Thin film interference in ultra-thin layers:
color coatings, tunable absorbers, and thermal emitters

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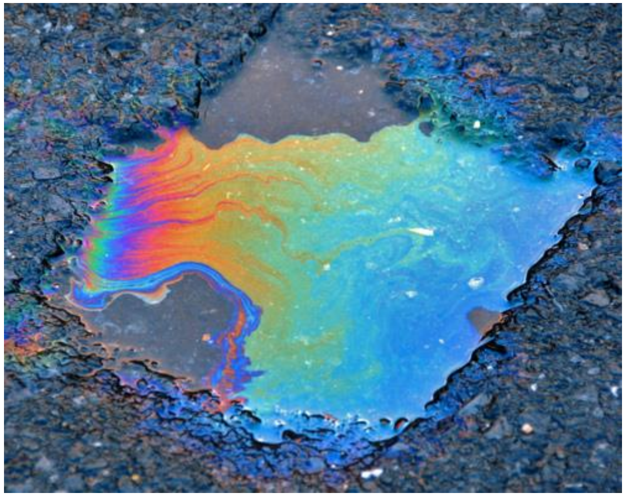
NanoLight [Benasque] **March 4, 2014**

Overview

- **Thin film interference in lossy films**
- **Ultra-thin color coatings**
- **Ultra-thin tunable perfect absorber in the infrared**
- **Anomalous thermal emitter**

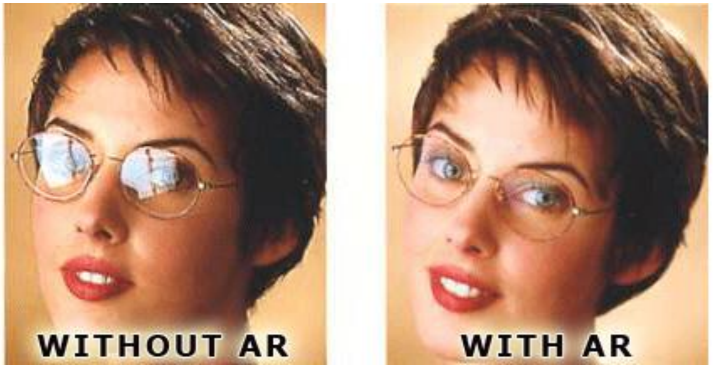
Overview



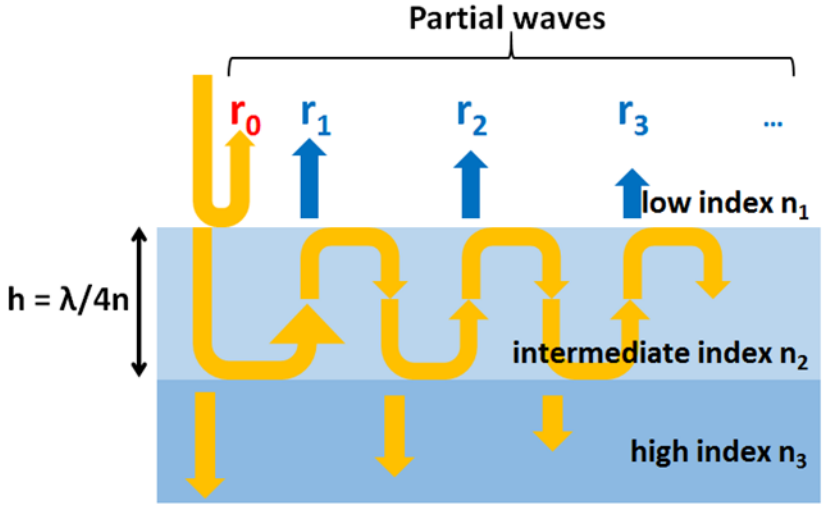
- **Thin film interference in lossy films**
- Ultra-thin color coatings
- Ultra-thin tunable perfect absorber in the infrared
- Anomalous thermal emitter

Anti-reflection (AR) coating

- One simple application: anti-reflective coatings



- Simplest/thinnest conventional AR coating: quarter-wave film
  - (optimized for a particular wavelength)



$$\tilde{r} = \frac{\tilde{r}_{12} + \tilde{r}_{23} e^{2i\tilde{\beta}}}{1 + \tilde{r}_{12}\tilde{r}_{23} e^{2i\tilde{\beta}}} \quad \text{with} \quad R = \left|\tilde{r}\right|^2$$

$$r_{12} = \frac{n_1 - n_2}{n_1 + n_2} \qquad \tilde{\beta} = \frac{2\pi}{\lambda}\tilde{n}_2 h$$

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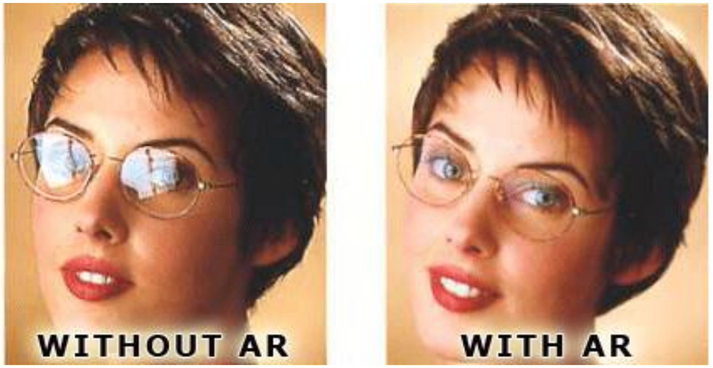

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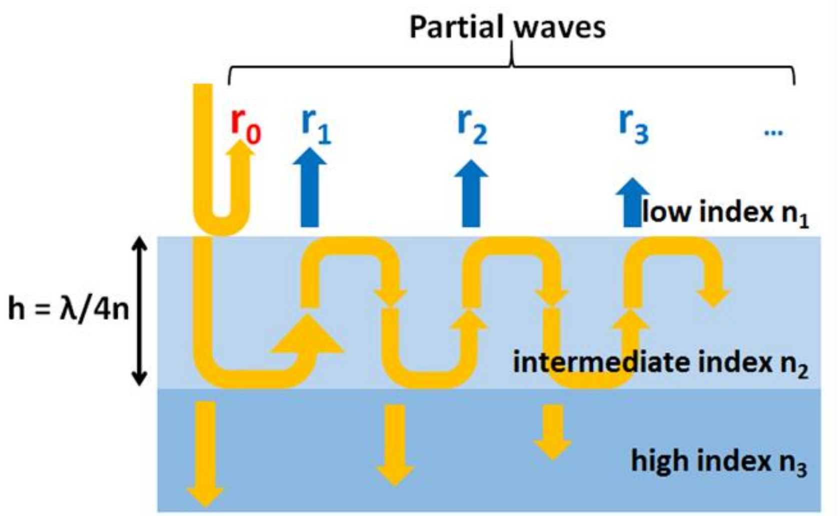
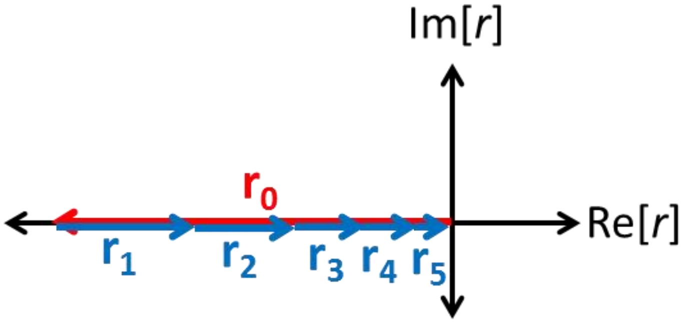


Phasor diagram



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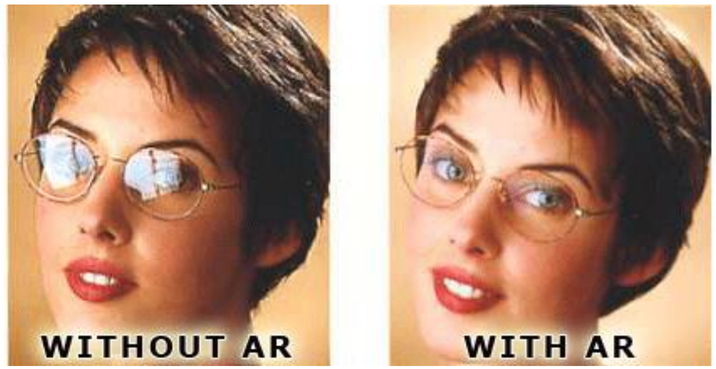

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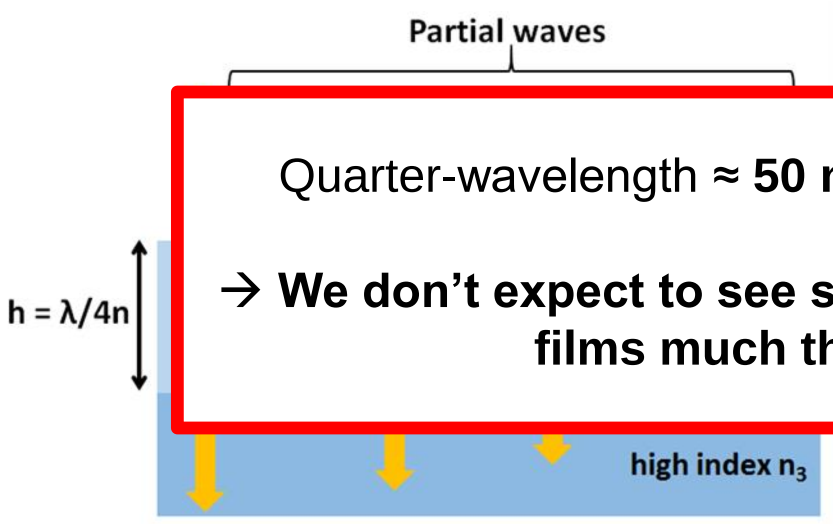

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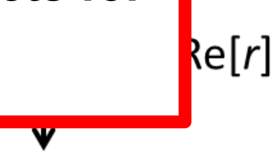
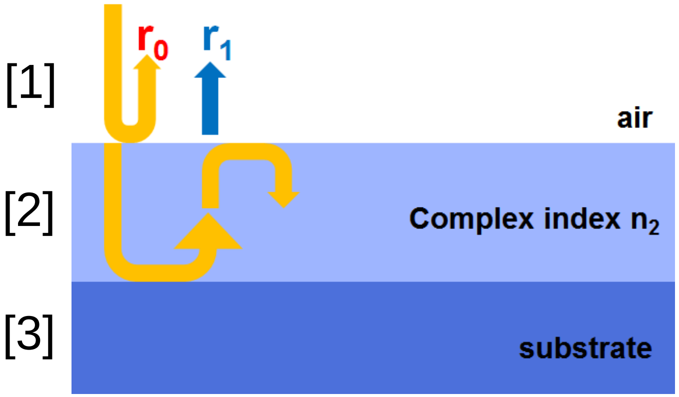


Quarter-wavelength ≈ **50 nm to 150 nm in the visible**

→ **We don't expect to see strong interference effects for films much thinner than this**

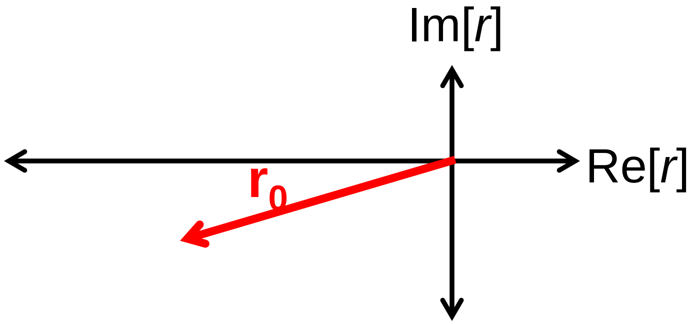
Interference in lossy films

- What if the film becomes very lossy?
  - Reflection coefficient from the 1-2 interface becomes complex-valued
  - Phasor $\mathbf{r_0}$ points away from the real axis



$$r_{pq} = \frac{\tilde{n}_p - \tilde{n}_q}{\tilde{n}_p + \tilde{n}_q}$$

$$\tilde{n}_p = n_p + ik_p$$



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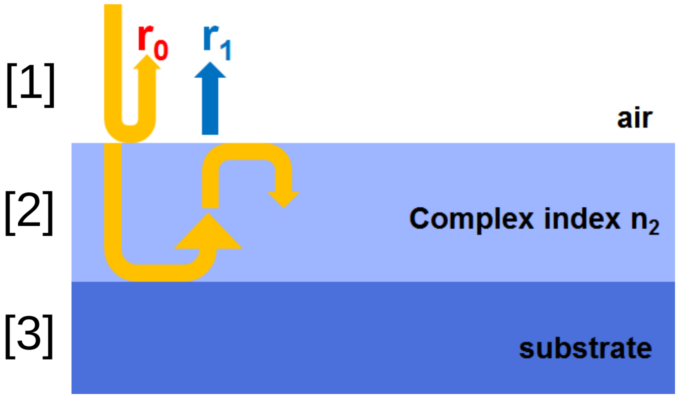

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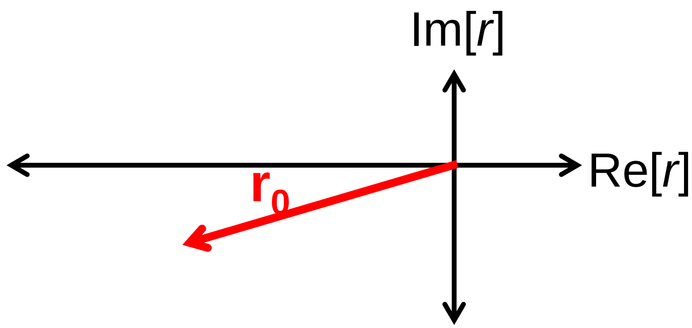

- The reflection coefficient is also complex-valued at the 2-3 interface, and even more-so if the substrate index is complex (but not $\rightarrow\infty$)

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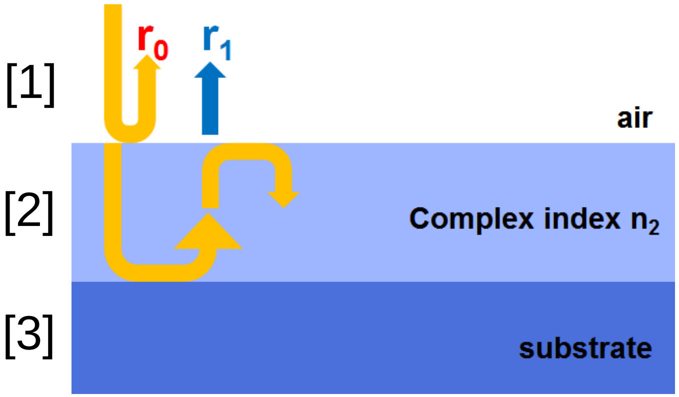

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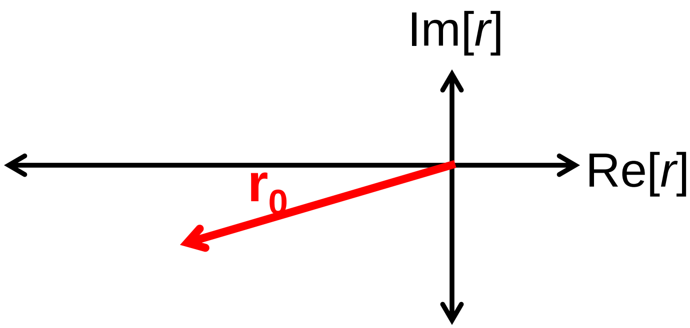
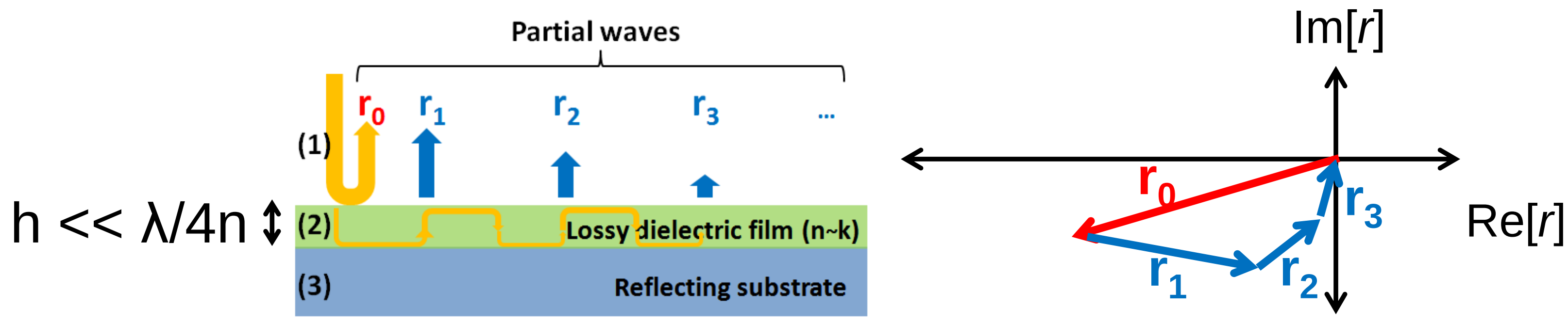


- The reflection coefficient is also complex-valued at the 2-3 interface, and even more-so if the substrate index is complex (but not → ∞)

- Must account for both interface reflection phase shifts and gradual phase accumulation via propagation
  - New interference condition → loss cannot be treated as a perturbation

Lossy dielectrics + finite metals

- Metals with finite conductivity and lossy dielectrics have weird interface reflection phase shifts (i. e. not 0 or π)
  - Different interference condition compared to the lossless case: **“resonance” can exist for films significantly thinner than λ/4**



- Takeaway message: it is possible to **suppress reflection** by using **interference** in a system involving an **ultra-thin, highly-lossy layer**

M. A. Kats et al, **APL** 101, 221101 (2012)

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- Thin film interference in lossy films
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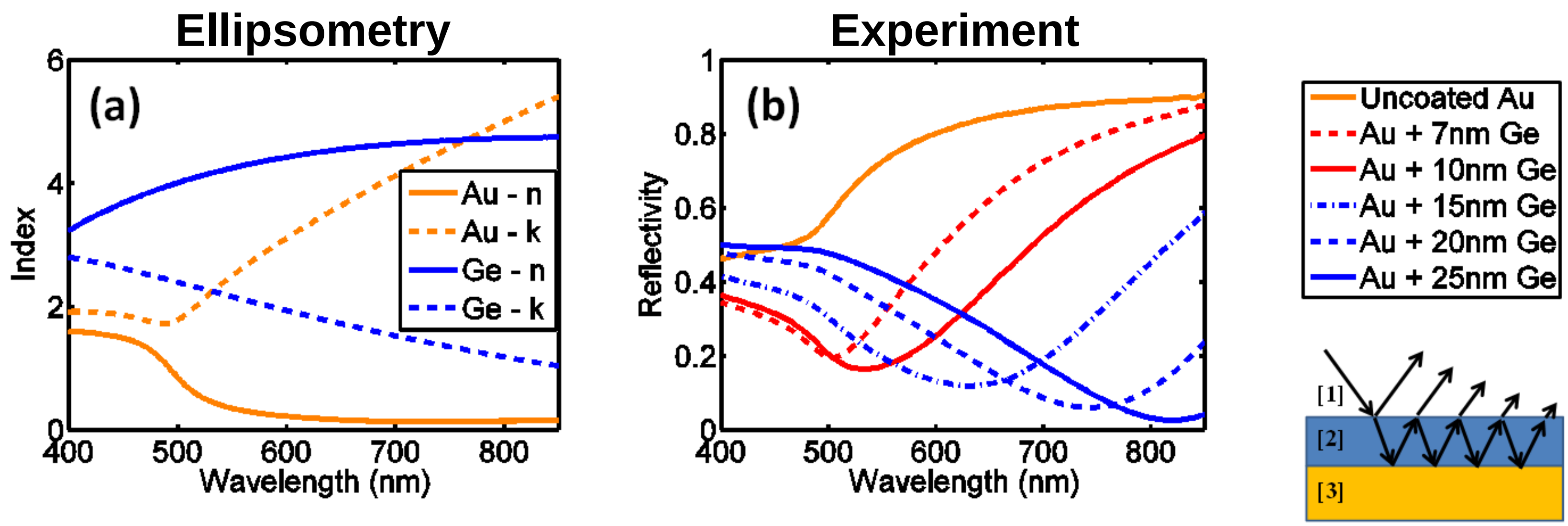
Our first experimental system

- Lossy dielectric → Amorphous germanium
- Lossy metal → Gold



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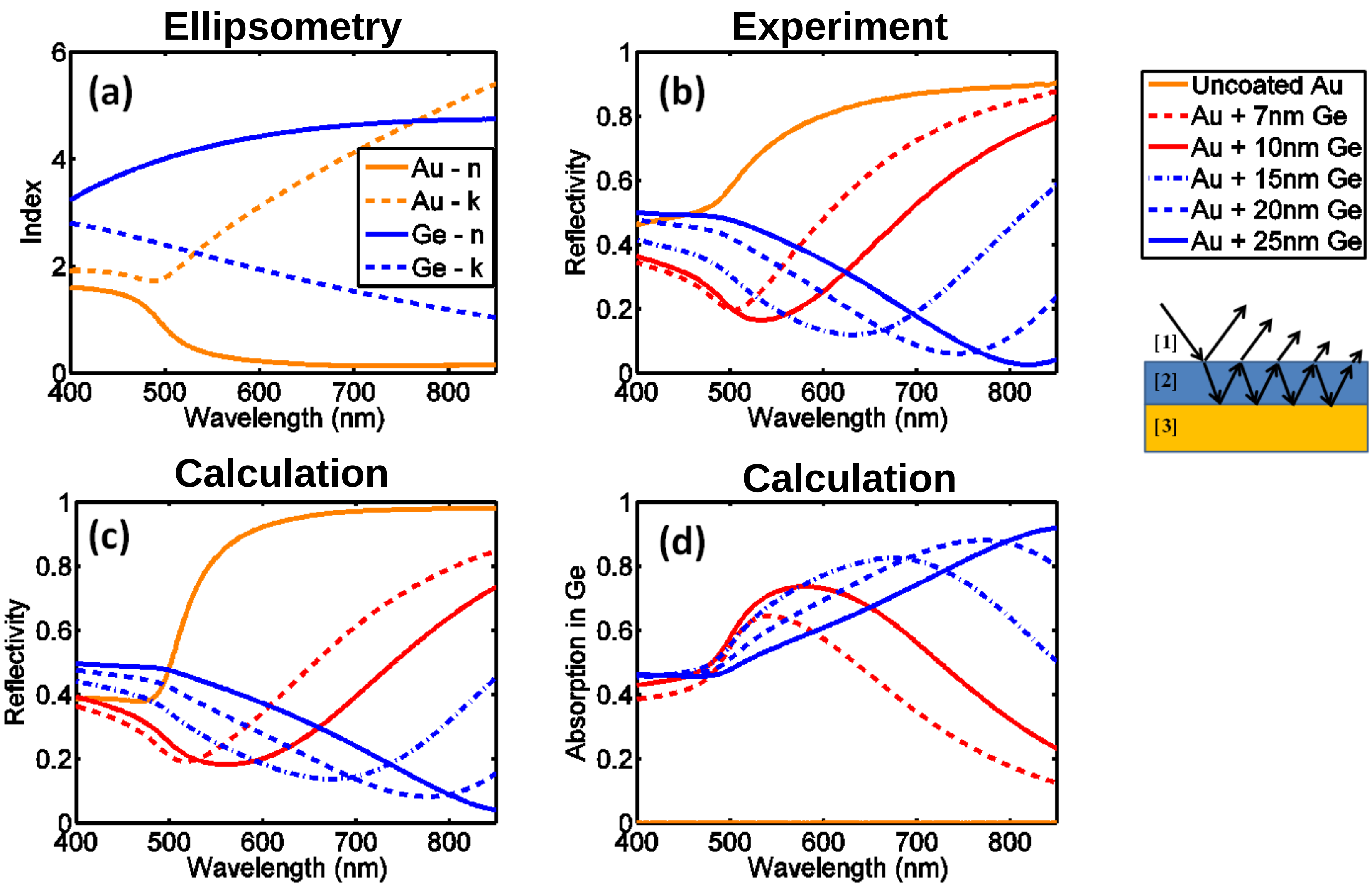
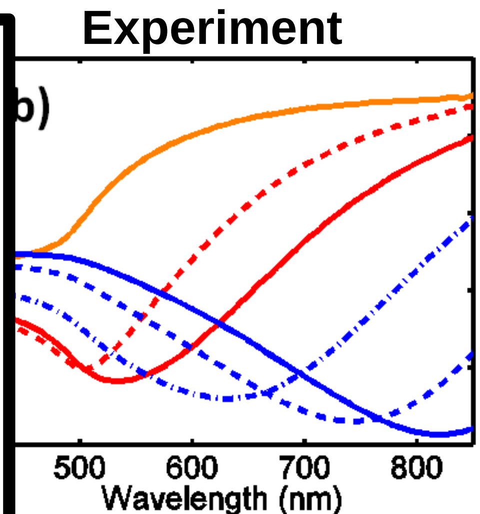
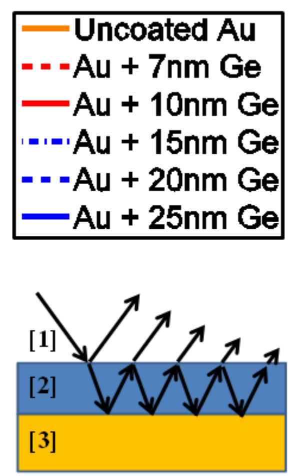


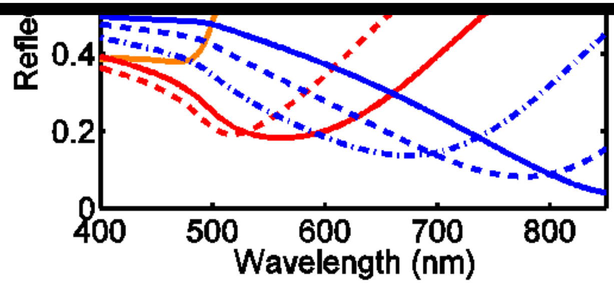
Our first experimental system

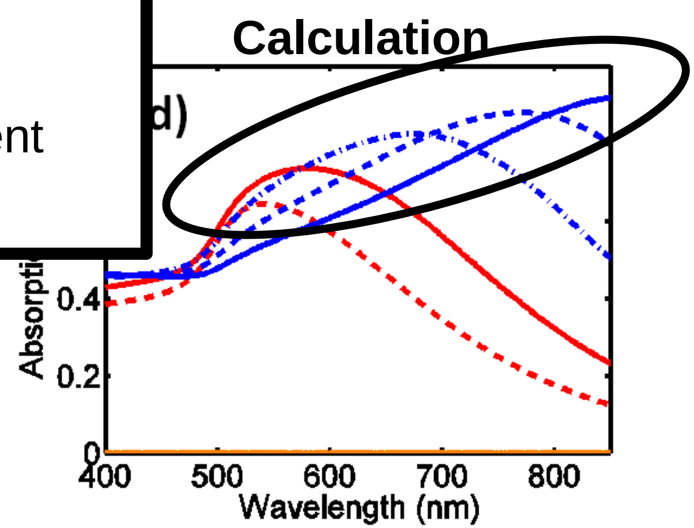
- Lossy dielectric → Amorphous germanium
- Lossy metal → Gold

> - 60 - 90% absorption within a 10-20 nm layer of semiconductor
> - Continuous film; no patterning
> - Immediate applications in mind
>   - Photodetectors
>   - Solar cells
>   - Localized heating
> - Note: absorption enhancement **without** field enhancement



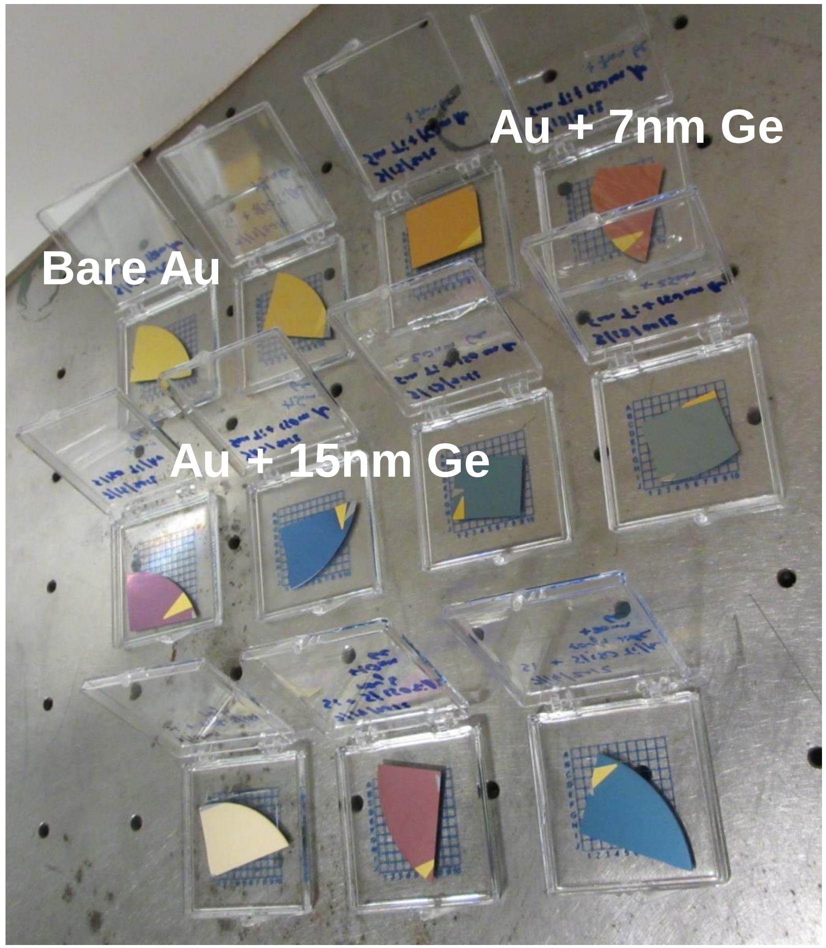






Coloring gold

- "Colored" gold films by coating with 5-20 nm germanium films
  → much thinner than λ/4



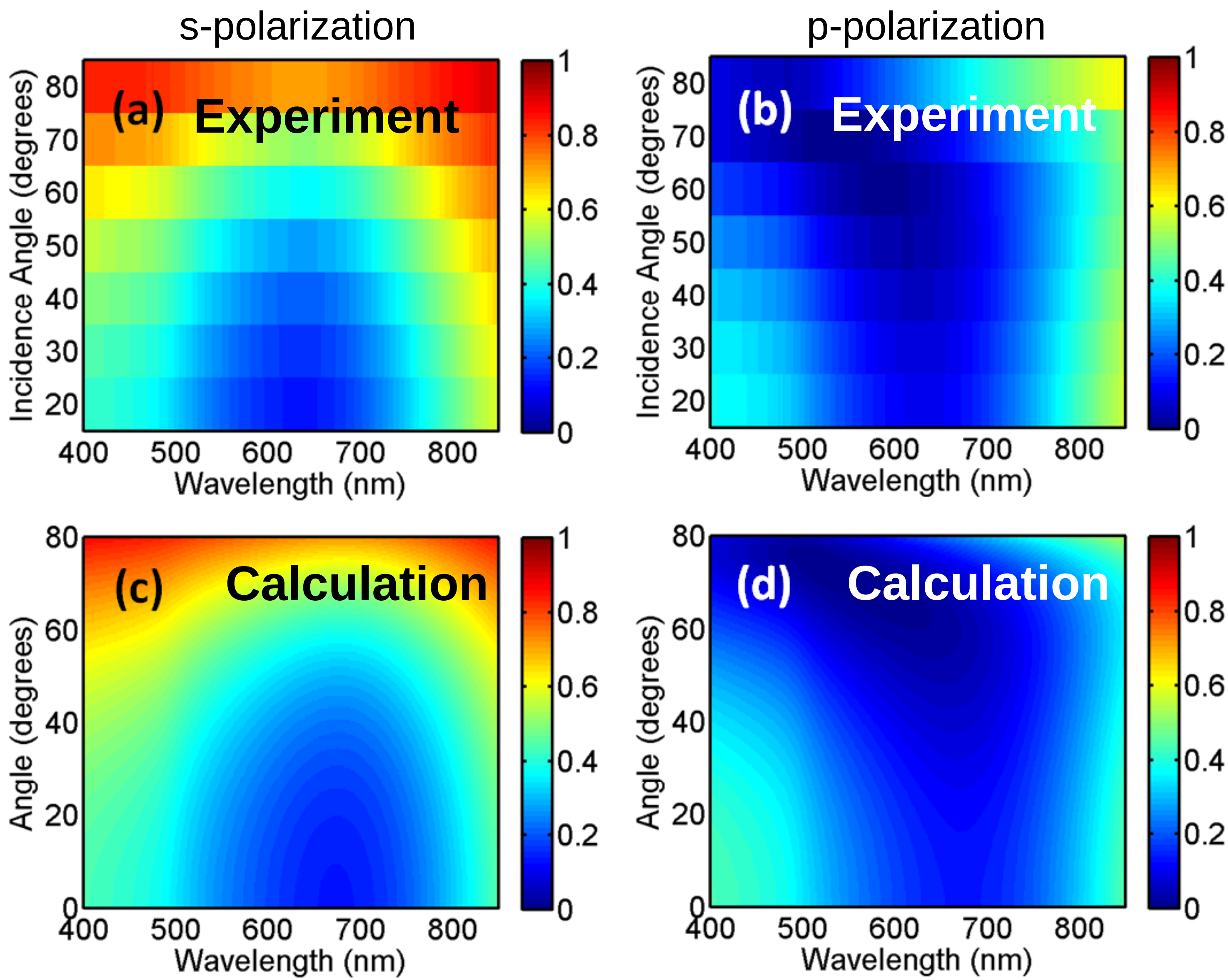
Polished substrate

Rough substrate
(still works!)

M. A. Kats et al, **Nat. Materials** 12, 20 (2013)

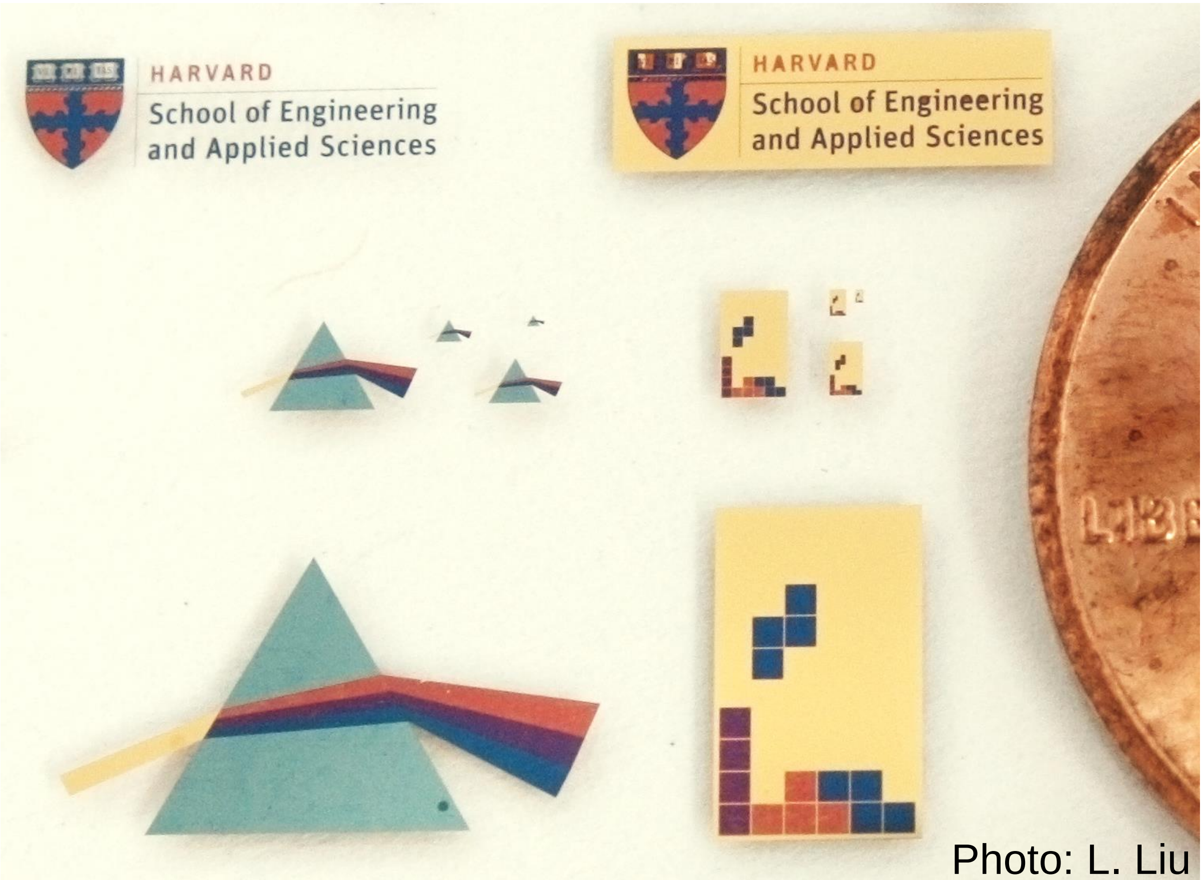
Angle-dependent reflectivity spectra

- Au + 15 nm of germanium



Nanometer thickness optical coatings

- Patterning ultra-thin coatings to create images, labels, etc



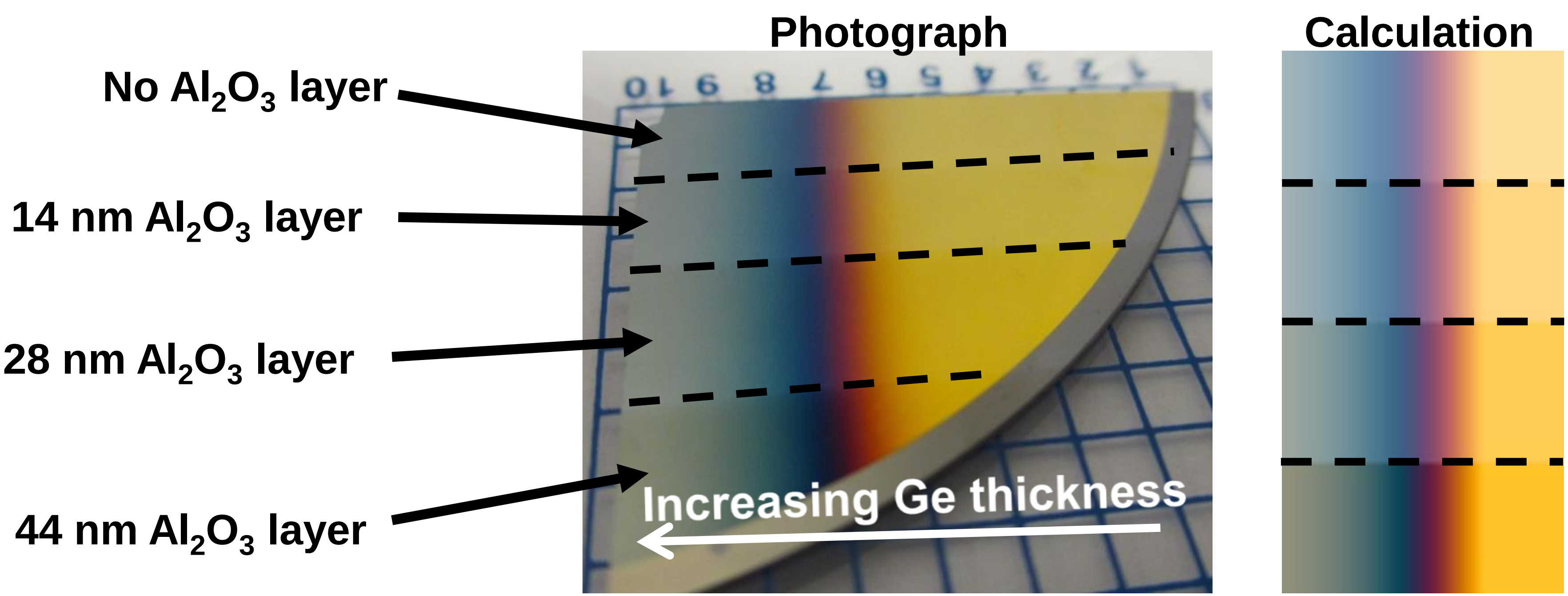
- The difference between blue and purple, and purple and pink is only ~4 nm continuous film of germanium (~ 8 atomic layers)!

M. A. Kats et al, **Nat. Materials** 12, 20 (2013)

Color gradients with ultra-thin coatings

- Ge film of gradient thickness on gold (top section)

- Overcoat with thin Al_2O_3 layers
  - Increased color contrast
  - Protection from the elements
  - Can be replaced by transparent electrode (e.g. ITO)

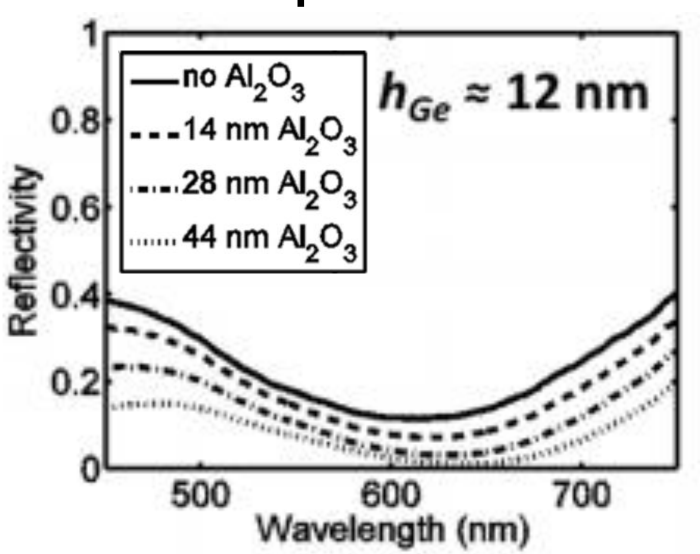


M. A. Kats et al, **APL** 103, 101104 (2013)

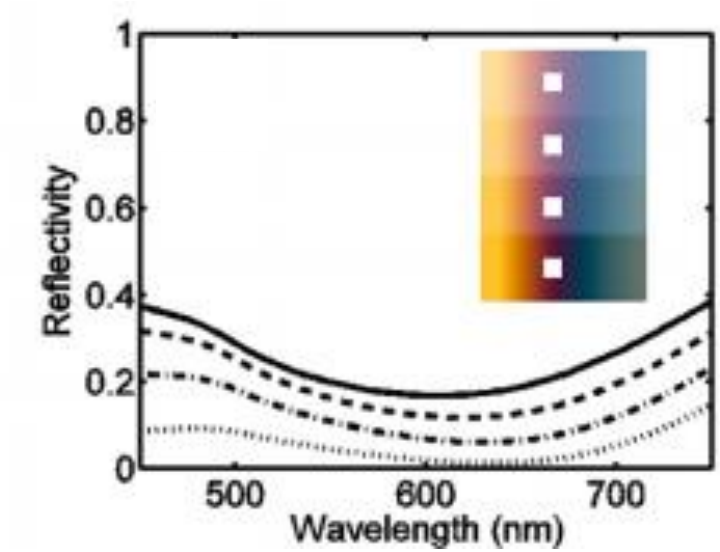
Additional layer of transparent dielectric

- **Au / 12 nm Ge / 44 nm Al_2O_3** overcoat → **R = 0 - 15%** across the **entire visible spectrum** with most of the **light absorbed in the germanium film**

Experiment



Calculation



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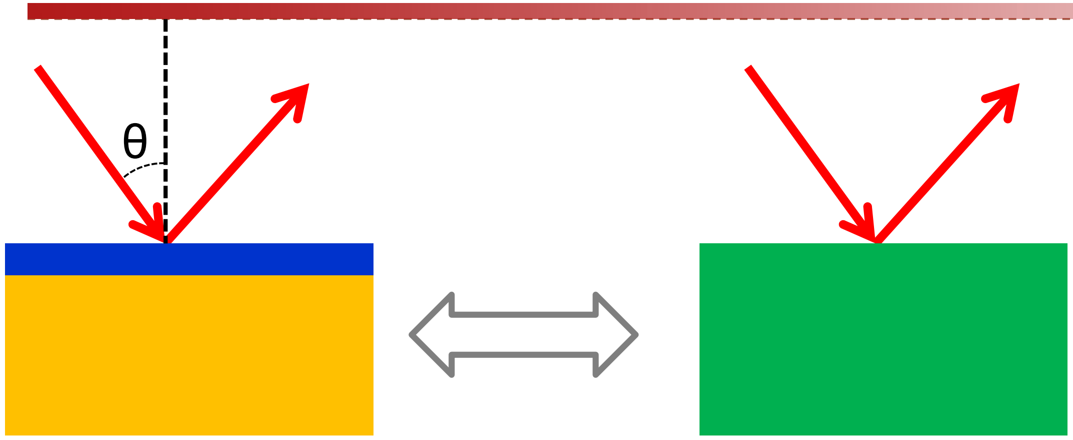
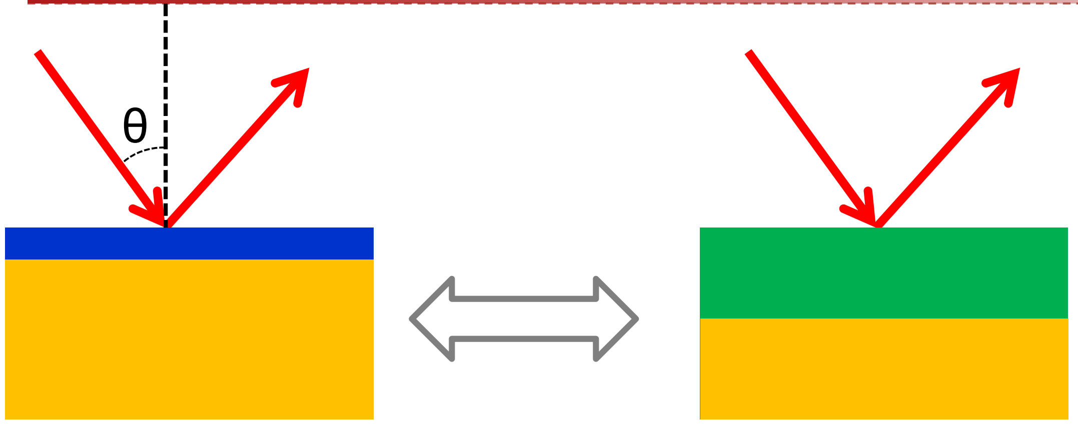
Structural color masquerading as a pigment



Gold + 15 nm of Ge **Equivalent material**

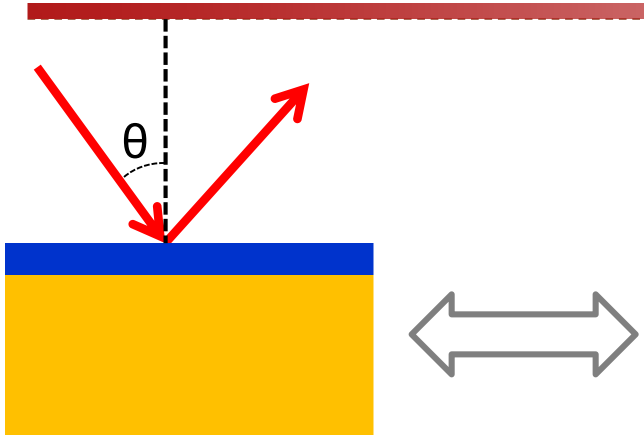
Structural color masquerading as a pigment



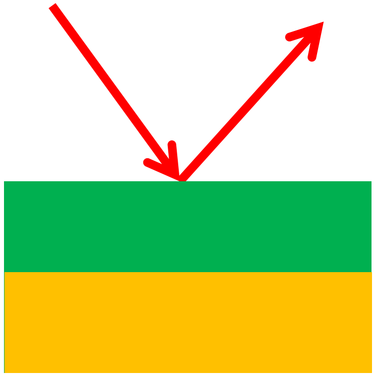
Gold + 15 nm of Ge

Color by pigment

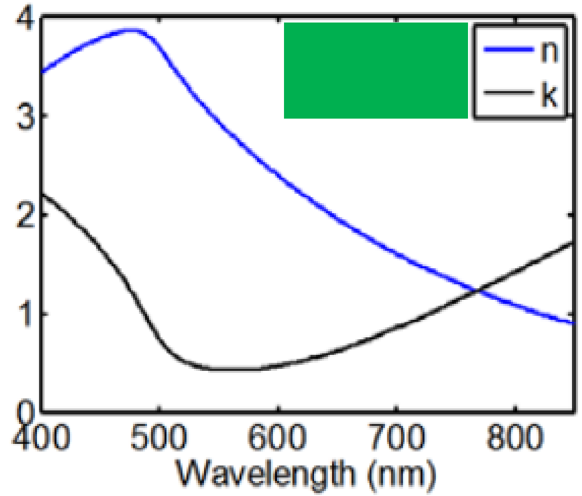
Structural color masquerading as a pigment



Gold + 15 nm of Ge



Color by pigment



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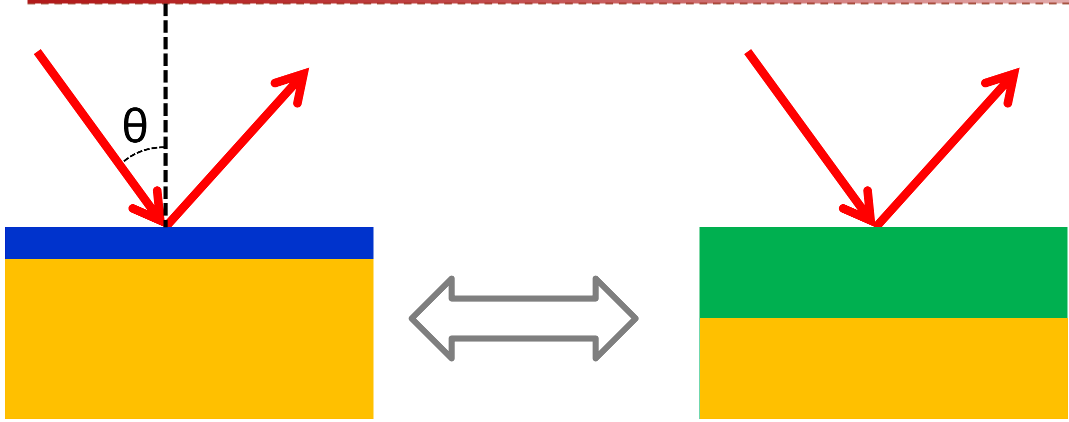
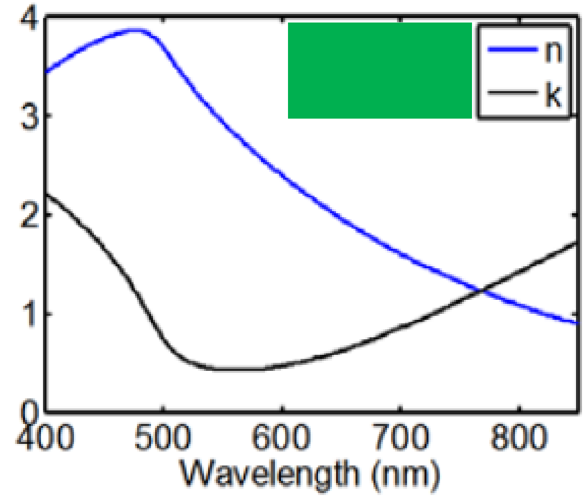
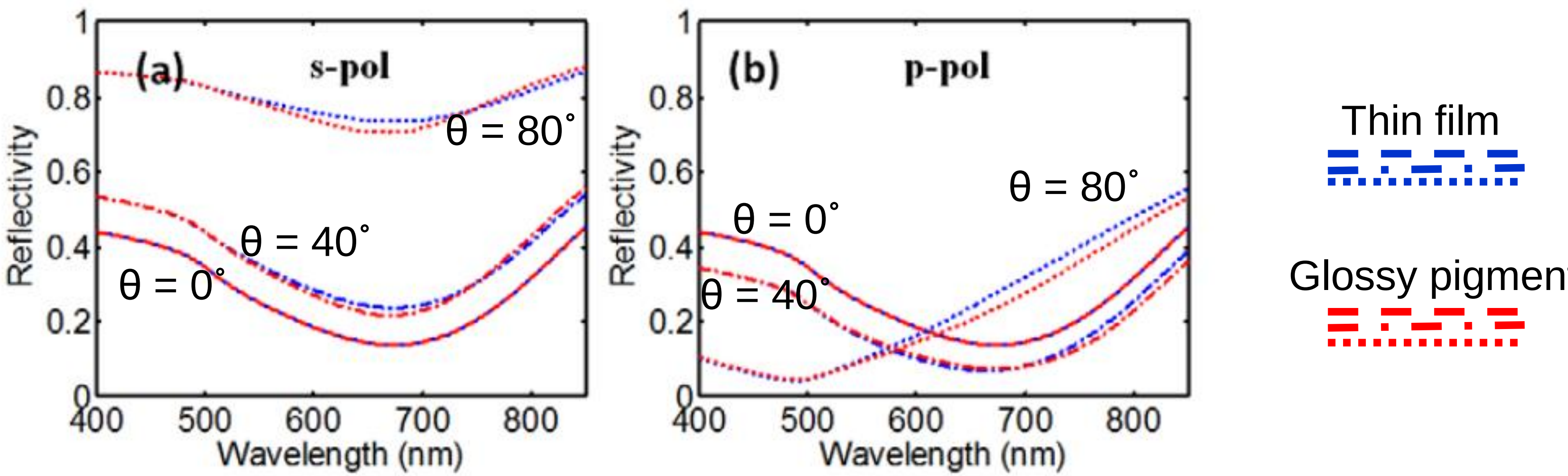


Gold + 15 nm of Ge | **Color by pigment**





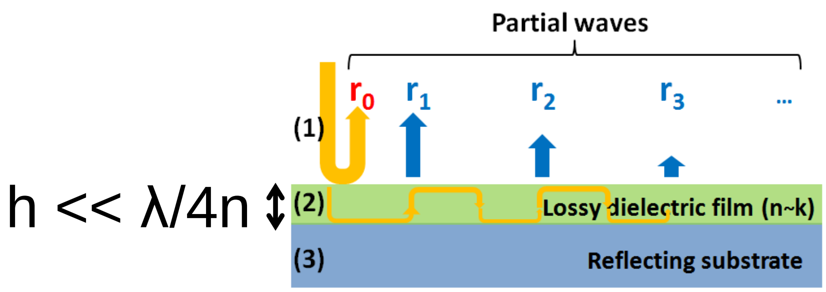
- Optically it is impossible to determine if you're looking at a solid material, a flat pigment, or a multi-layer system with ultra-thin films

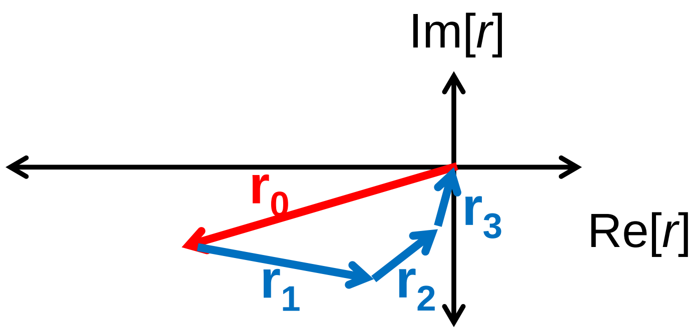
Overview

- Thin film interference in lossy films
- Ultra-thin color coatings
- **Ultra-thin tunable perfect absorber in the infrared**
- Anomalous thermal emitter

Lossy dielectrics + finite metals

- Metals with finite conductivity and lossy dielectrics have weird interface reflection phase shifts (i. e. not 0 or π)
  - Resonance can exist for films significantly thinner than λ/4
  - To achieve full suppression of a wavelength, the film should be very lossy

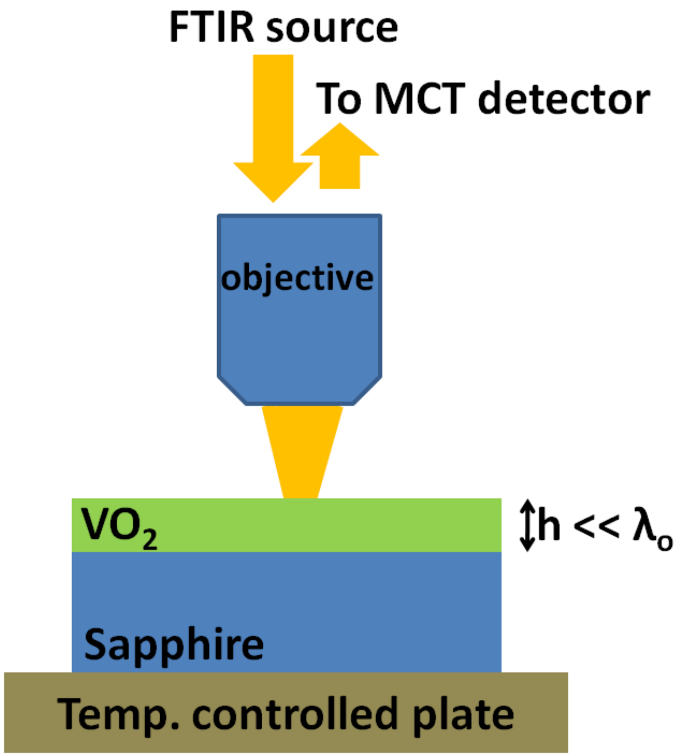




- Takeaway message: it is possible to achieve **large (even perfect) absorption** by using **thin film interference** in a system involving an **ultra-thin, highly-lossy layer**

Making a tunable perfect absorber

- Our experimental system comprises a thin (180 nm vs. λ ~ 5-15 μm) film of vanadium dioxide (VO_2) on sapphire
  - VO_2 serves as highly-absorbing layer (tunable)
  - Sapphire is highly-reflecting due to phonon activity in the IR

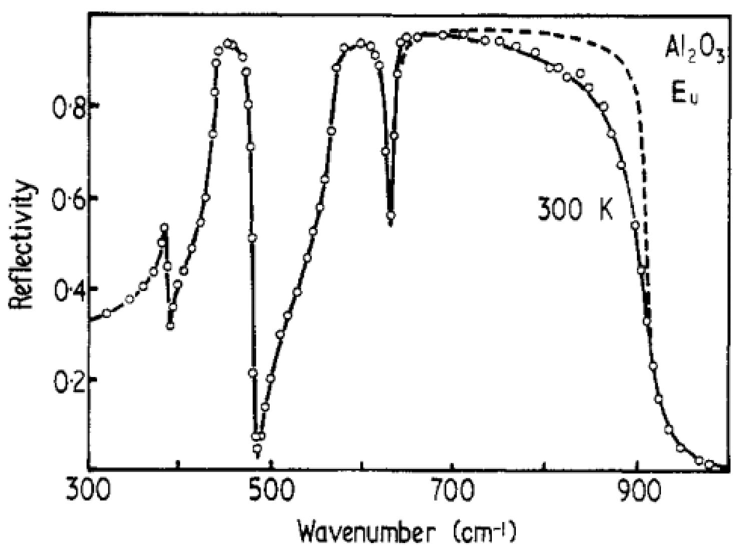


Why sapphire?

- In the IR, what reflectors give us non-trivial optical phase shifts upon reflection?

$$r_{23} = \frac{\tilde{n}_2 - \tilde{n}_3}{\tilde{n}_2 + \tilde{n}_3}$$

- At λ = 12 um, conventional metals do not work
  - n_{Au} ~ 15 + 60i, n_{Fe} ~ 6 + 40i, etc → all pretty much PEC-like..
  - **Sapphire (crystalline Al_2O_3) fits the bill!**

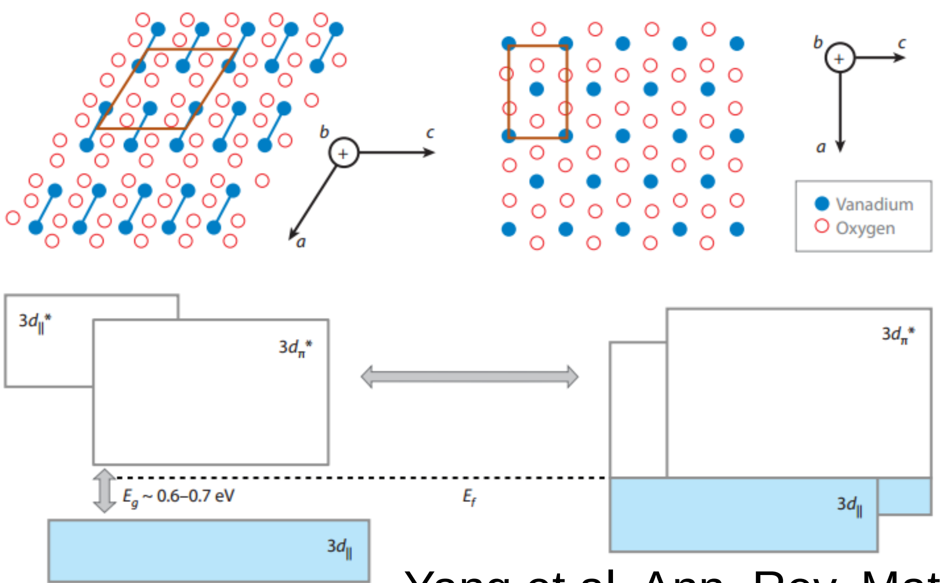


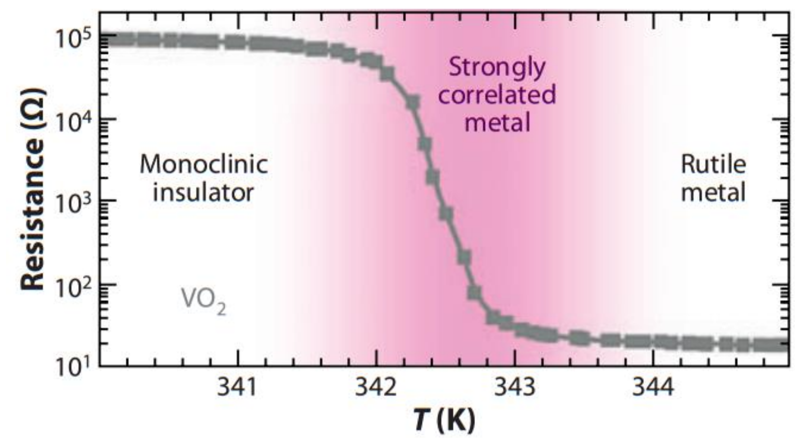
→ Multi-phonon activity in Sapphire
→ **At 12 um, *n* ~ 0.1 + 0.8i**

Gervais and Piriou, J. Phys. C (1974)

Vanadium dioxide (VO_2)

- VO_2 is a correlated metal oxide which experiences phase change upon heating to past ~70 °C (reversible, but with hysteresis)
- Conductivity changes by >10,000 from the insulating to conducting state



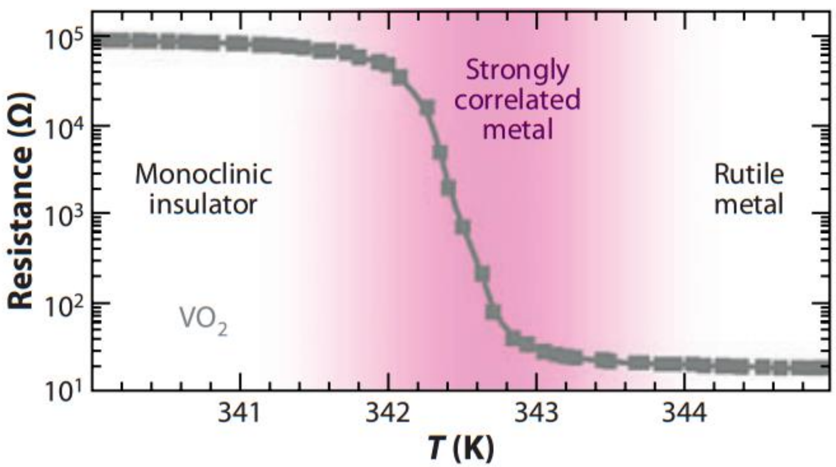


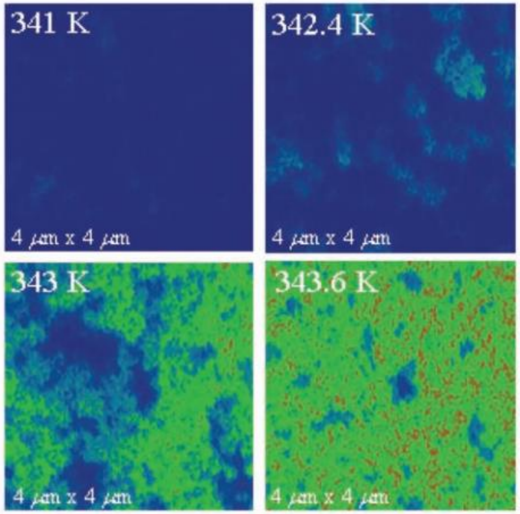
Yang et al, Ann. Rev. Mat. Res. (2011)

VO_2 samples from Ramanathan group @ Harvard

VO_2 in the transition region

- What happens in the transition region of VO_2?



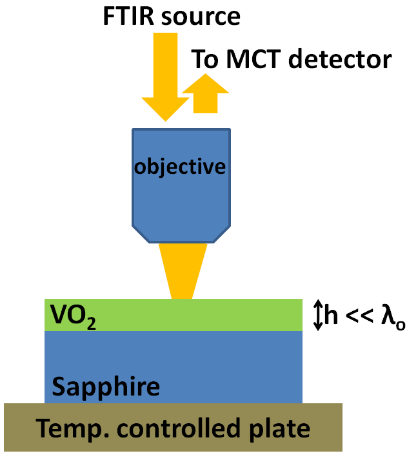


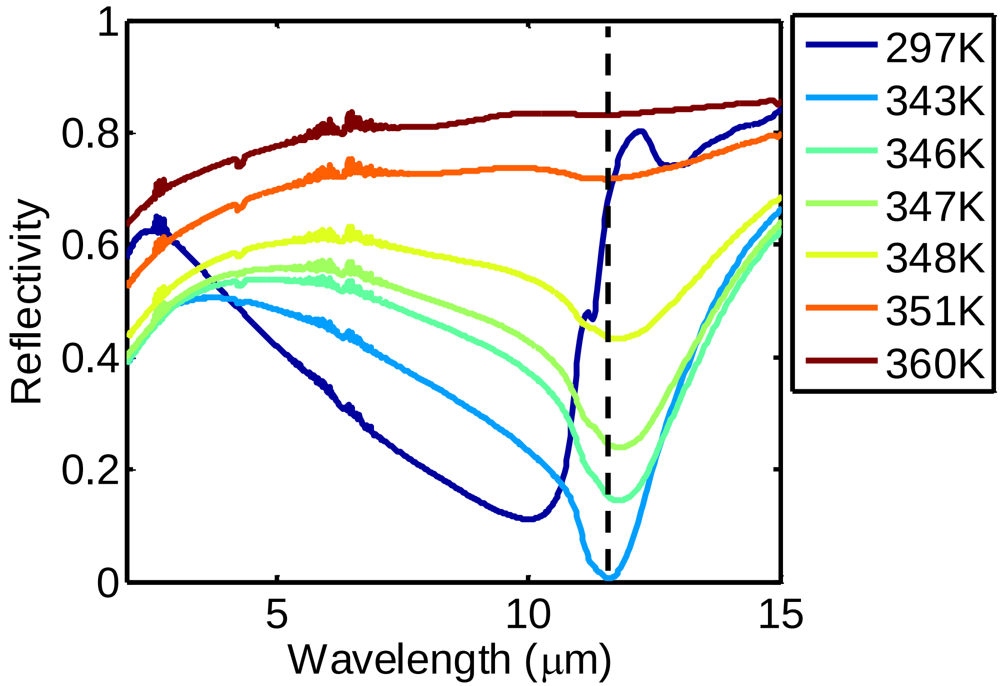
Qazilbash, Basov, et al, Science (2007)

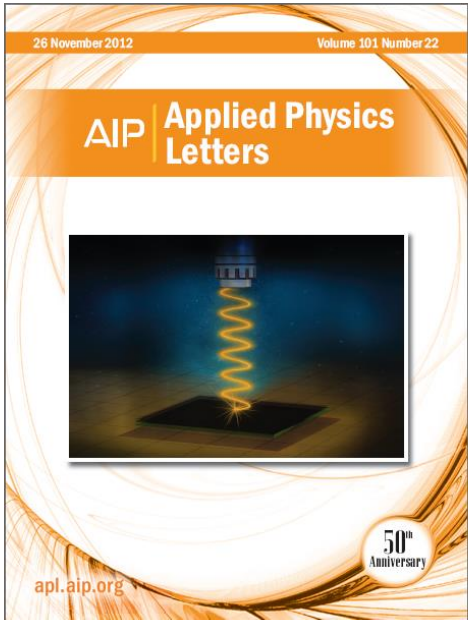
- Nanoscale islands of metal-phase VO_2 begin to form within a background of dielectric-phase VO_2, which then grow and connect
  - The mixture can be viewed as a ***disordered, natural metamaterial***
  - The ratio of co-existing phases can be controlled → ***tunable medium***

Tunable perfect absorber

- Temperature control of VO_2 allows significant tuning of its refractive index, and hence the sample reflectivity
- Reflectivity tuning from ~80% to 0.25% at 11.6um
  → on/off ratio of more than 300
  → entire structure is simply 180nm of VO_2 on sapphire



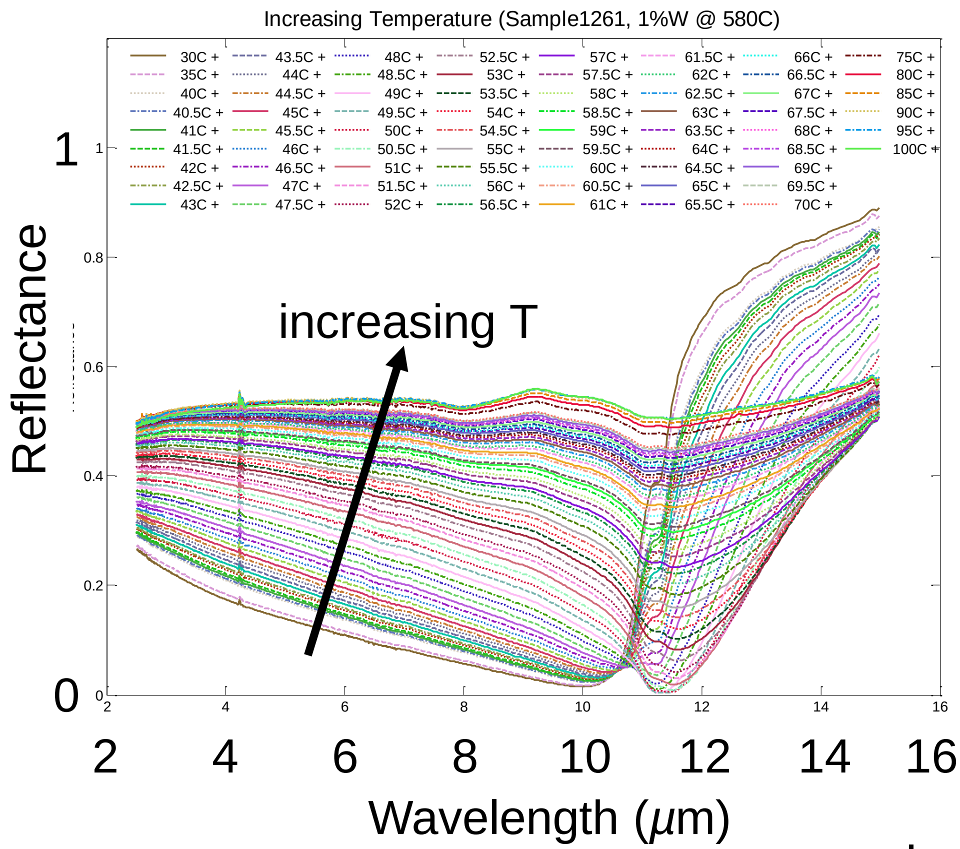




M. A. Kats et al, **APL** 101, 221101 (2012)

Changing the transition temperature

- Doping VO_2 with tungsten (W) → lower transition temperature
  - 1% W incorporated into VO_2 during growth → perfect absorption condition at ~50 °C rather than ~70 °C



In collaboration with:
C. Ronning, J. Rensberg
H. Schmidt, I. Skorupa

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- Ultra-thin tunable perfect absorber in the infrared
- **Anomalous thermal emitter**

IR absorber in reverse: thermal emitter

- Spectrum/intensity of thermal radiation emitted by an object is given by Planck's law:

$$I(K,T) = 2hc \underbrace{\frac{K^3}{e^{hcK/k_B T} - 1}}_{\text{Blackbody contribution}} \underbrace{\varepsilon(K)}_{\text{emissivity}}$$

K: spectroscopic wavenumber (= f/c)

- Thermodynamic statement: Kirchhoff's law of thermal radiation

$$\varepsilon(K) = a(K)$$

$a(K)$ ← absorptivity

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spectroscopic wavenumber (= f/c)

Blackbody contribution

emissivity

- Thermodynamic statement: Kirchhoff's law of thermal radiation

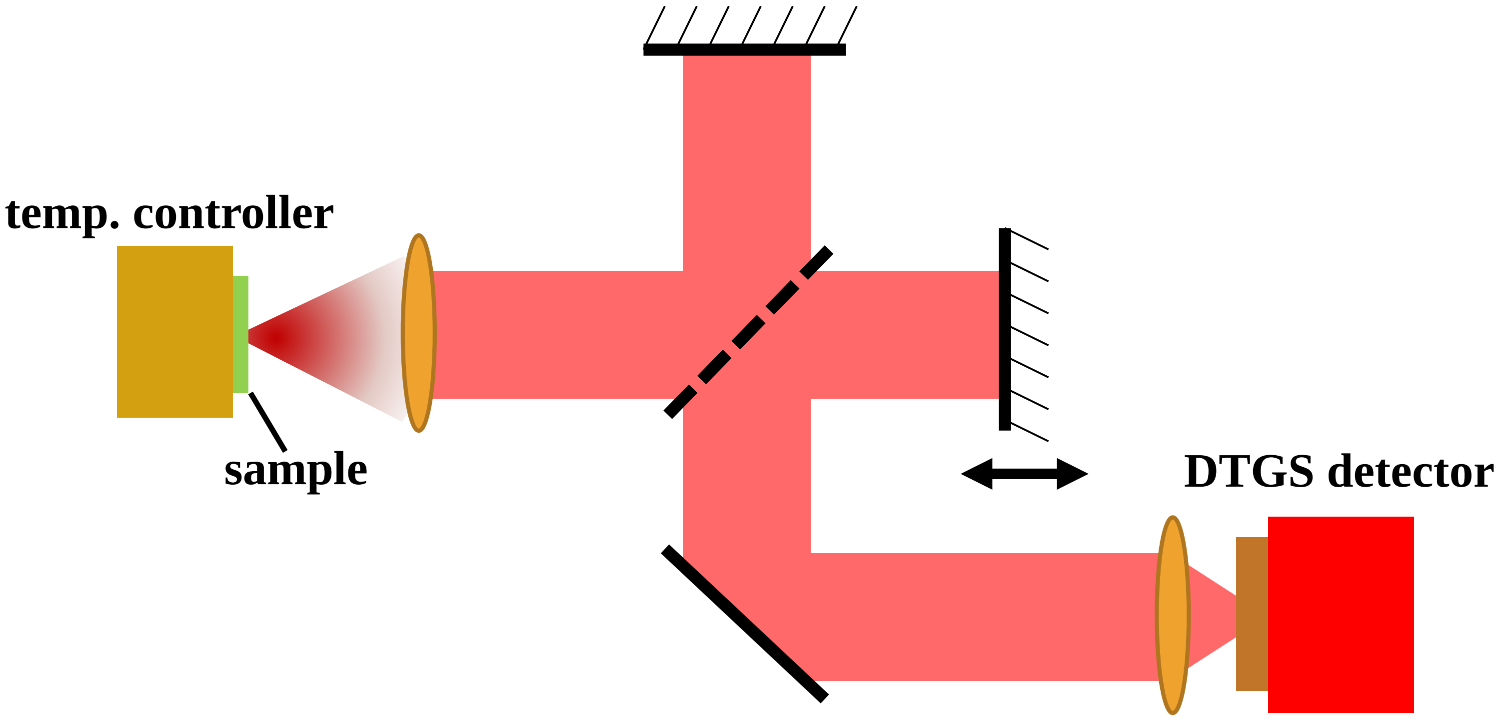
$$\varepsilon(K) = a(K)$$

← absorptivity

- Our VO_2/sapphire structure has temperature-dependent infrared absorptivity, and hence its emissivity is expected to also vary with temperature
  - **Anomalous behavior such as non-monotonic thermal emission with temperature**

Thermal emitter: experimental setup

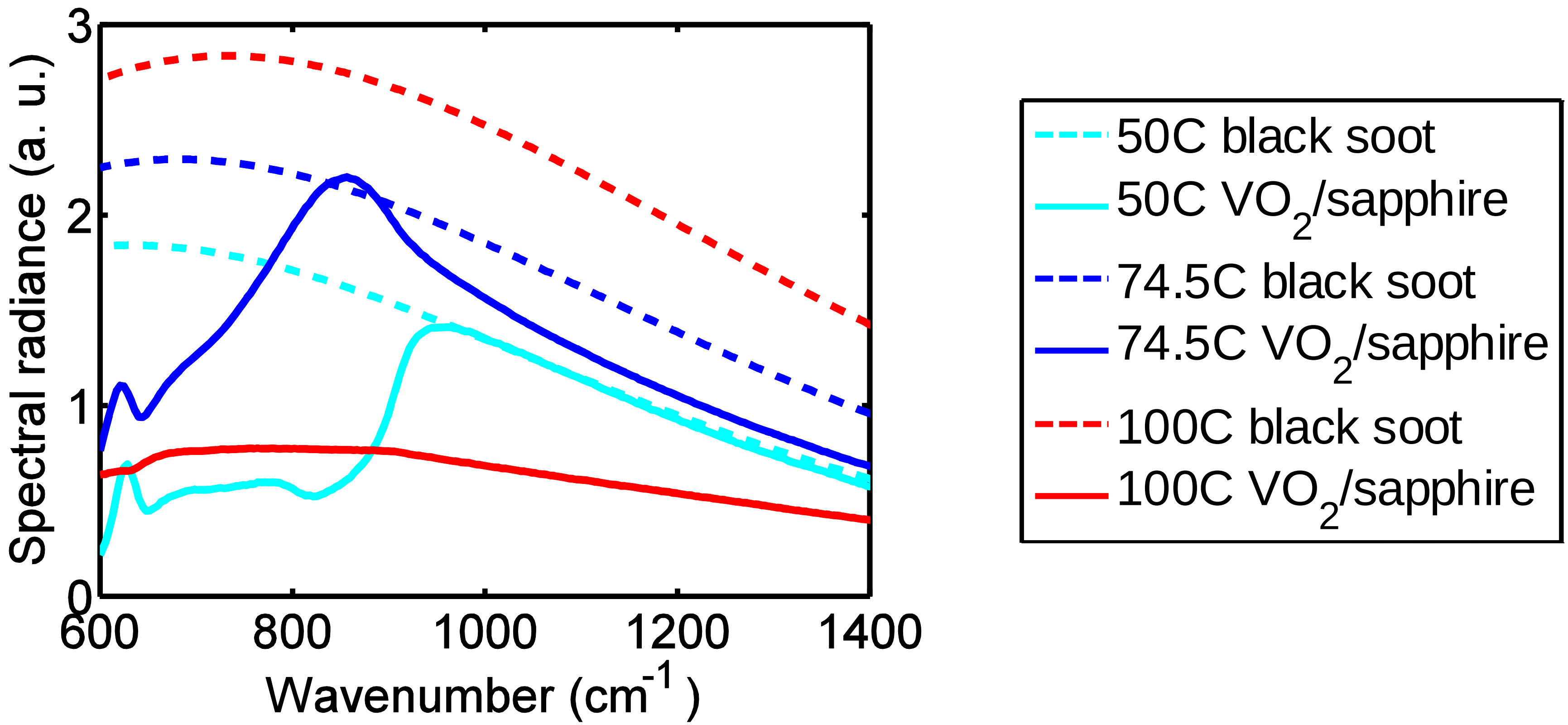
Fourier transform infrared spectrometer (FTIR)



- Data analysis must account for thermal emission from the detector and optics, and the frequency-dependent response of the instrument
- Can use a wafer blackened by candle soot as blackbody-like reference ($\varepsilon \approx 0.96$ in the IR)

Thermal emitter: experimental results

- Extracted spectral radiance (distribution of thermal emission)

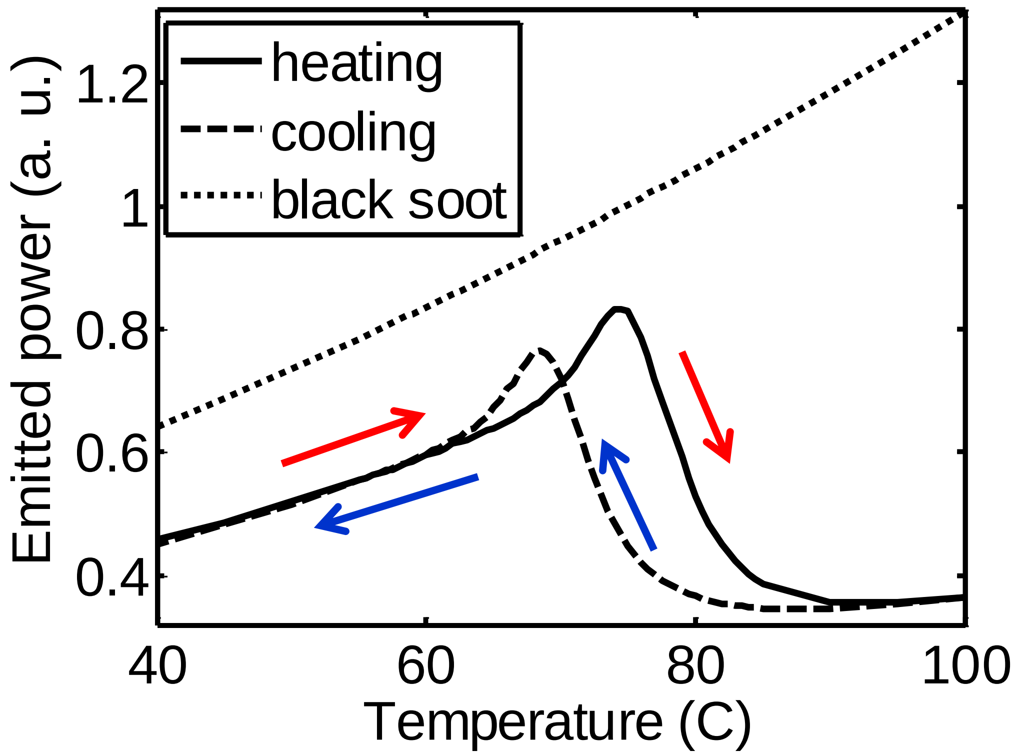


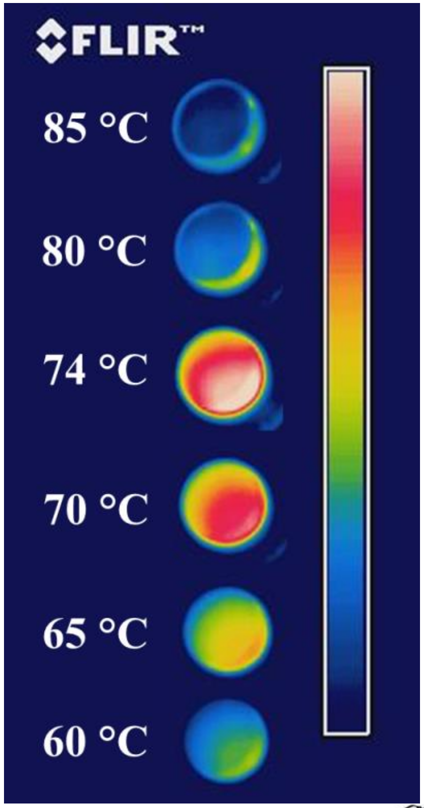
- Thermal emission peak @ "perfect absorption" condition
- At some point emissivity surpasses our black soot reference
- Total emitted IR light goes up, then down with increasing temperature

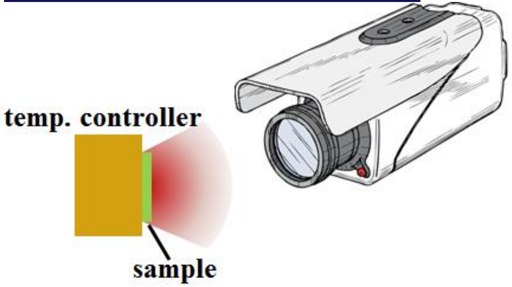
<u>M. A. Kats</u> et al, **Physical Review X** 3, 041004 (2013)

Thermal emitter: experimental results

- Integrated emitted power over the 8-14 μm atmospheric transparency region







- Multiple unusual features:
  - Local maximum in the emitted power
  - Negative differential thermal emittance over ~10°
  - Hysteresis (intrinsic to VO_2)

M. A. Kats et al, **PRX** 3, 041004 (2013)

Thermal emitter: experimental results

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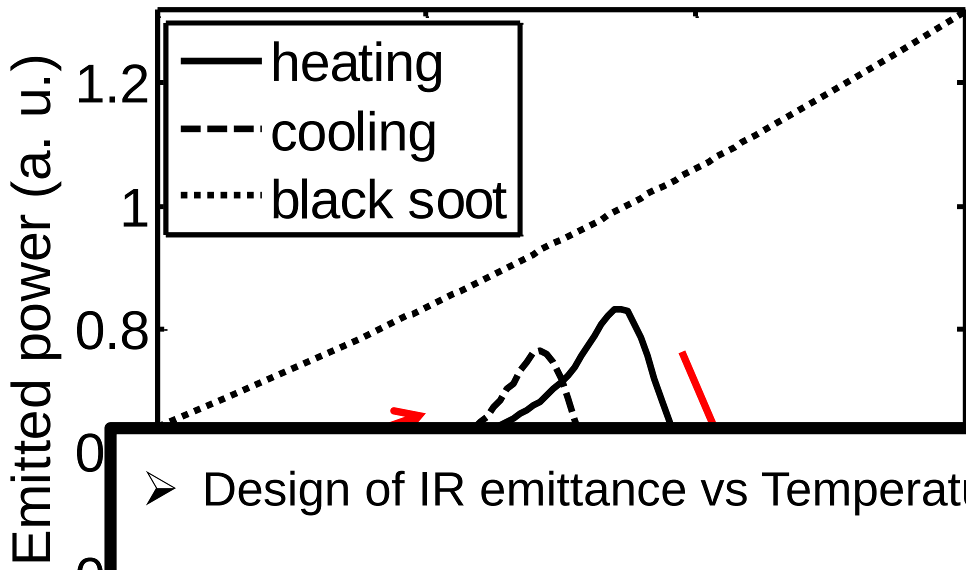
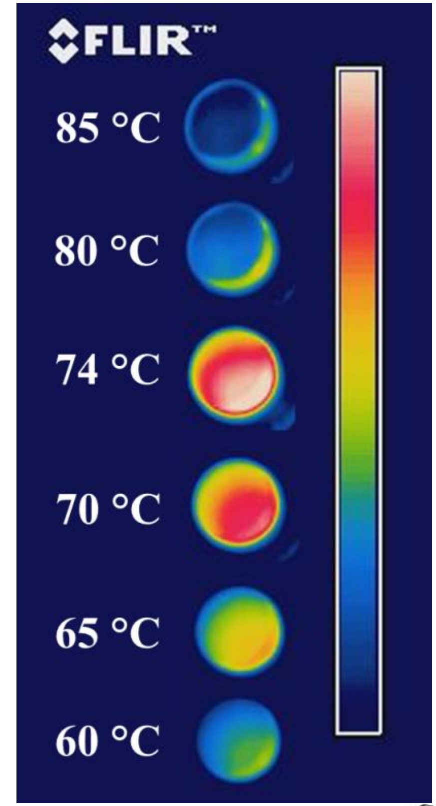
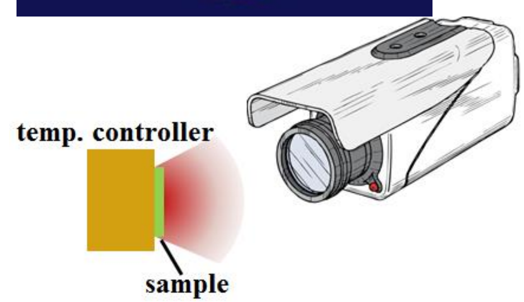


- Design of IR emittance vs Temperature
  - Efficient temperature regulation (passive or active)
  - Infrared camouflage





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Summary

- Described existence of strong optical interference in ultra-thin, highly-absorbing films
- Demonstrated ultra-thin optical interference coatings comprising lossy semiconductor films on gold substrates
  - Large optical absorption within nanometer-thick layers
  - Thin film interference without iridescence
- Demonstrated a tunable absorber in the infrared based on VO_2 and sapphire
  - Used the phase transition of VO_2 as a tunable, disordered, “natural metamaterial”
- Demonstrated an anomalous thermal emitter
  - “Perfect” blackbody-like emission,
  - Negative differential thermal emittance

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