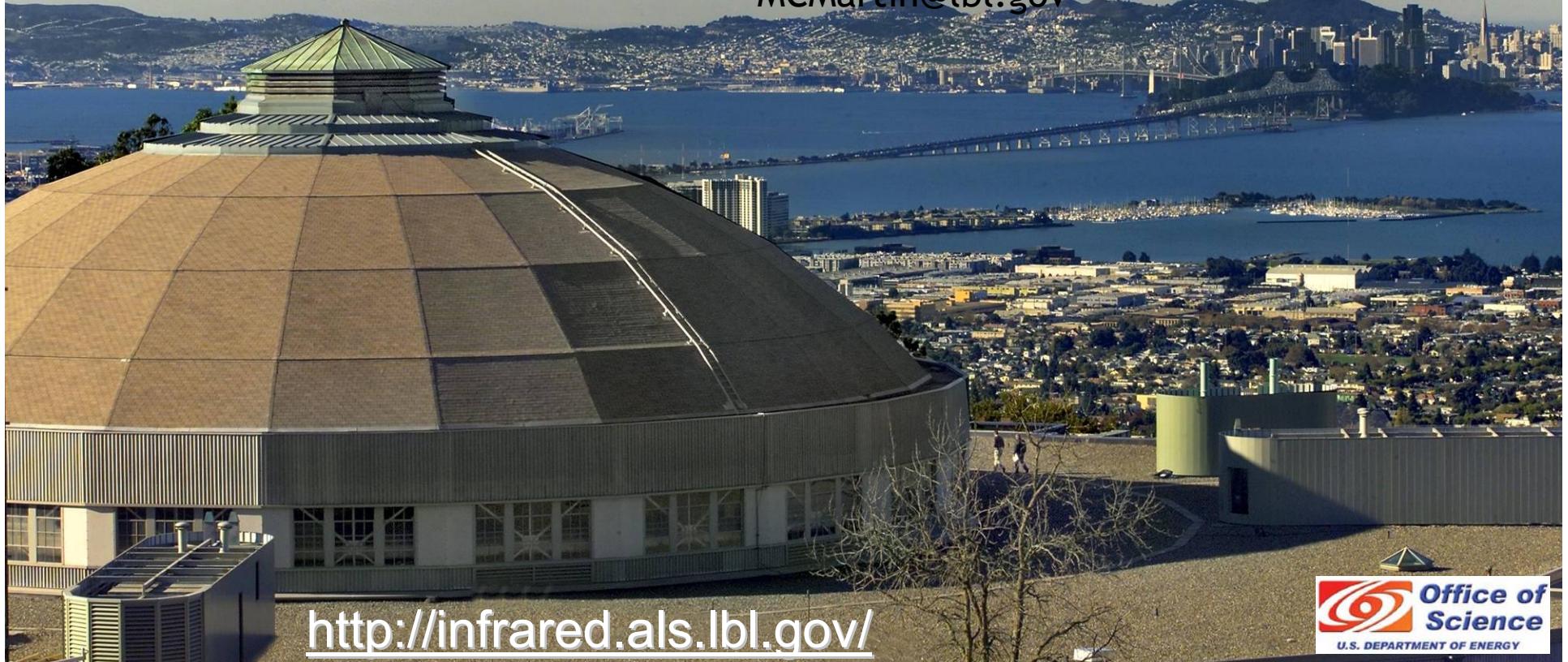


Current Infrared Studies of Novel Materials at the ALS: Metamaterials, Organic conductors, and Graphene

Michael C. Martin

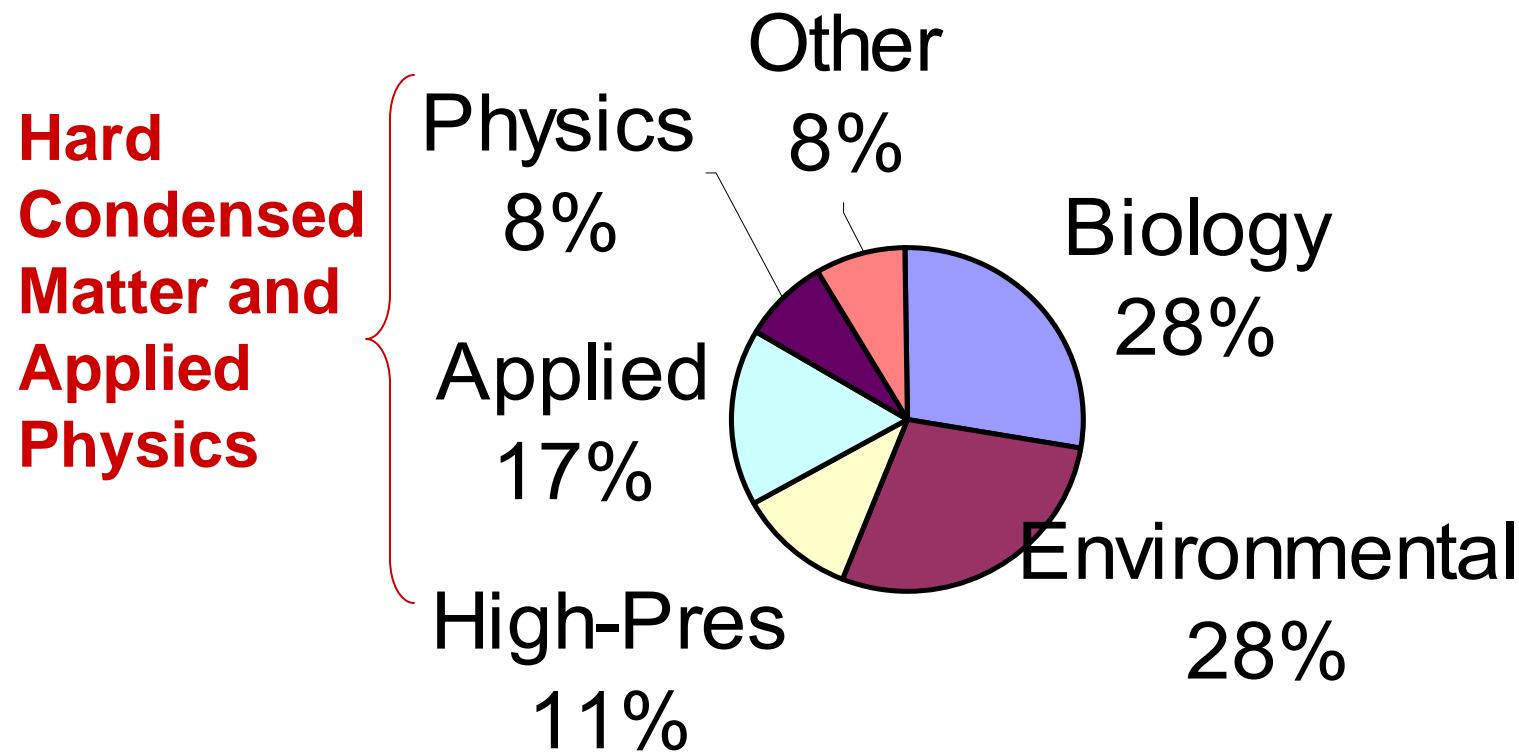
Advanced Light Source, Lawrence Berkeley National Laboratory
MCMartin@lbl.gov



<http://infrared.als.lbl.gov/>



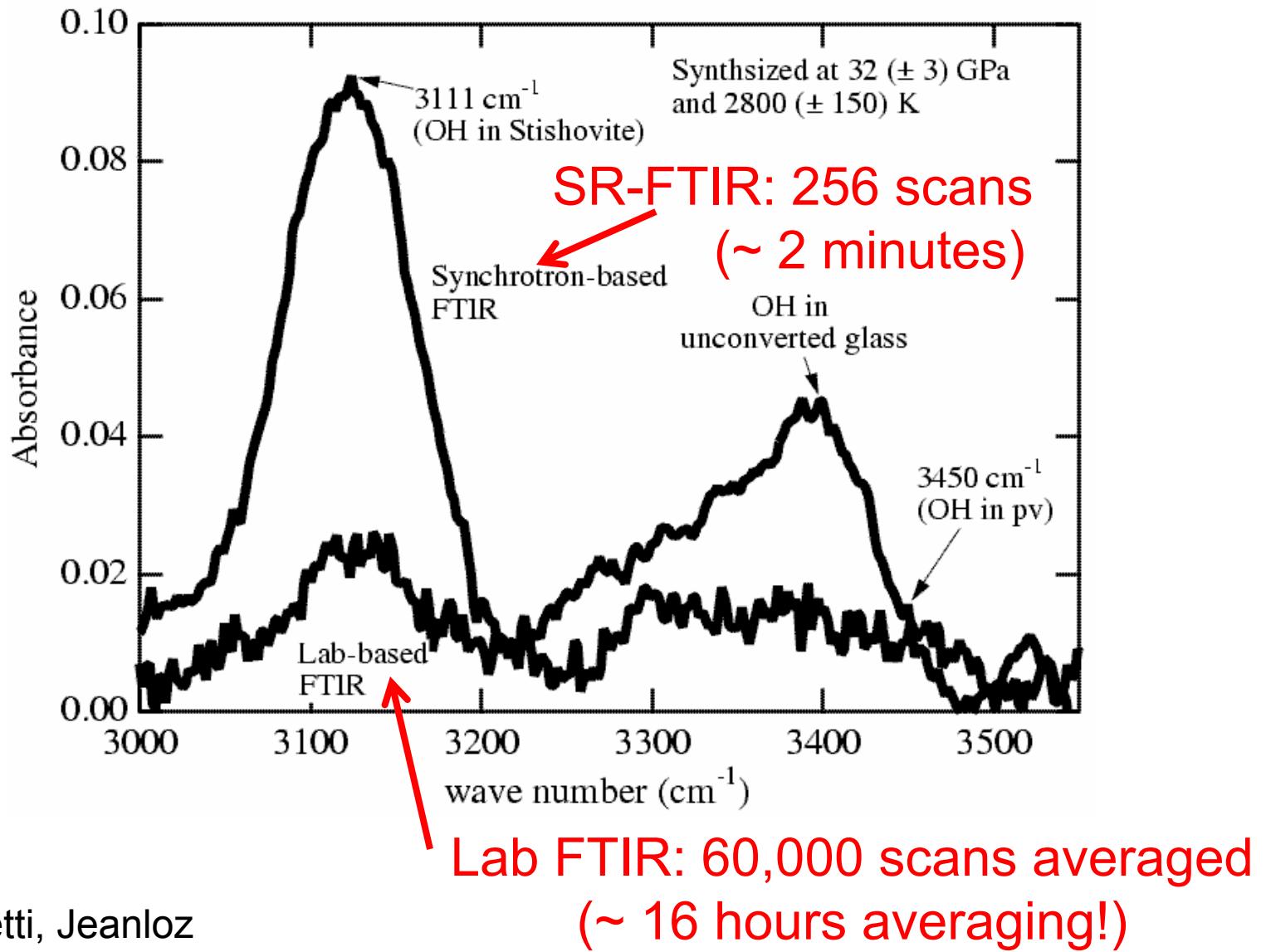
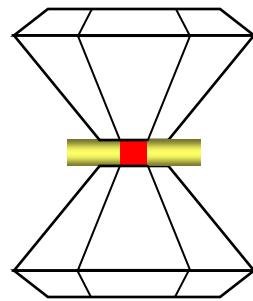
ALS IR Users (2007)



(The ALS IR beamlines are primarily mid-IR microscopy focused. NSLS-II will have this as well as more far-IR capabilities which will broaden the HCM&AP ‘slice’.)

Example of Synchrotron's High Brightness: Geophysics

Mineral sample (ocean basalt) in diamond anvil cell at high pressure (32 GPa)

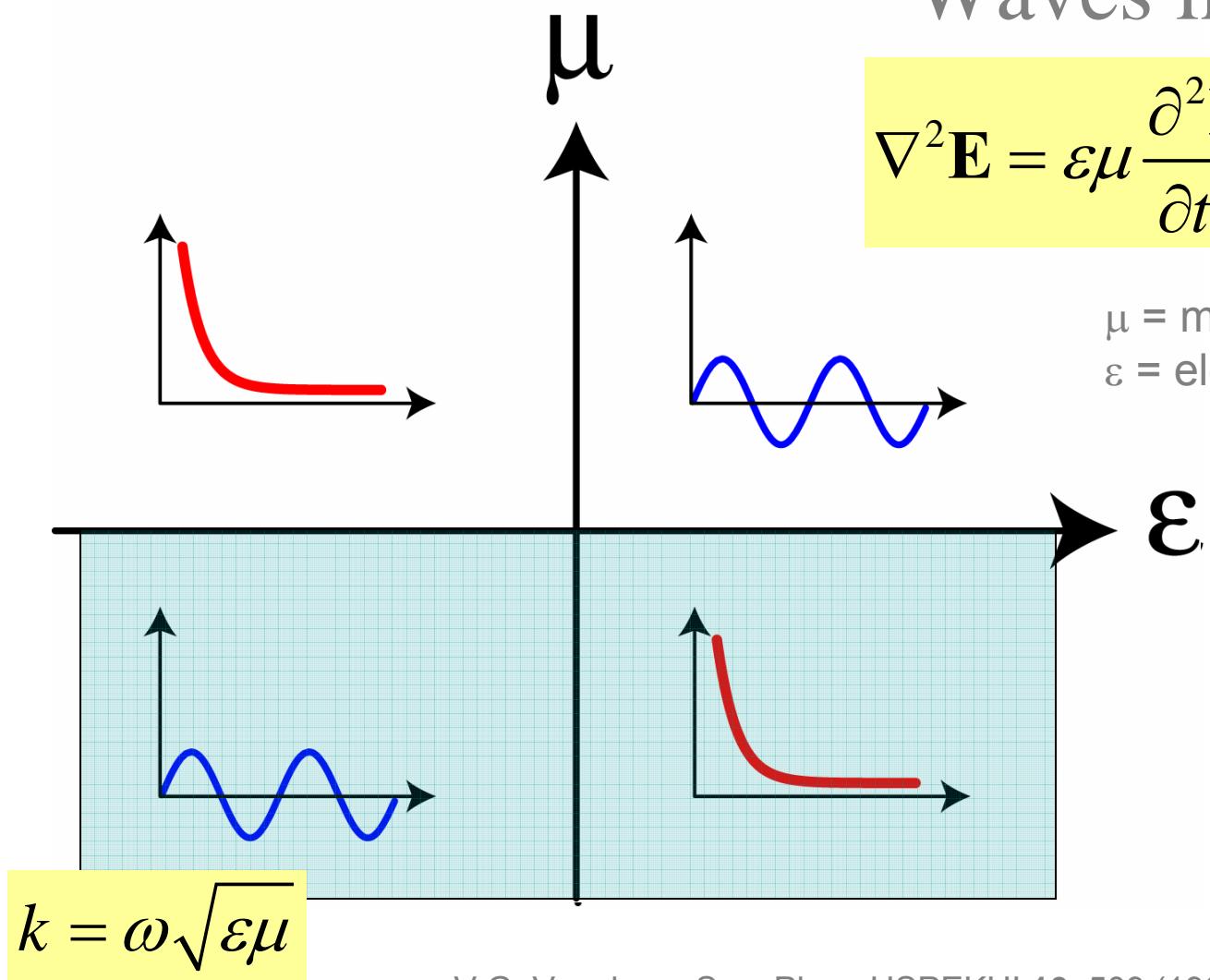


Left Handed Materials

Waves in Media:

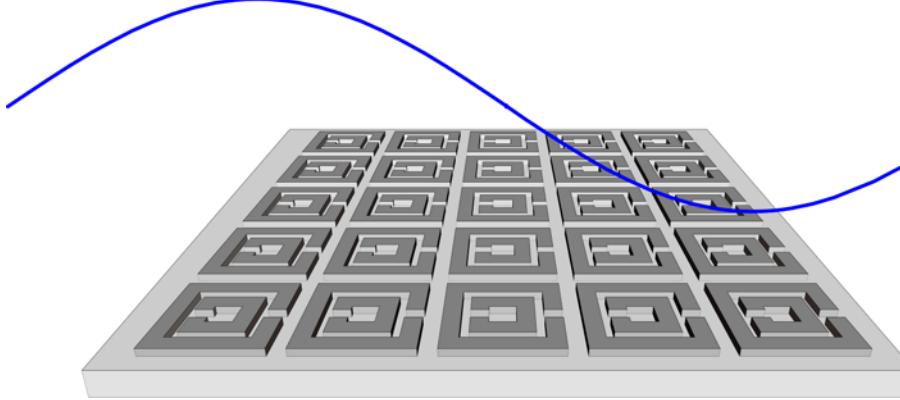
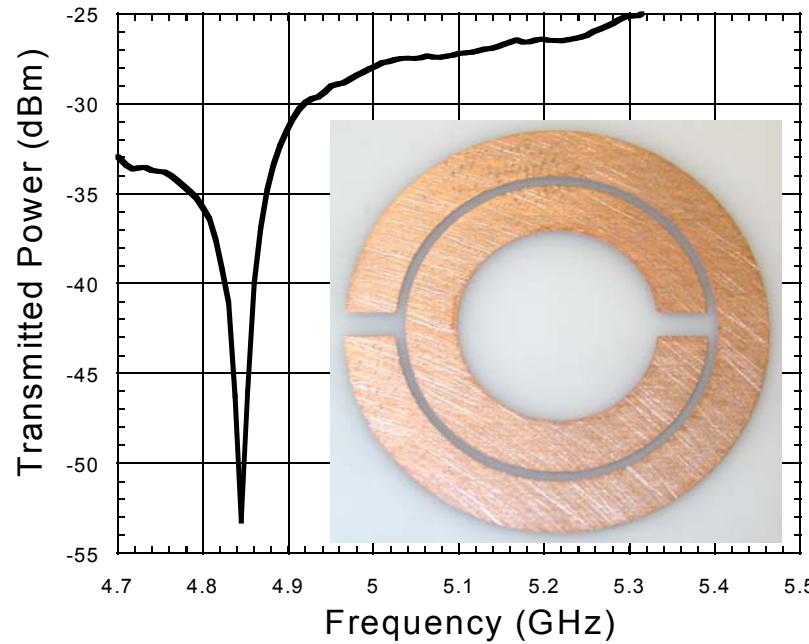
$$\nabla^2 \mathbf{E} = \epsilon \mu \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad n = \sqrt{\epsilon \mu}$$

μ = magnetic permeability
 ϵ = electric permittivity

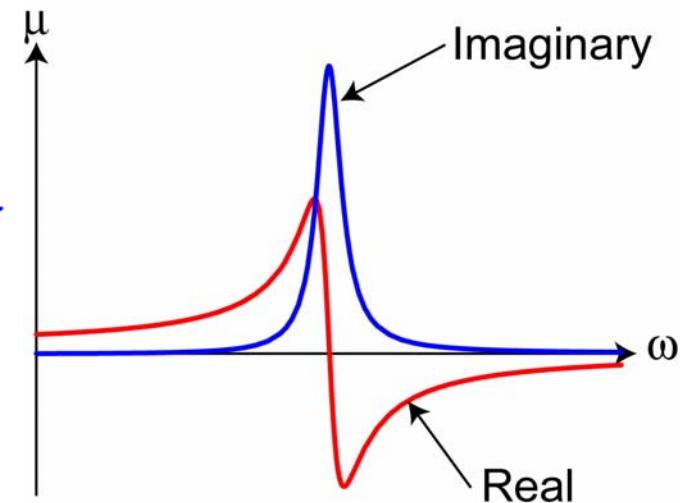


V.G. Veselago, Sov. Phys. USPEKHI **10**, 509 (1968).

A Magnetic “Atom”



Pendry et al. suggested that an array of ring resonators could respond to the magnetic component of incident radiation, displaying an effective negative permeability.



J. B. Pendry, A. J. Holden, D. J. Robbins, W. J. Stewart, “Magnetism from conductors and enhanced non-linear phenomena,” *IEEE Trans. MTT* **47**, 2075 (1999).

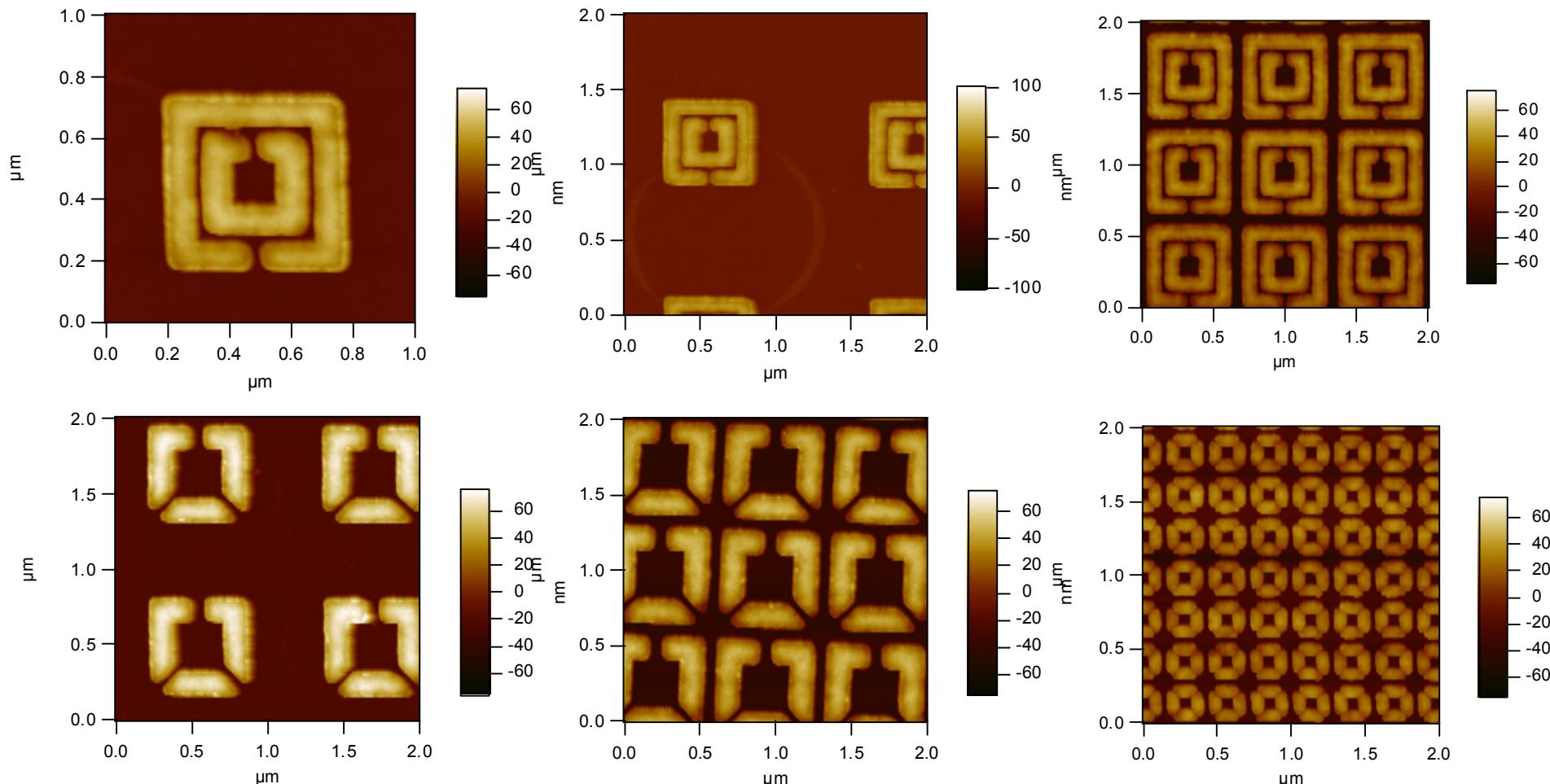
Nano-scale Metamaterials

Zhao Hao¹, Michael C. Martin¹, Bruce Hartneck², Stefano Cabrini², and Erik Anderson³

¹Advanced Light Source Division, ²Molecular Foundry, and ³Center for X-Ray Optics, LBNL

E-beam lithography, gold plated structures, free-standing SiN_x substrate (100 nm thick)

Sample AFM images of various structures:

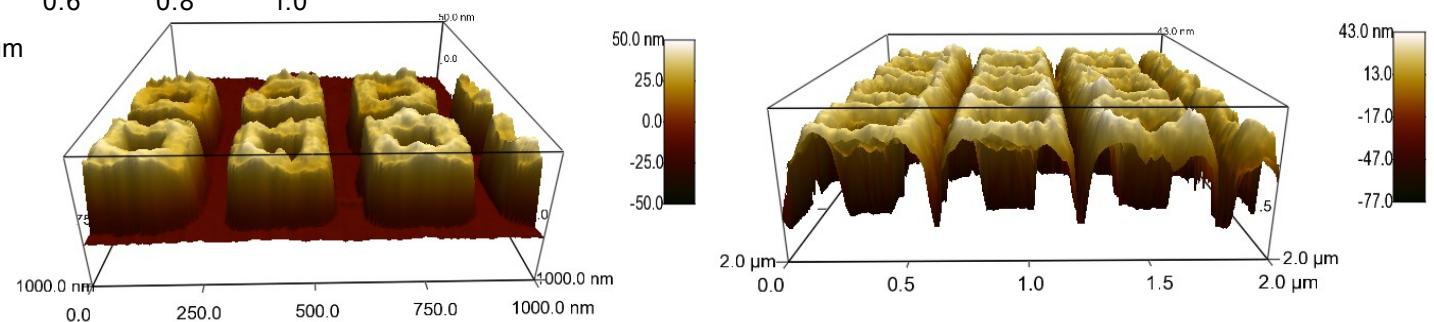
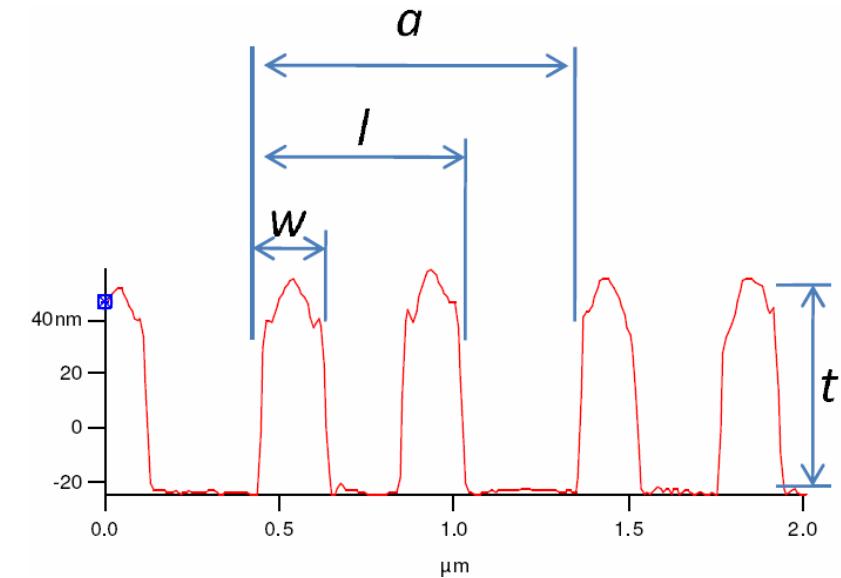
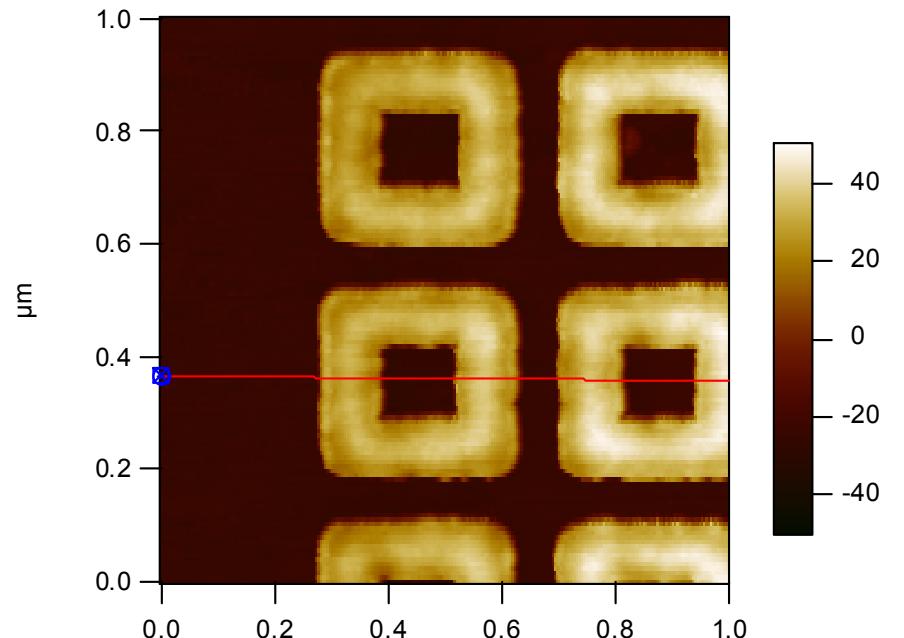


Line widths $w = 40, 60, 100$ nm; Lattice spacing a varies from $6 w$ to $10 w$; thickness $t \approx w$

Closed Ring Structures



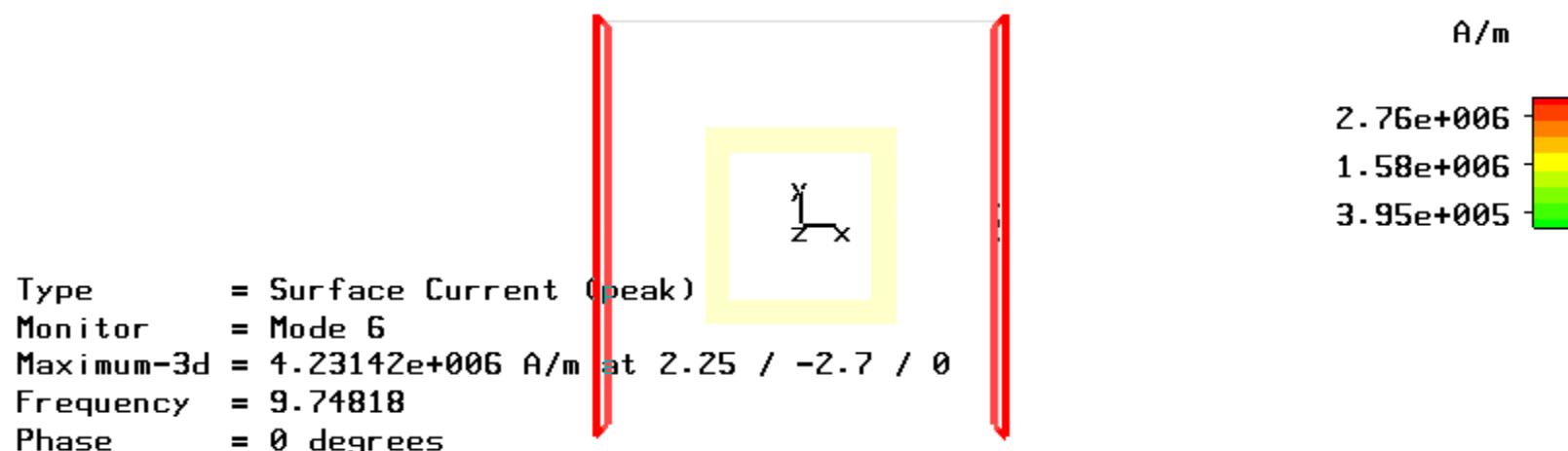
E-beam lithography, gold plated structures, free-standing SiN_x substrate (100 nm thick)
Sample AFM images of structures:



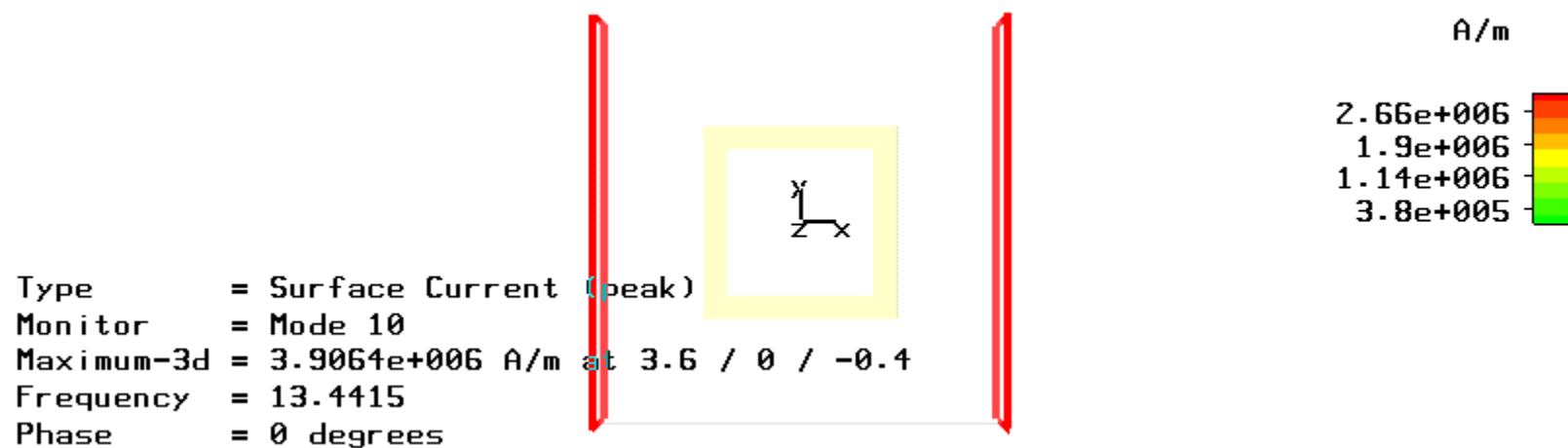
Z. Hao *et al.*, *Appl. Phys. Lett.* **91**, 253119 (2007).

Line widths $w = 40, 60, 100$ nm; Lattice spacing a varies from $6 w$ to $10 w$; thickness $t \approx w$

E1 surface current distribution



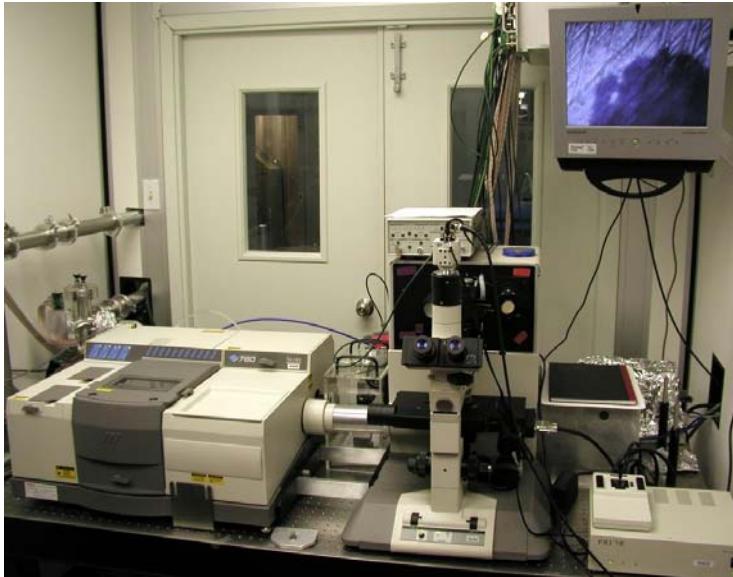
M1 surface current distribution



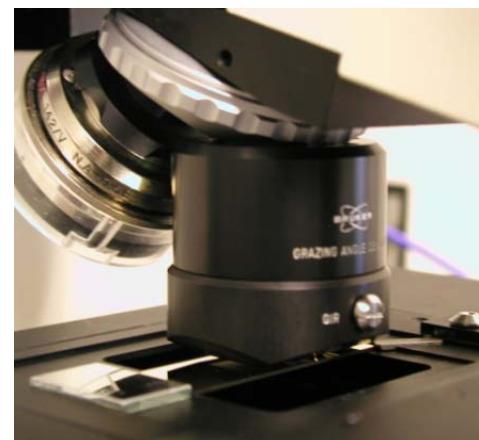
Measurement Setup



FTIR spectromicroscopy at ALS synchrotron BL1.4.3 and BL1.4.4



“Normal” Incidence
Objective:
 $\sim 26 \pm 8$ degree

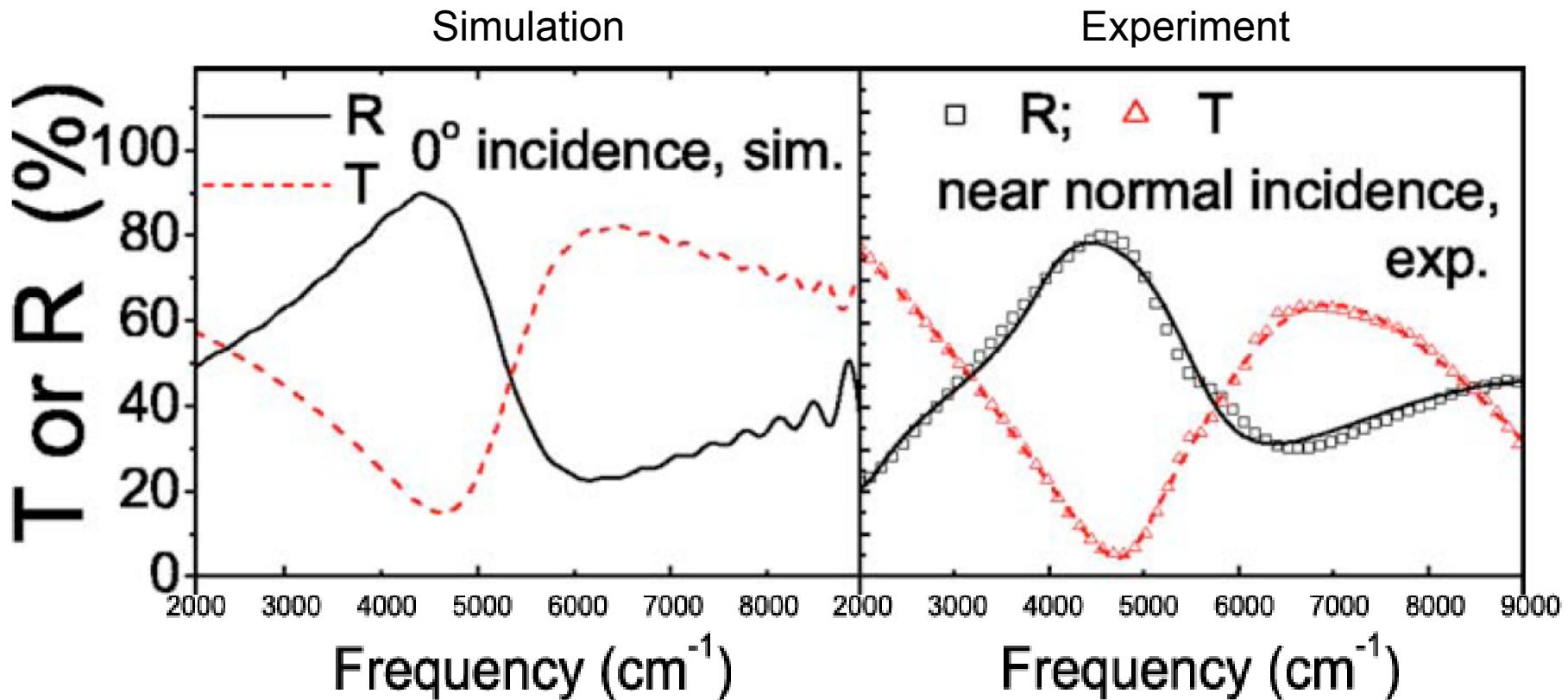
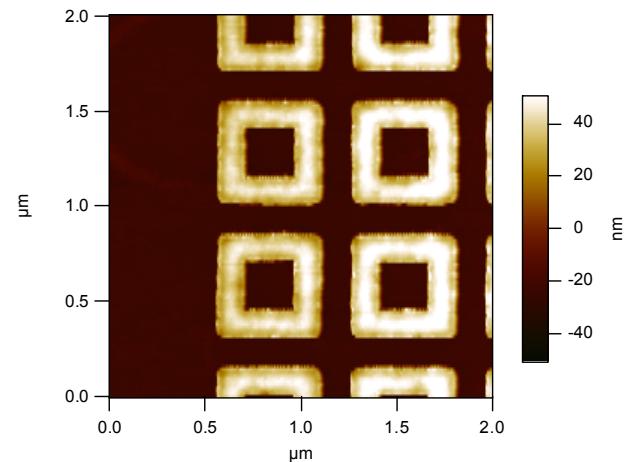


Grazing Angle
Objective:
 ~ 85 degree

With full input/output polarization control

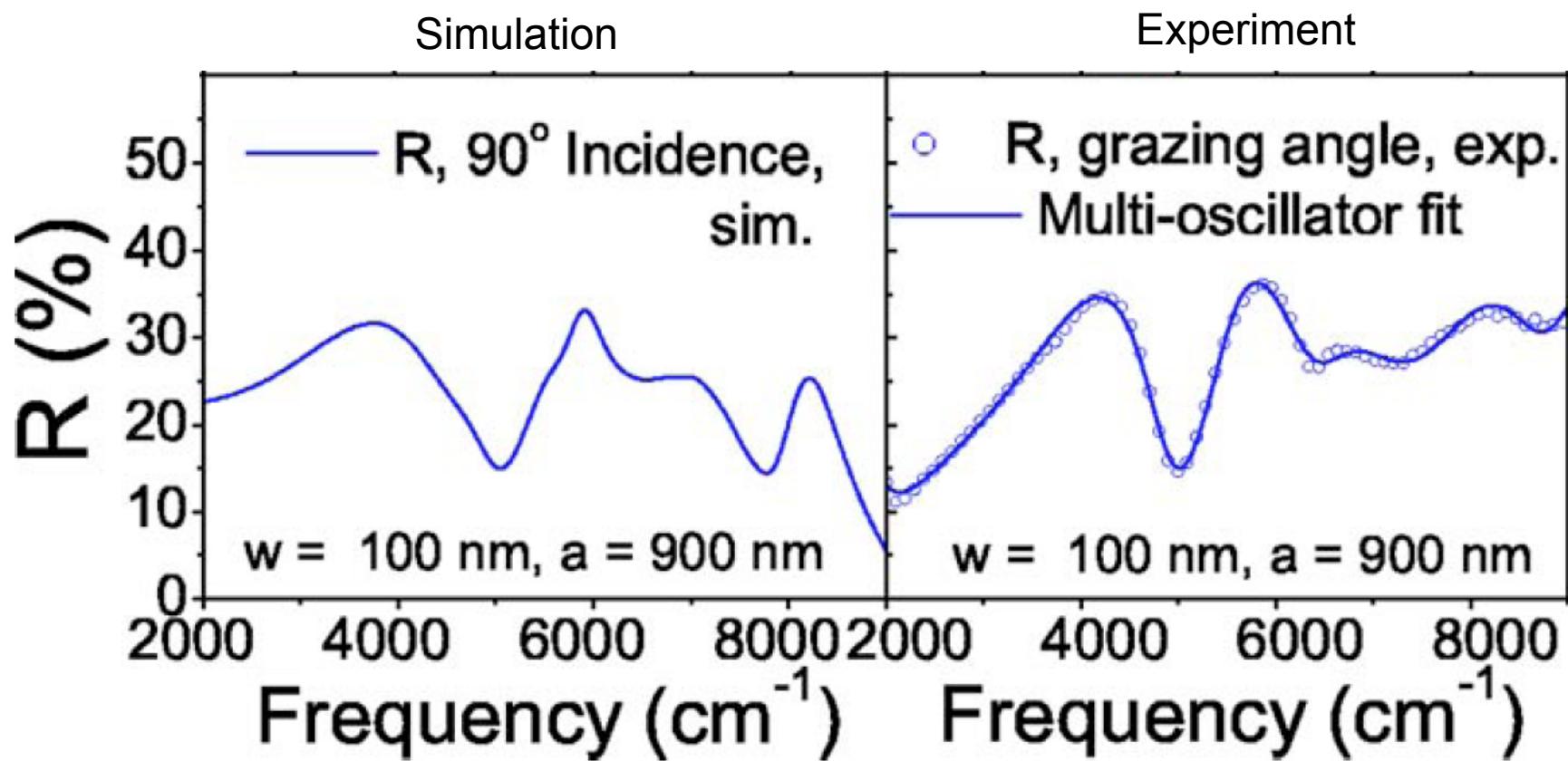
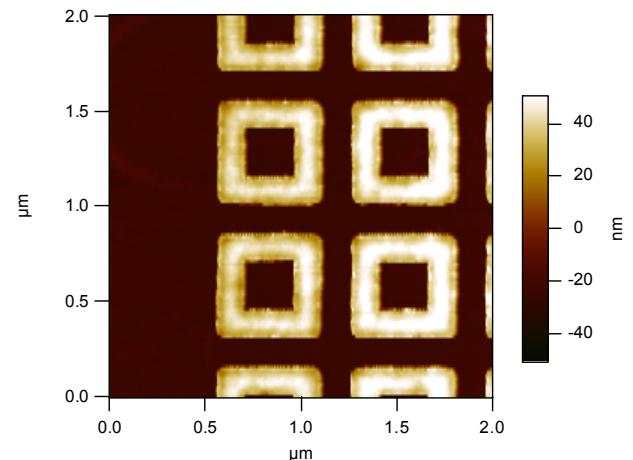
Near-normal incidence

w=100 nm, l=500 nm, a=900 nm and t=73nm,
on 100 nm thick free-standing SiN_x membrane

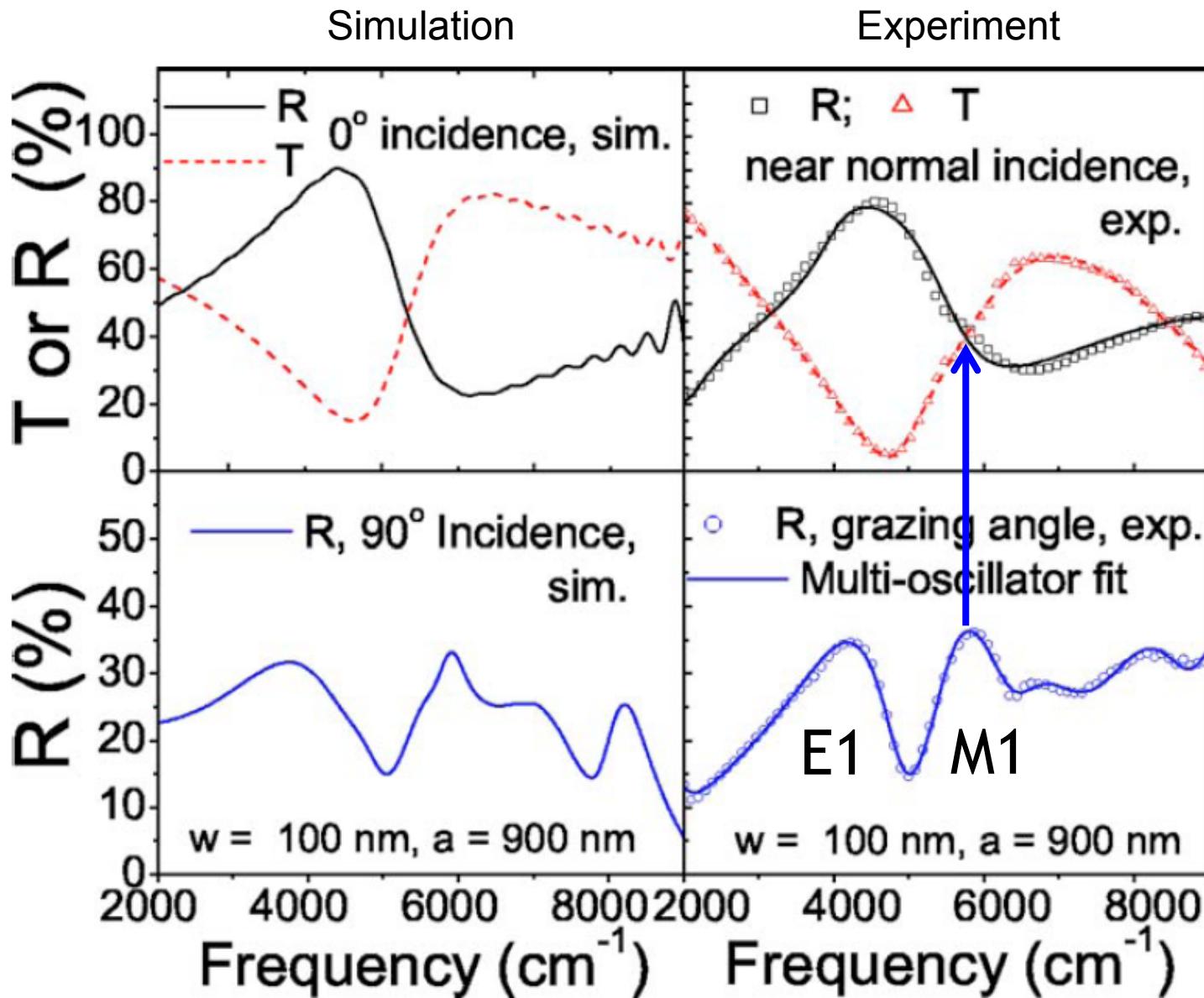


Grazing incidence

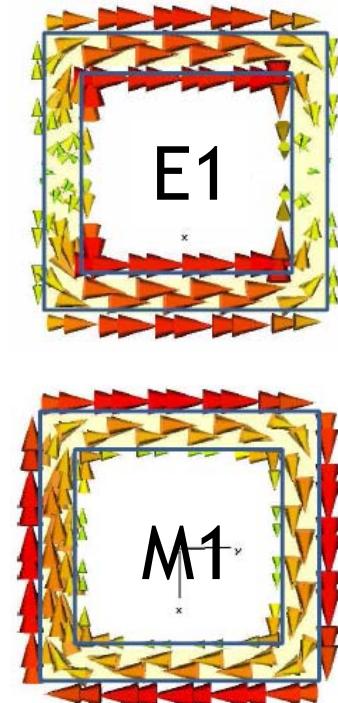
w=100 nm, l=500 nm, a=900 nm and t=73nm,
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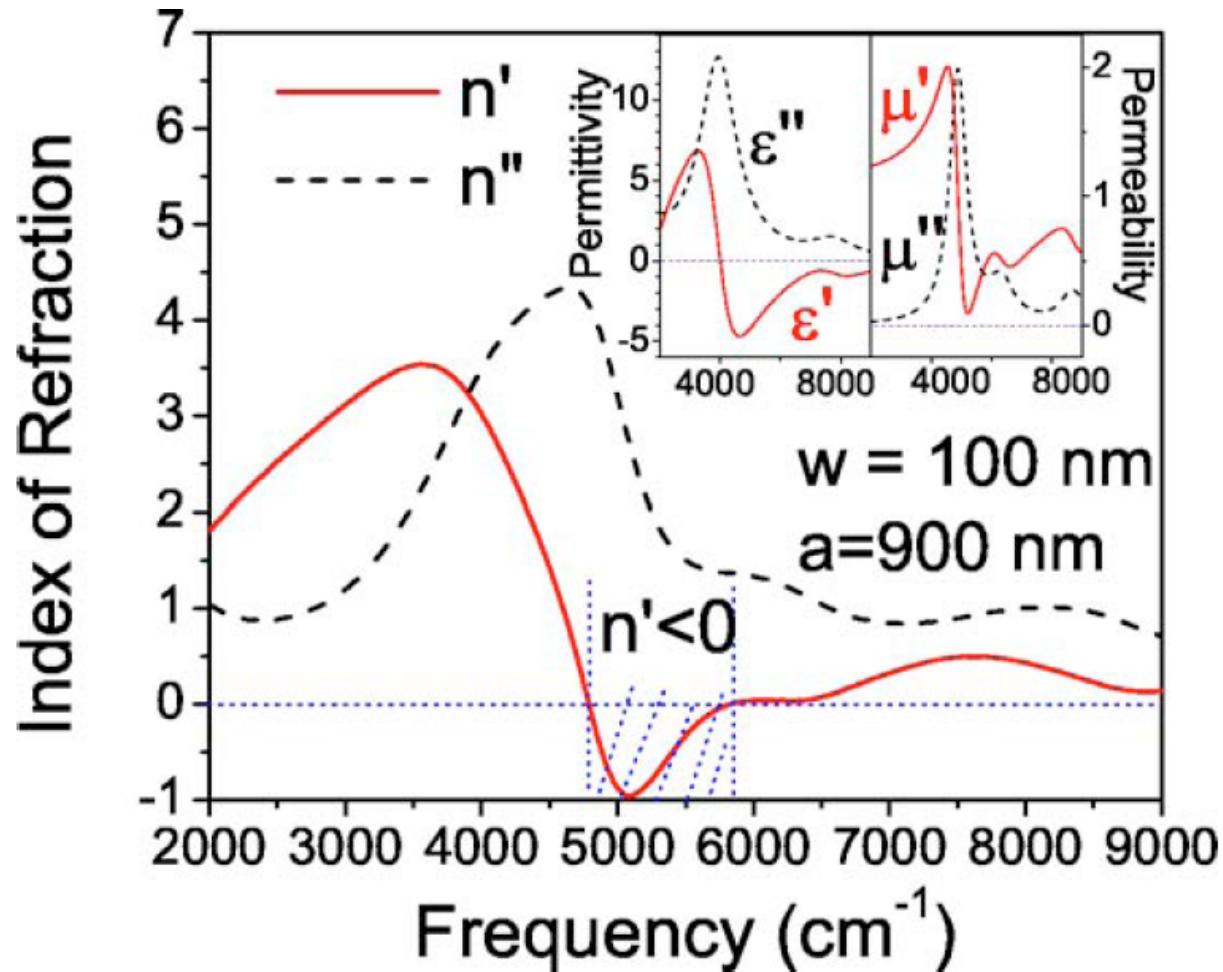
Compare Normal & Grazing



We can see that our 26 degrees “near-normal” incidence measurement includes some M1 seen in grazing incidence



Complex Index of Refraction



Z. Hao *et al.*, *Appl. Phys. Lett.*
91, 253119 (2007).

Negative index is achieved
where E1 and M1 overlap.

$5000 \text{ cm}^{-1} = 2 \mu\text{m wavelength} = 152 \text{ THz}$

Infrared Imaging of Charge Injection in Organic Field-Effect Transistors

Zhiqiang Li, Dimitri Basov

University of California, San Diego

Zhao Hao, Michael C. Martin

Advanced Light Source, Berkeley



Support:

Collaborators:

G. M. Wang

D. Moses

A. J. Heeger
(UCSB)

V. Podzorov

M.E. Gershenson
(Rutgers)

N.Sai

D. Meyertholen

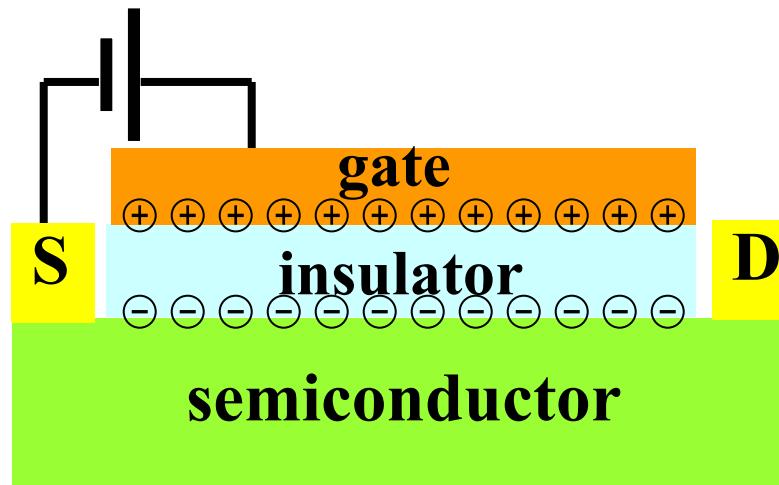
M. M. Fogler

M. Di Ventra
(UCSD)

FET principle

FET is ubiquitous

$\sim 10^{18}$ Si FETs manufactured every year
($> 10^8$ per person!)



Carrier density → conductance

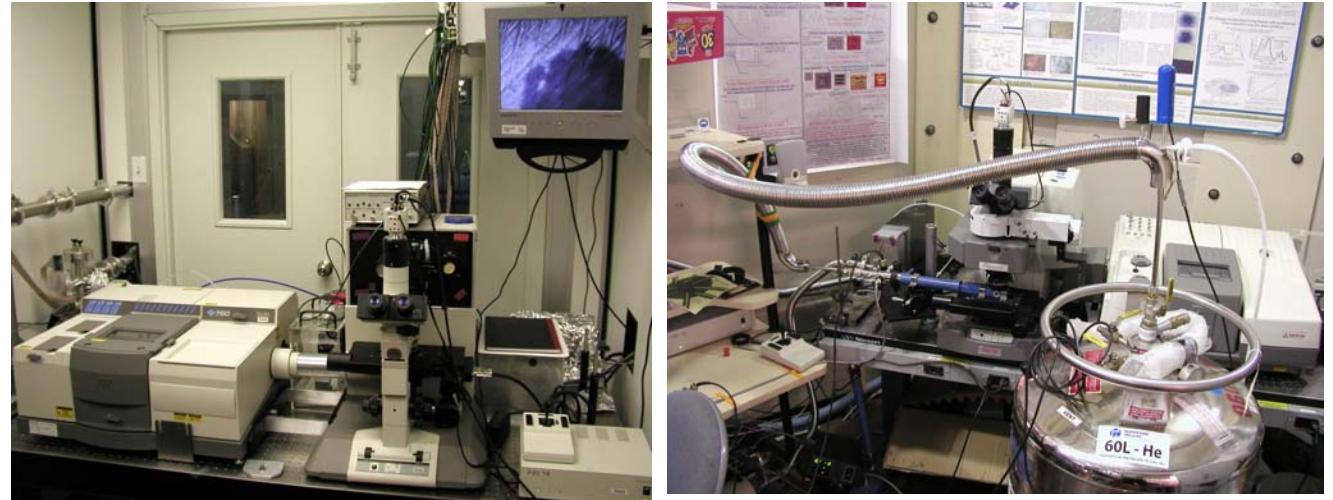
IR spectromicroscopy of FETs

1: Broad energy range.

Sub-THz THz Far-IR Mid-IR Near-IR visible/UV

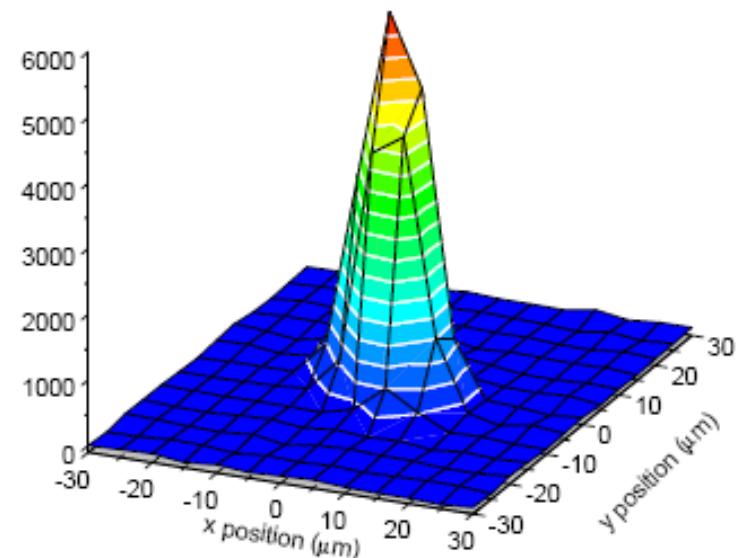
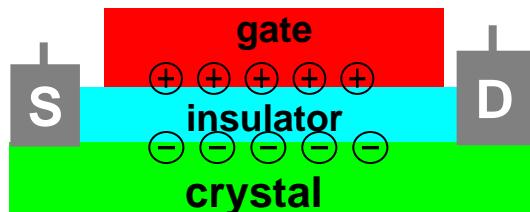
ALS IR Beamline 1.4

UCSD Basov lab

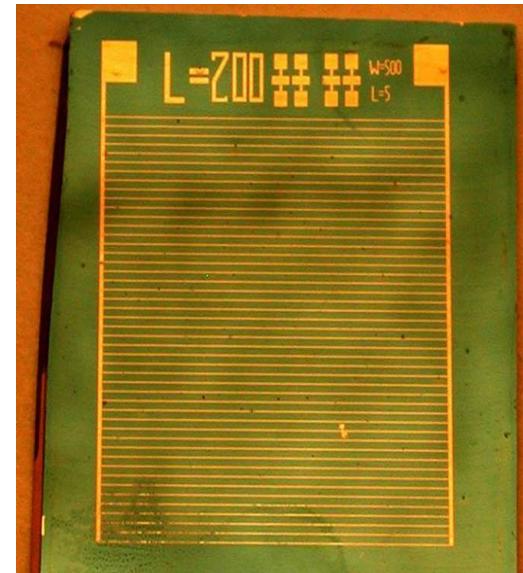
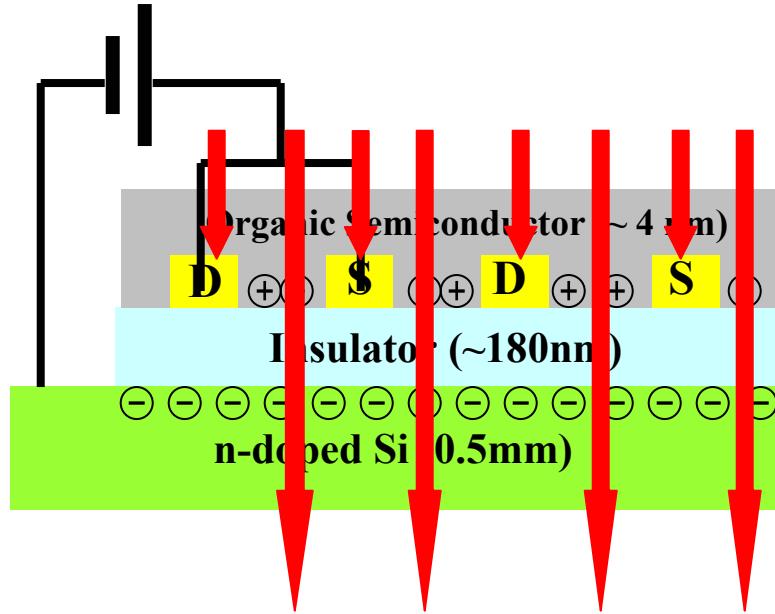


2: High spatial resolution,
high brightness.

ALS IR Beamline 1.4



Large area FET devices



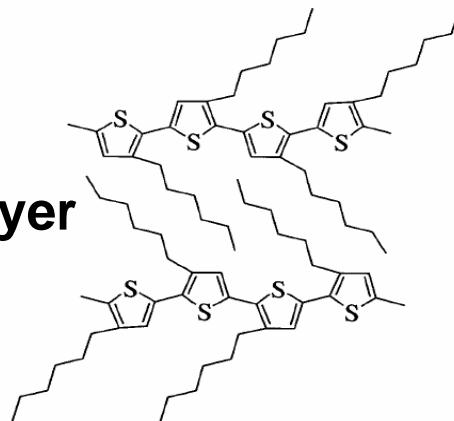
Organic conductor:
Poly(3-hexylthiophene) (P3HT)

Transmission as a function of gate voltage

$$T(\omega, V_{GS})$$

Direct probe of very thin charge accumulation layer

Insulator TiO_2 or SiO_2



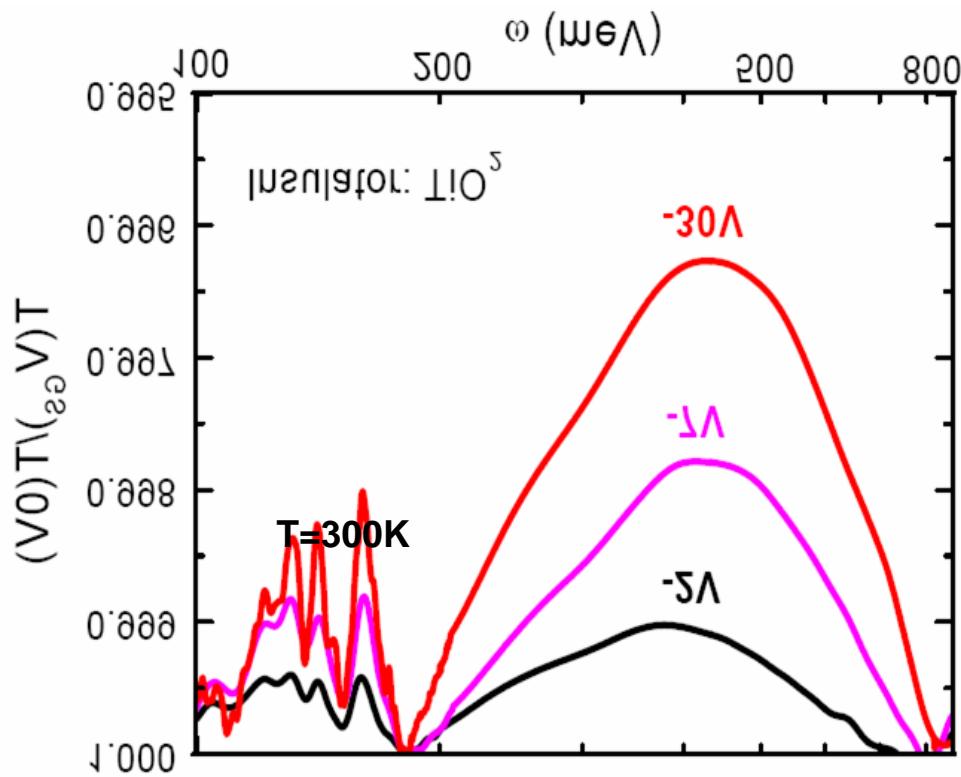
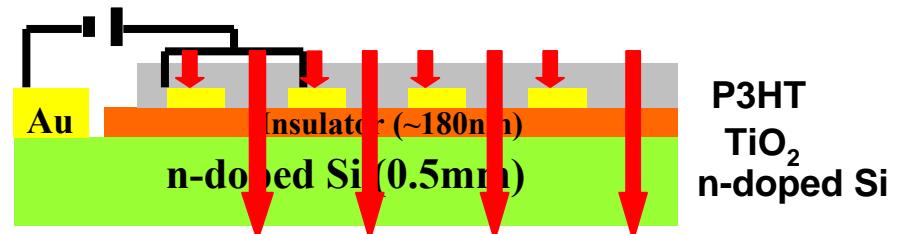
Z.Q. Li, et al, *Nano Letters* 6, 224 (2006).
Z.Q. Li, et al, *Appl. Phys. Lett.* 86, 223506 (2005).

FET mobility: up to $0.7 \text{ cm}^2/\text{V s}$

IR spectroscopy of charge injection in P3HT

Voltage induced absorption:

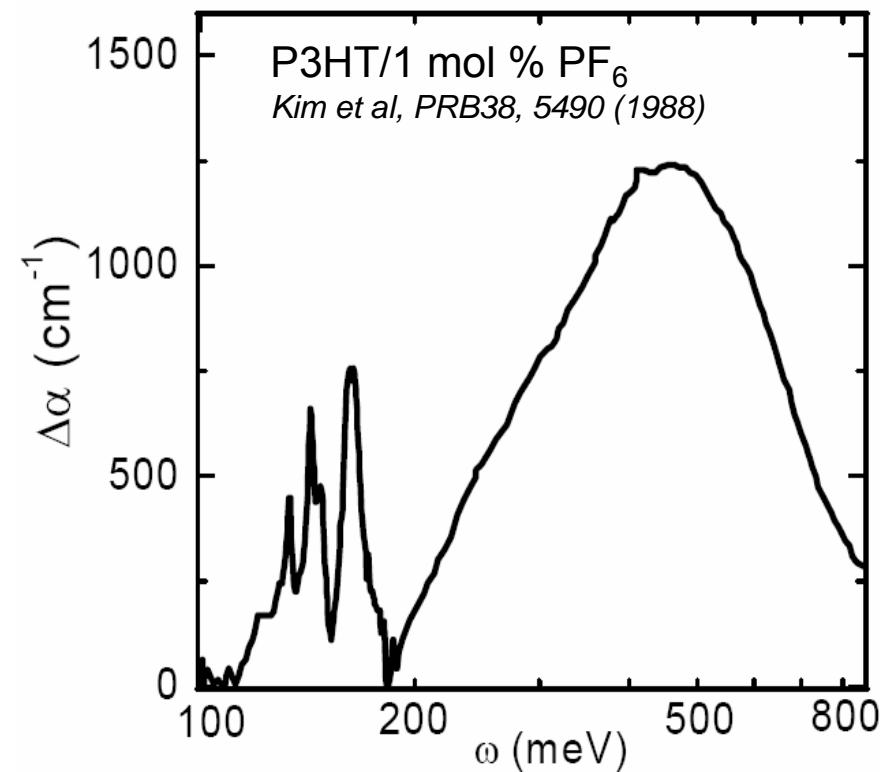
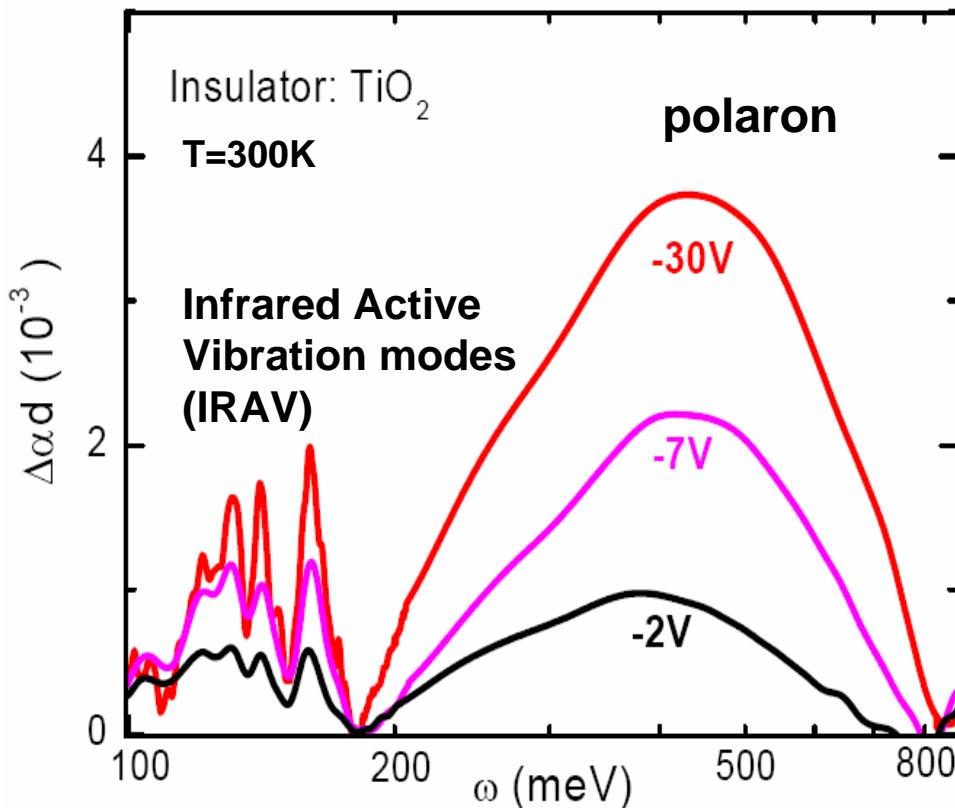
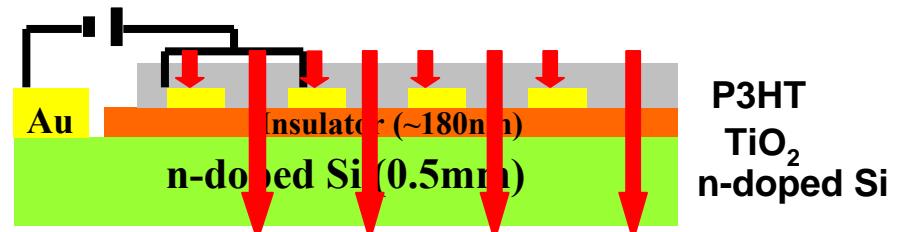
$$\Delta\alpha d \sim 1 - T(V)/T(0V)$$



Electronic excitations in P3HT FET

Voltage induced absorption:

$$\Delta\alpha d \sim 1 - T(V)/T(0V)$$

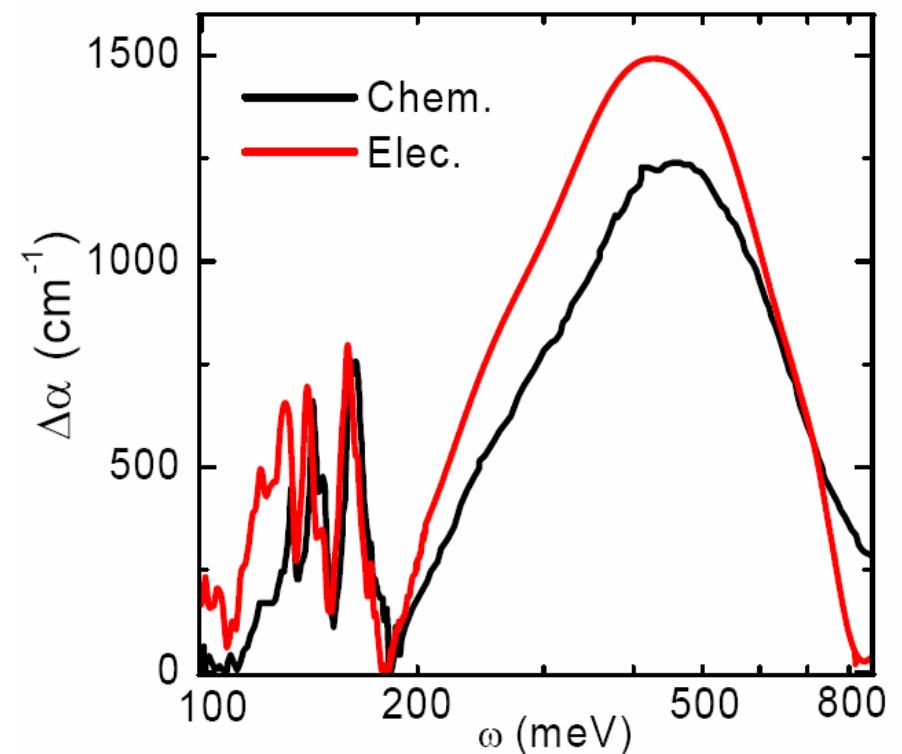
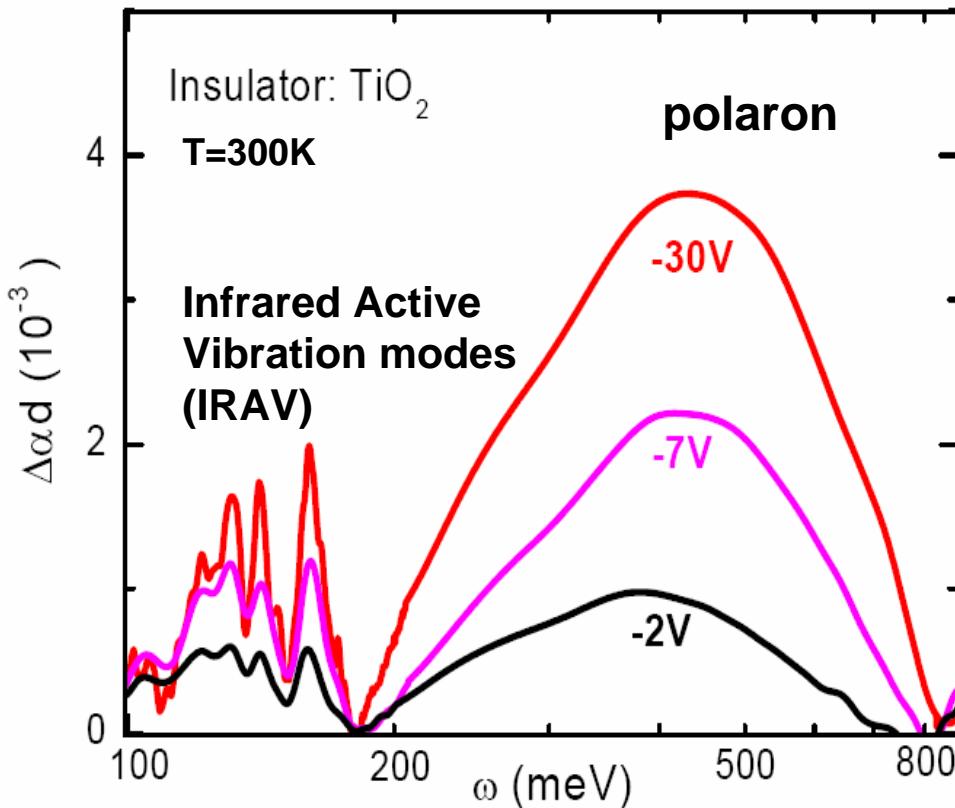
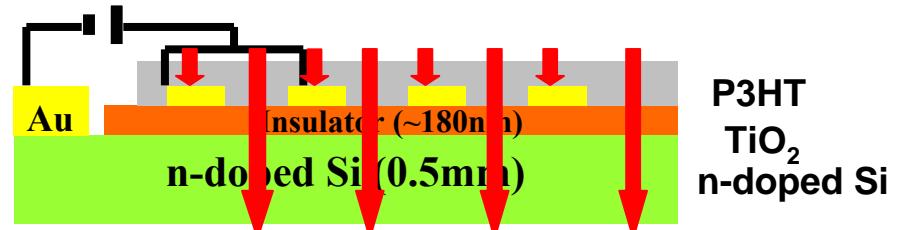


Z.Q. Li, et al, Nano Letters 6, 224 (2006).

Electronic excitations in P3HT FET

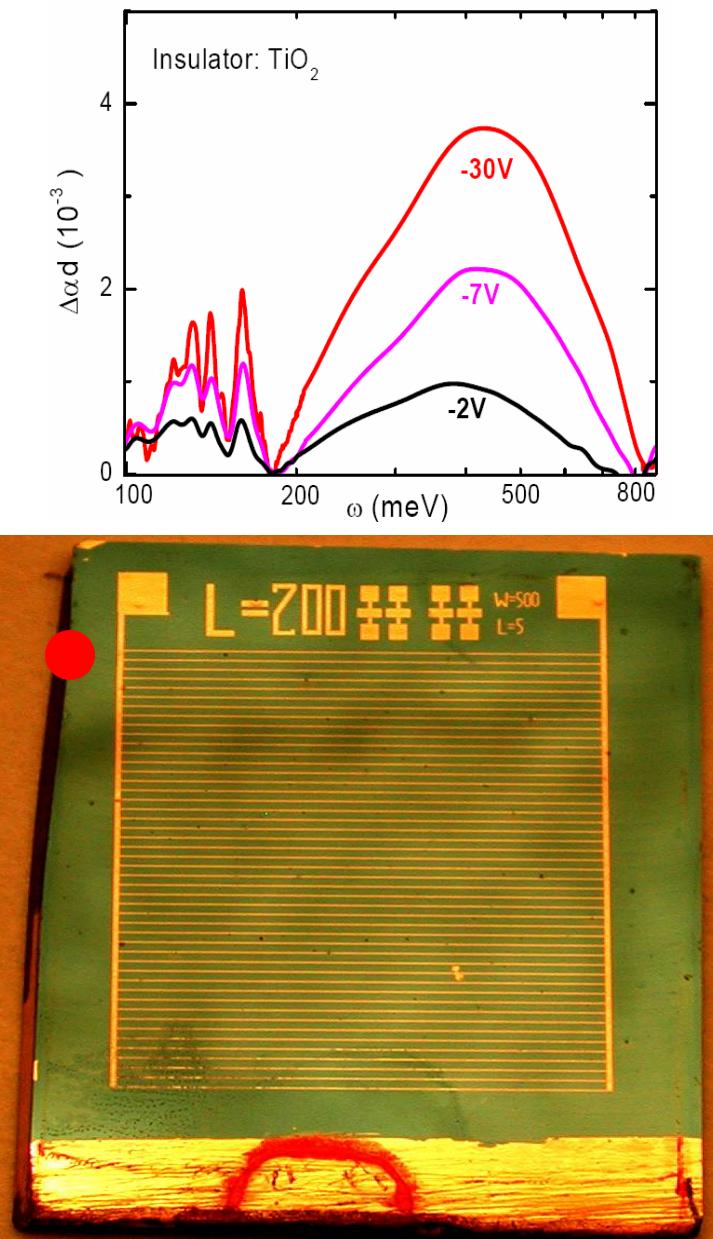
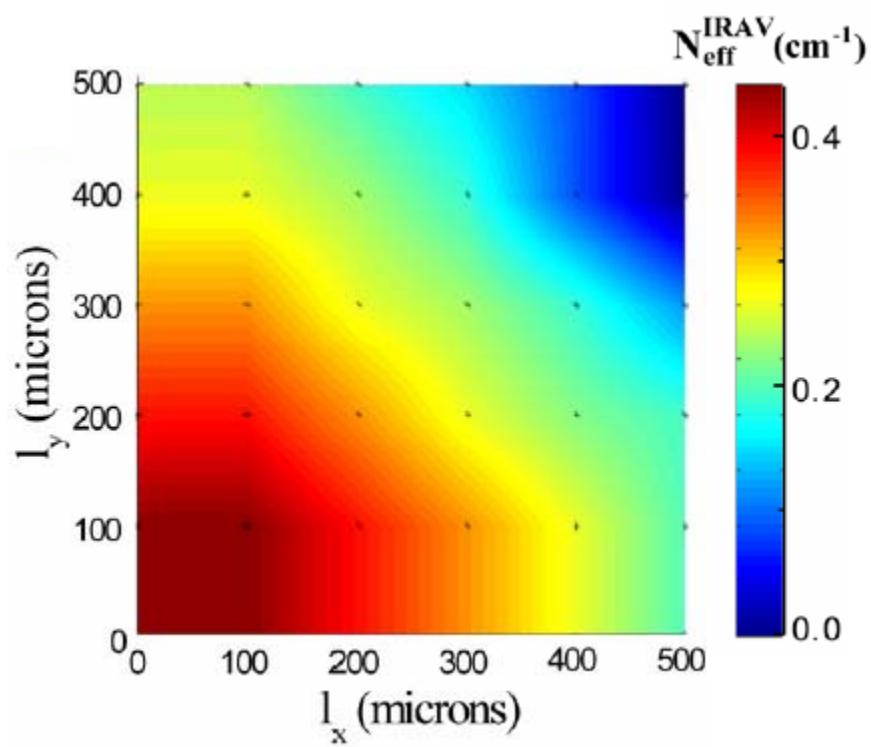
Voltage induced absorption:

$$\Delta\alpha d \sim 1 - T(V)/T(0V)$$

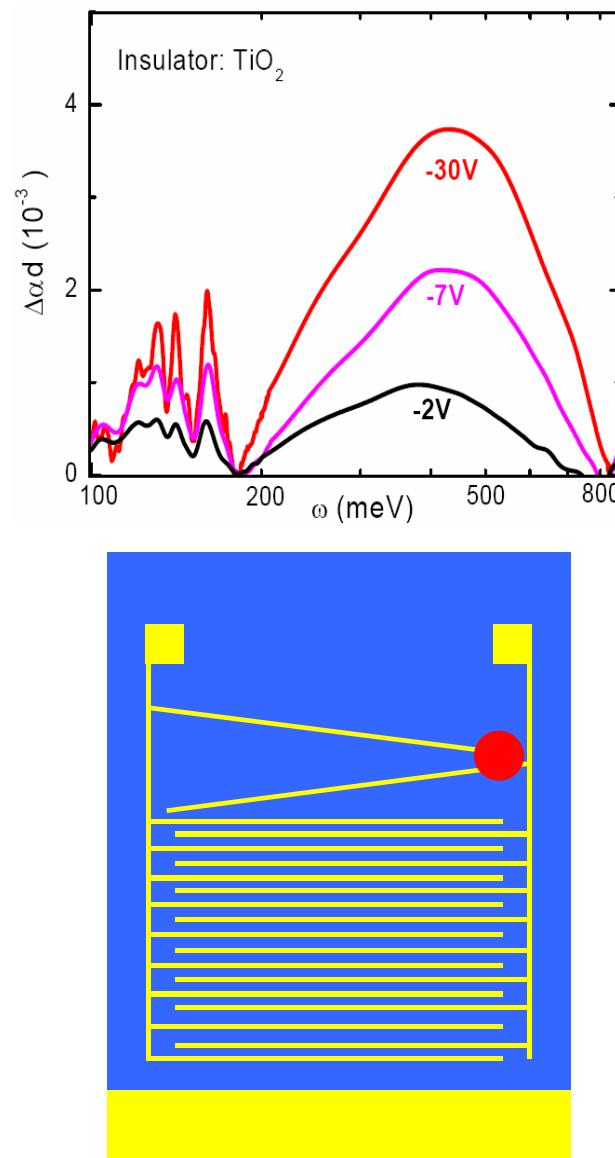
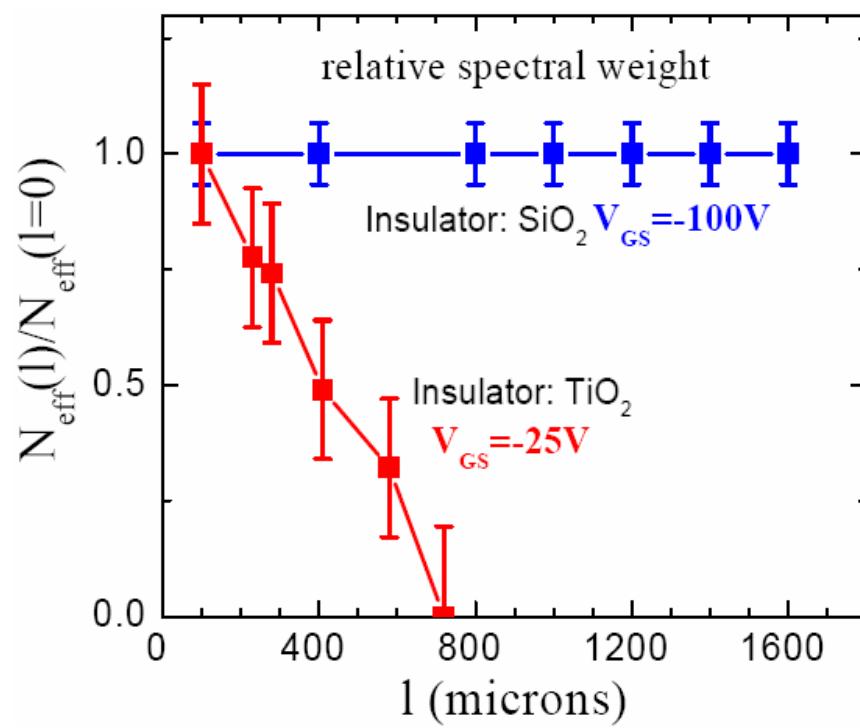


Z.Q. Li, et al, Nano Letters 6, 224 (2006).

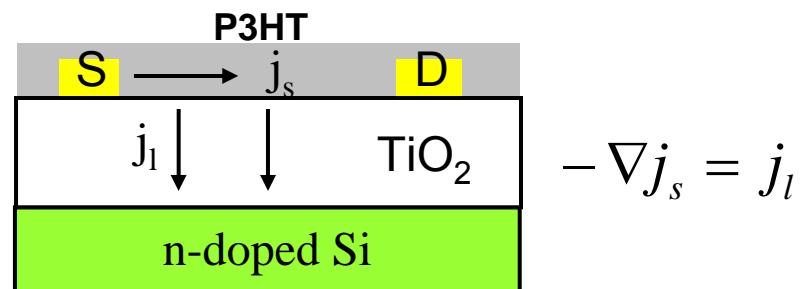
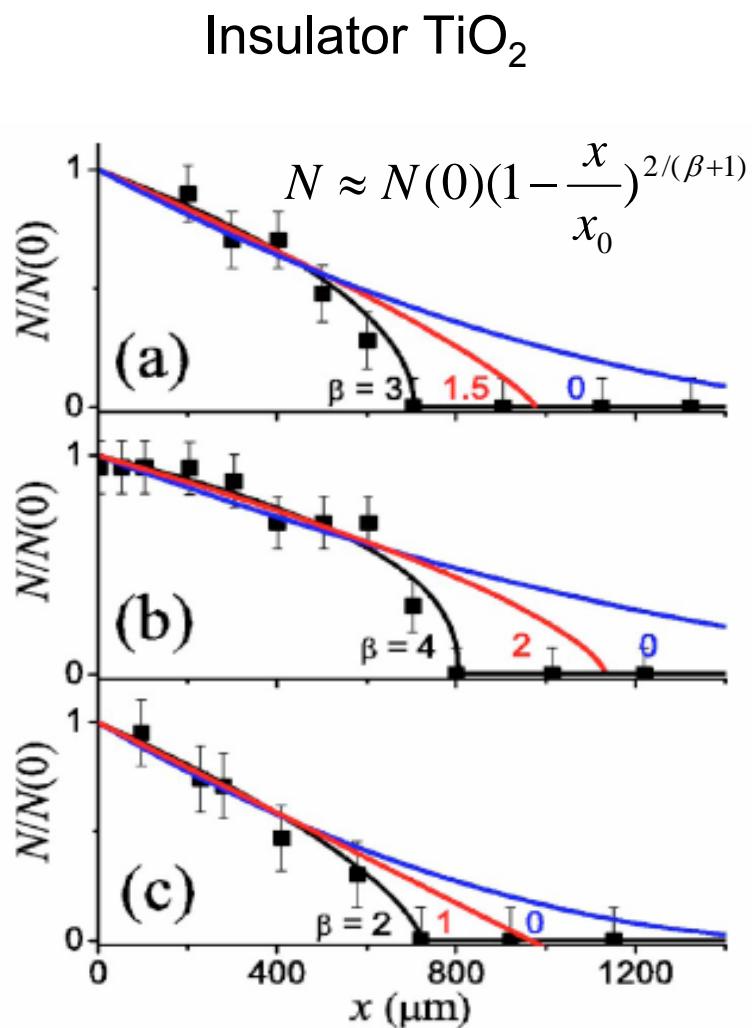
Microscopic study of charge injection



Microscopic study of charge injection

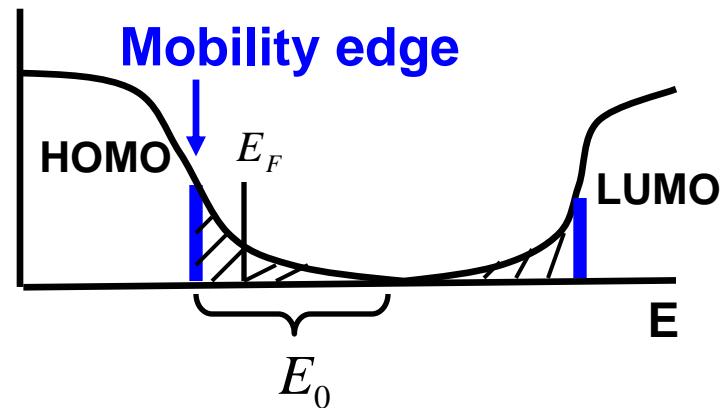


Microscopic study of charge injection



$$\nabla(N\nabla N) = N / (e\mu\rho_l)$$

DOS



Charge-induced localized states: bipolarons

$$\mu \sim N^\beta$$

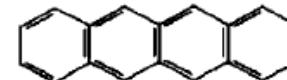
$$\beta = E_0 / k_B T - 1 \geq 0$$

A. D. Meyertholen, et al., Appl. Phys. Lett. 90, 222108 (2007).
N. Sai, et al., Phys. Rev. B 75, 045307 (2007).

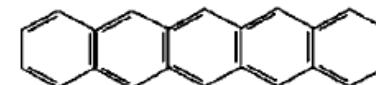
Charge transport in organic molecular crystals

**Small molecule organic
semiconductors:**

Tetracene

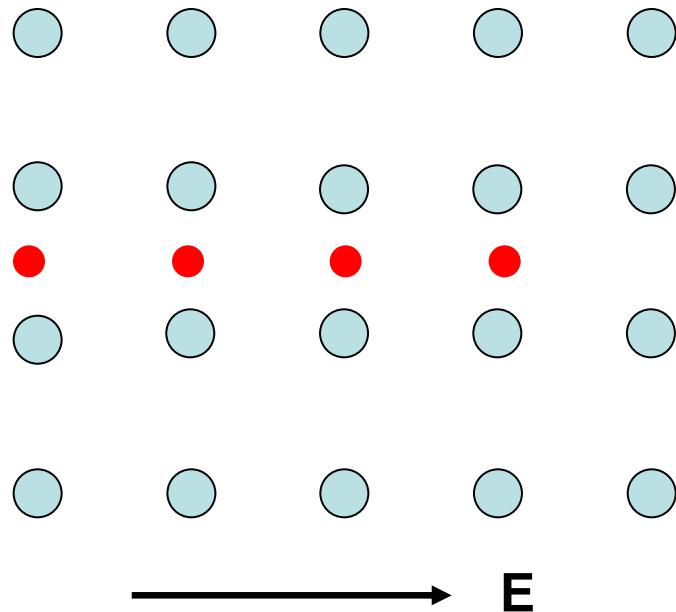


Pentacene



What is the nature of excitations responsible for charge transport?

Small polarons



Effective mass:

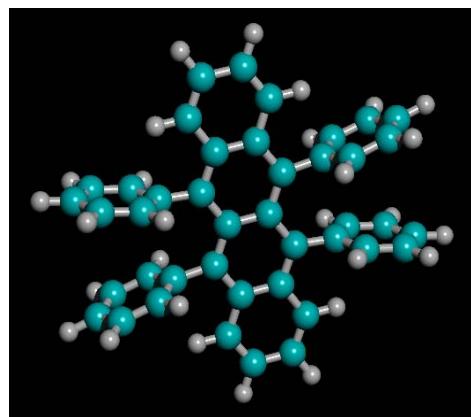
10-1000 band mass

E. A. Silinsh & V. Capek
(AIP Press, New York, 1994).

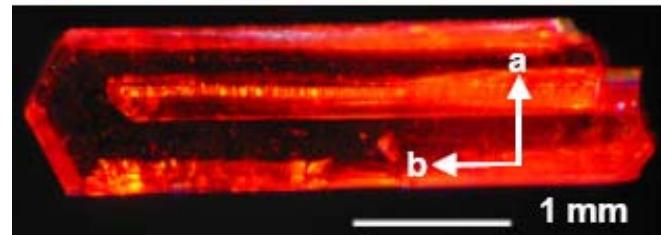
M. Pope, & C. E. Swenberg
(Oxford University Press, New York,
London, 1999).

IR study of single crystal rubrene FETs

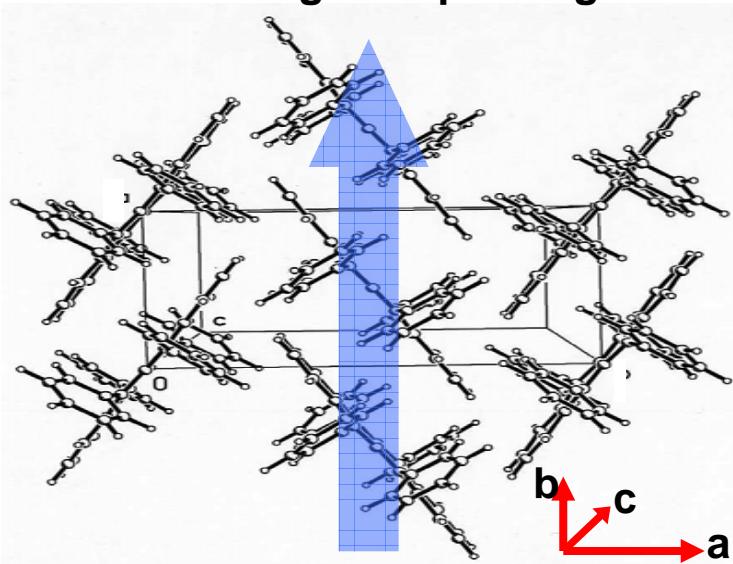
Rubrene: $C_{42}H_{28}$



V. Podzorov, et al, APL 82, 1739 (2003).

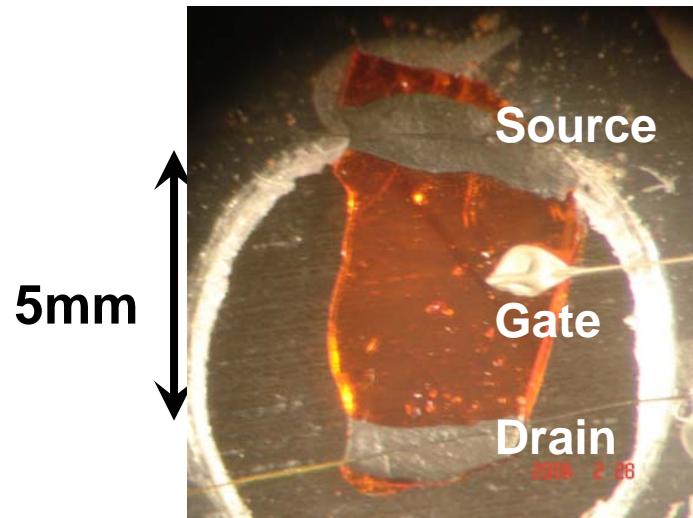


herringbone packing



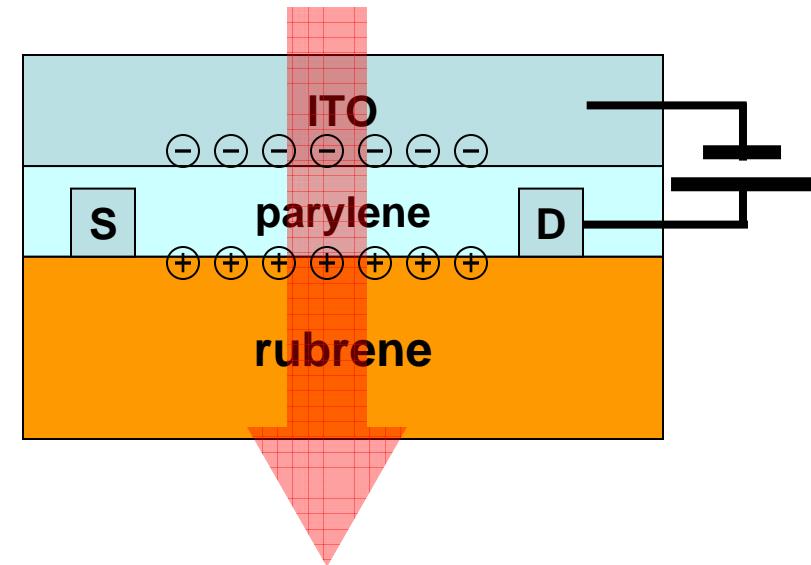
M. E. Gershenson et al, Rev. Mod. Phys. 78, 973 (2006).
V. Podzorov et al, PRL 93, 086602 (2004).

IR study of single crystal rubrene FETs



b axis $\mu \approx 5 \text{ cm}^2 / \text{Vs}$

ITO = Indium Tin Oxide

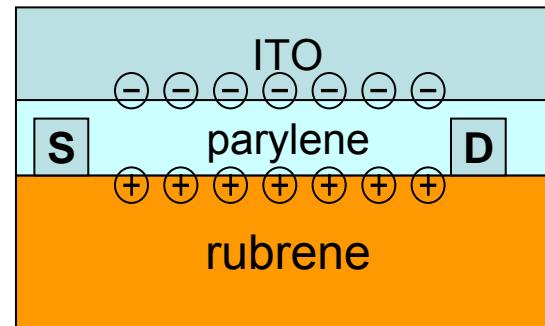
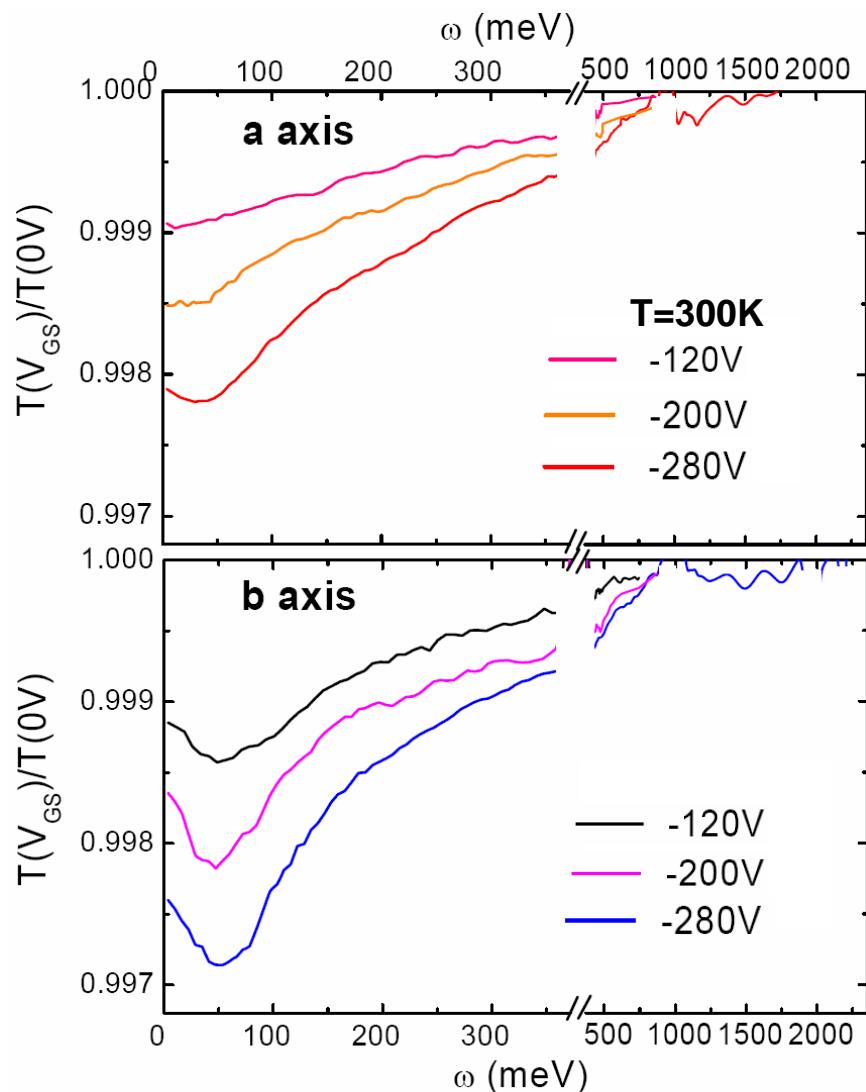


Transmission as a function of gate voltage

$$T(\omega, V_{GS})$$

Z.Q. Li, et al, PRL 99, 016403 (2007) .

IR response of rubrene FETs

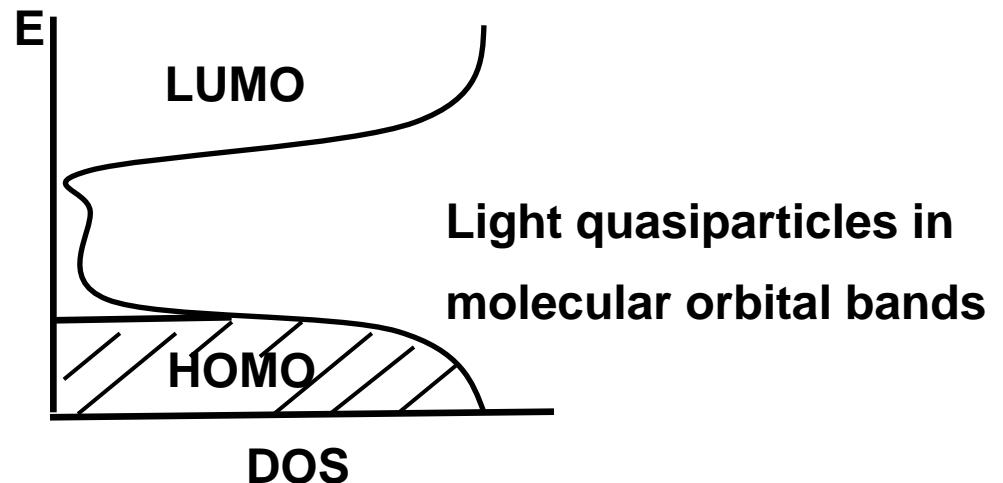
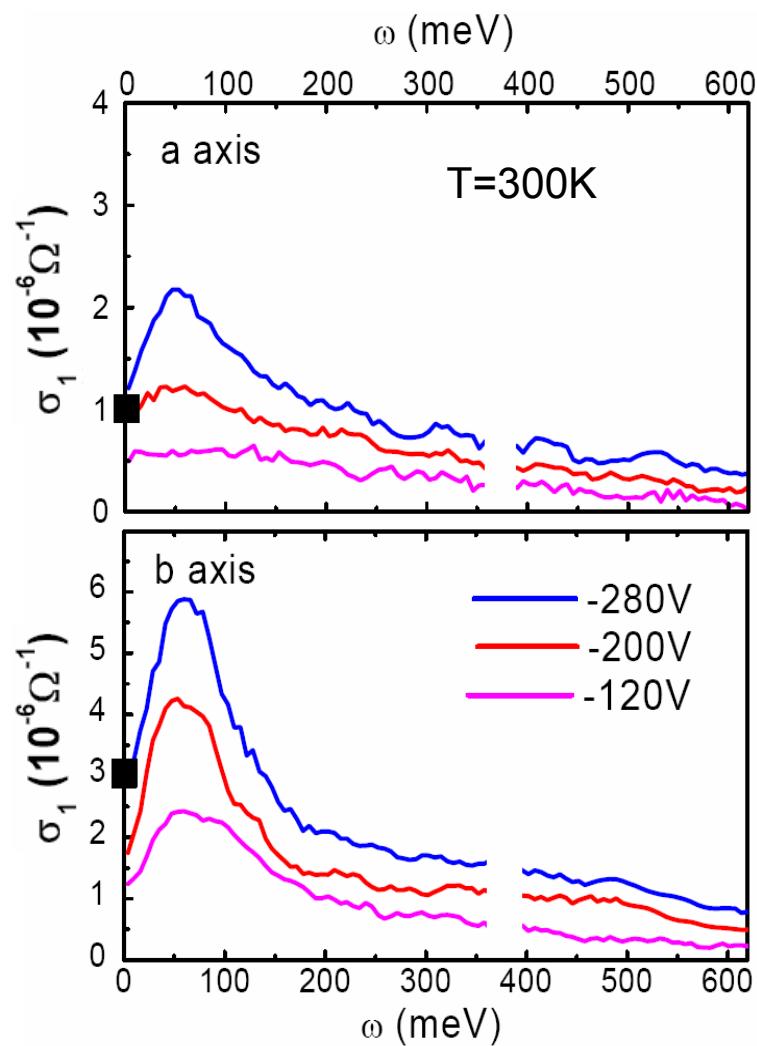


**(1) Reflection, transmission
and ellipsometric measurements**

(2) Multi-layer modeling

**Optical constants of the
accumulation layer in rubrene**

Charge transport in rubrene FETs



- 1: No low-energy gap in the optical conductivity
- 2: Anisotropy of transport properties and optical conductivity.
- 3: Small values of effective masses

$$\frac{n_{2D}}{m^*} = \frac{2}{\pi e^2} \int_0^{\Omega_c} \sigma_I(\omega) d\omega$$

$$m_a^* \approx 1.85 m_e \quad m_b^* \approx 0.80 m_e$$

No prominent polaronic effects at 300K.

Spectroscopy and Charge Injection in Graphene

Zhiqiang Li, Dimitri Basov
University of California, San Diego



**Eric A. Henriksen, Z. Jiang, P.
Kim, H. L. Stormer**

Columbia University, New York
National High Magnetic Field Lab, Tallahassee
Bell Labs, Alcatel-Lucent, Murray Hill



Zhao Hao, Michael C. Martin
Advanced Light Source, Berkeley



[Data to be published soon ...]

Synchrotron FTIR and HCM&MP



Synchrotron FTIR

- Microscopy on small samples or effect regions
- Broad optical conductivity capabilities
- Combined with:
 - cryogenics, high-fields, high pressure,
 - current-injection, optical pumps, THz pumps, ...

Many Opportunities for Hard Condensed Matter & Materials Physics Applications.

MCMartin@lbl.gov



<http://infrared.als.lbl.gov/>

