Alexey Belyanin
Lecture 4

Unconventional nanostructures and new avenues

- Graphene
- Carbon nanotubes
- Plasmonics

Graphene

Yet another amazing form of carbon

Nobel Prize in Physics 2010

Andre Geim

Konstantin Novoselov

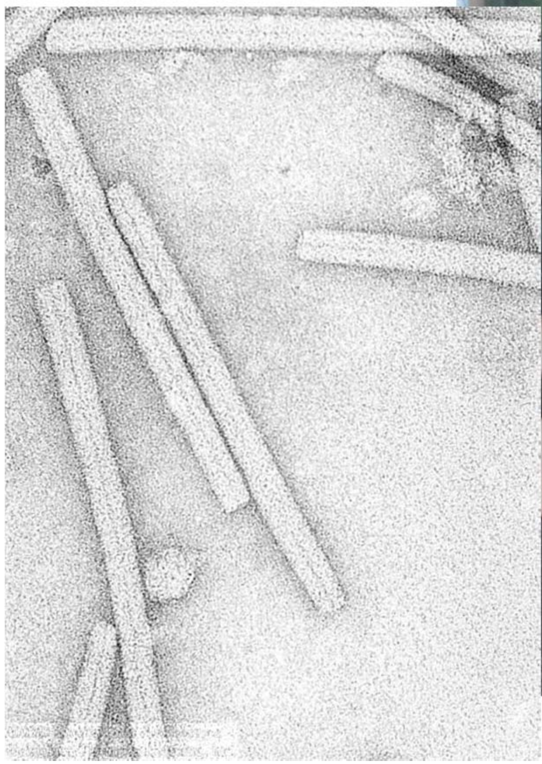
Univ. of Manchester, UK

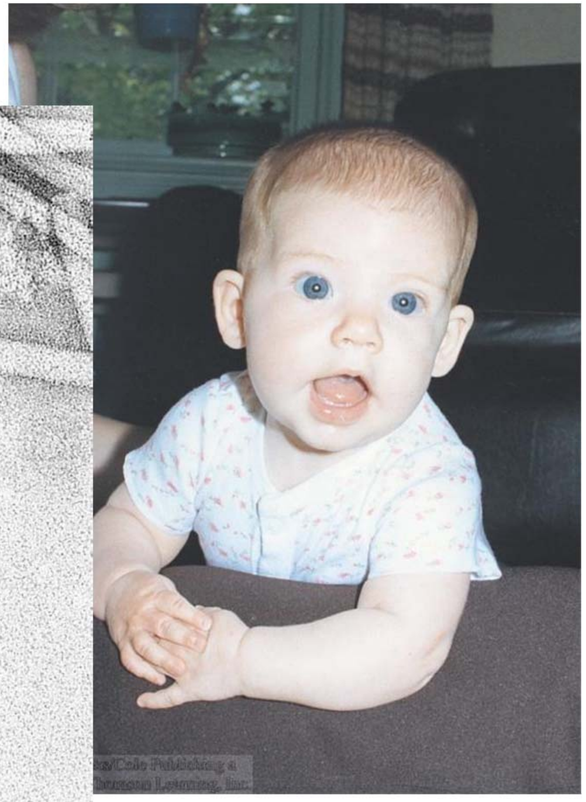
Carbon: the Element of Life

Has unique flexibility for bonding and ability to make complex compounds

All life forms on Earth, from viruses to complex mammals (including humans) are based on carbon chemistry.

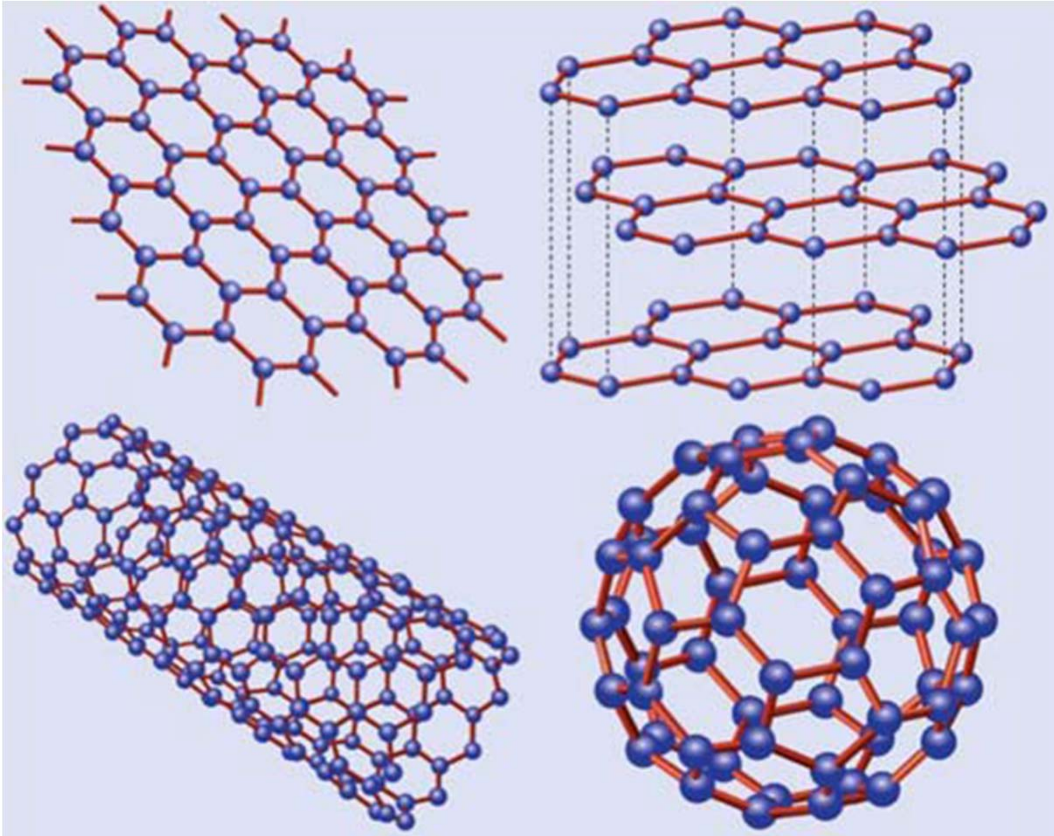
The Tobacco Mosaic Virus contains a single strand of RNA, about 0.1 mm long

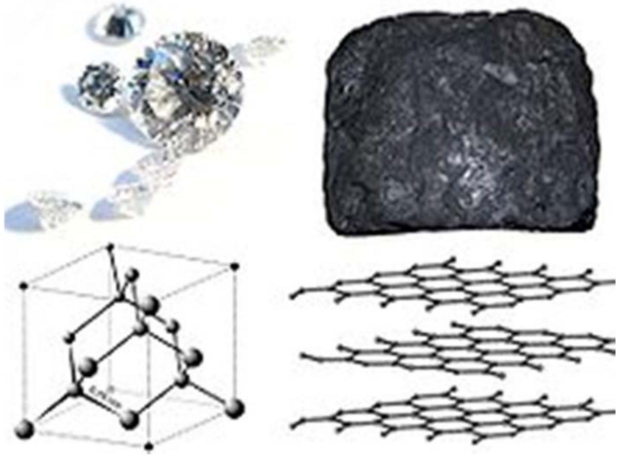




This complex mammal contains about 3 billion miles of DNA.

Even pure carbon can be present in a variety of forms:



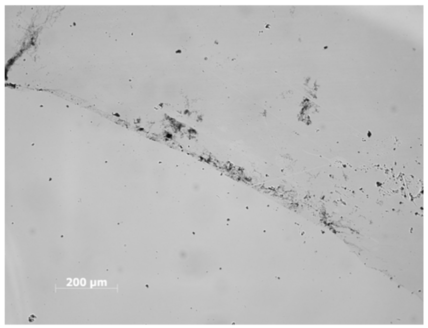


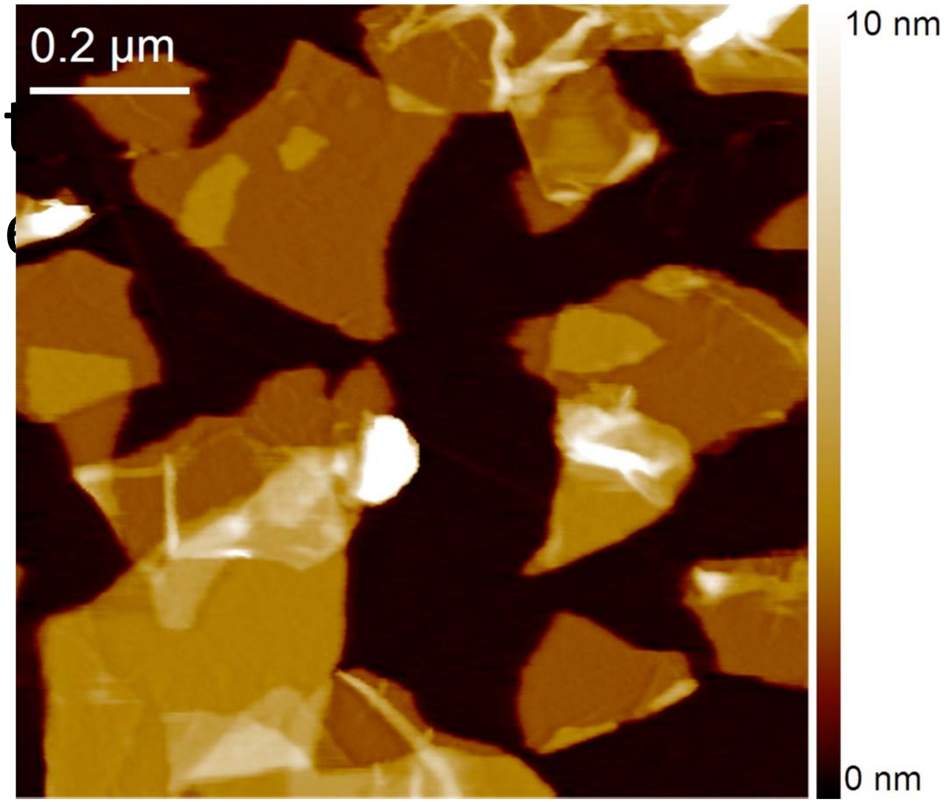
Diamond vs.	**graphite**
Cubic Lattice, Very tight, inflexible	Honeycomb Sheets that easily slide (pencil)

Graphene (top left) is a 2D honeycomb lattice of carbon atoms. Graphite (top right) can be viewed as a stack of graphene layers.
Carbon nanotubes are rolled-up cylinders of graphene (bottom left). Fullerenes C_{60} (bottom right) are molecules consisting of wrapped graphene by the introduction of pentagons on the hexagonal lattice. (From Castro-Neto et al. 2009)

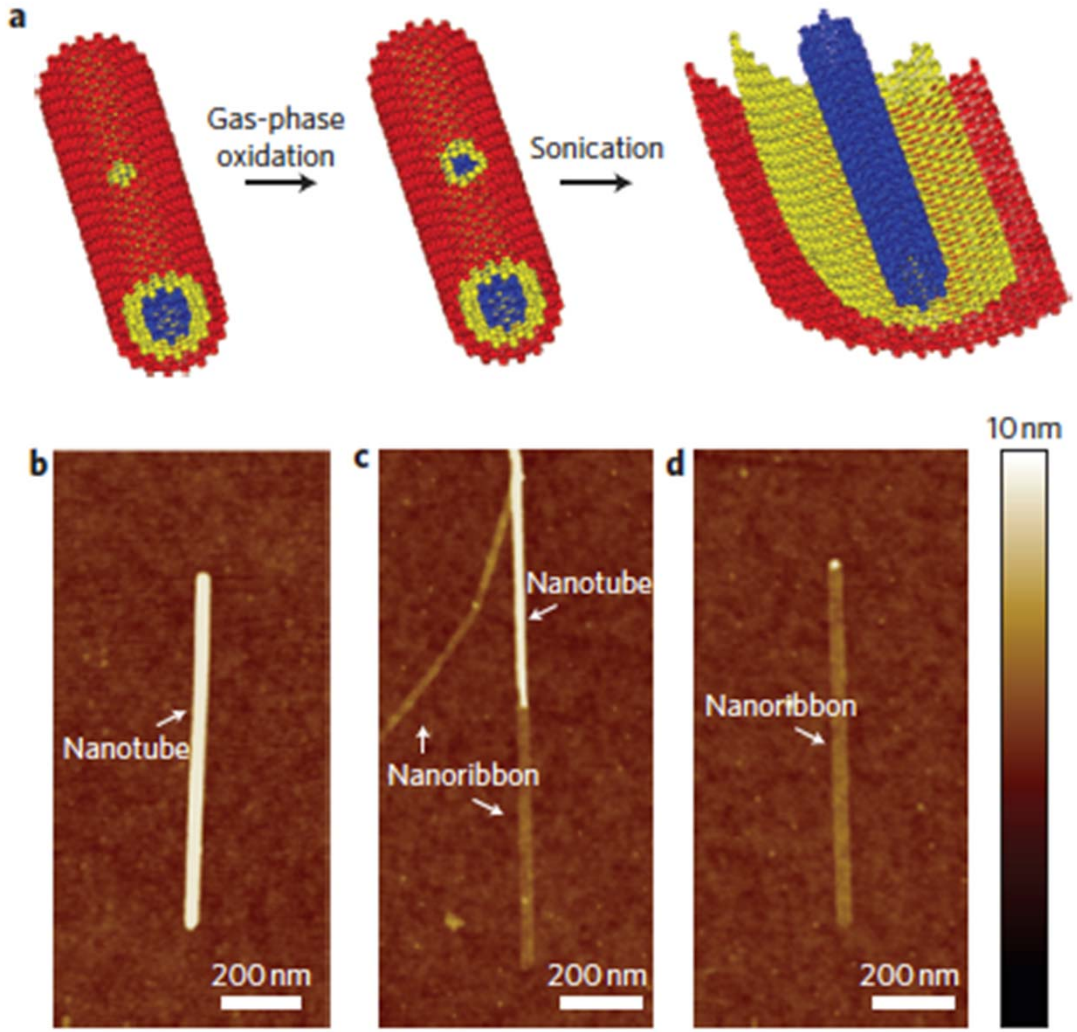
How Geim and Novoselov produced it

- They used Scotch tape to repeatedly split graphite crystals into increasingly thinner flakes
- Then placed the flakes t substrate to prevent the





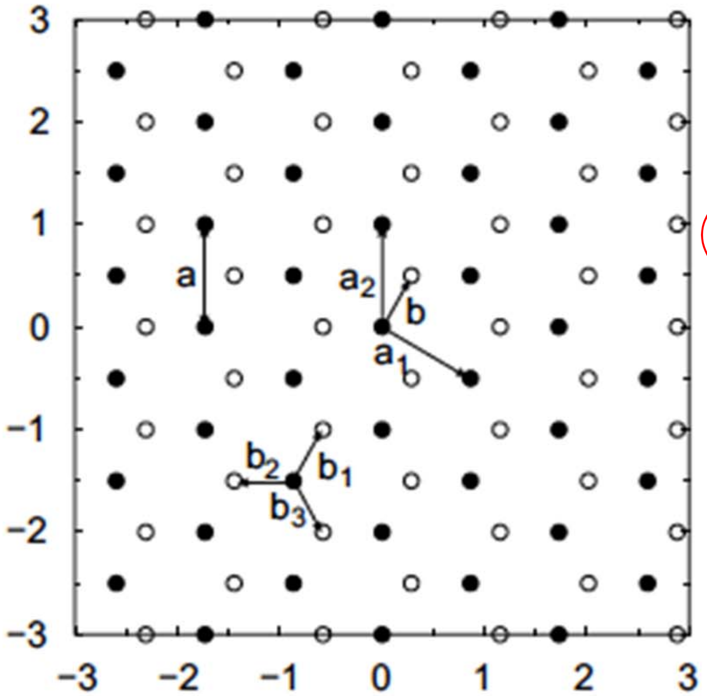
Unzipping a nanotube

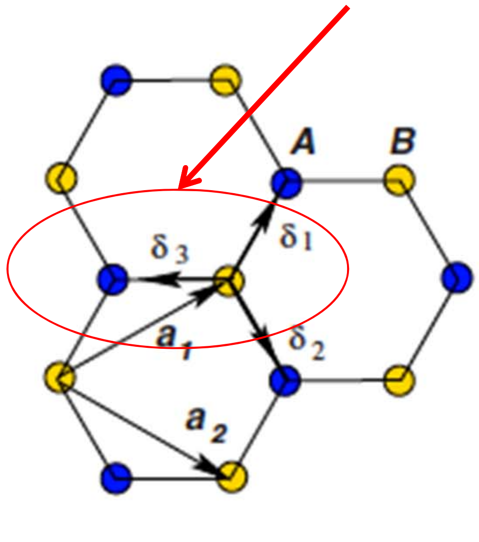


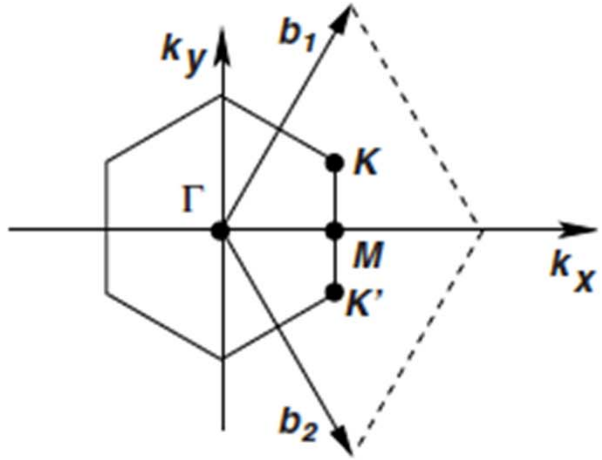
Nature Nanotech. Jiao et al. 2010

Graphene structure

Unit cell: two atoms







Brillouin zone

Castro-Neto et al. 2009

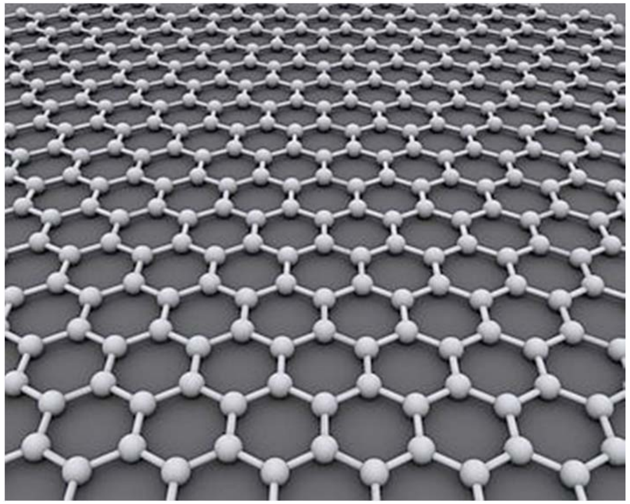
Wallace 1947

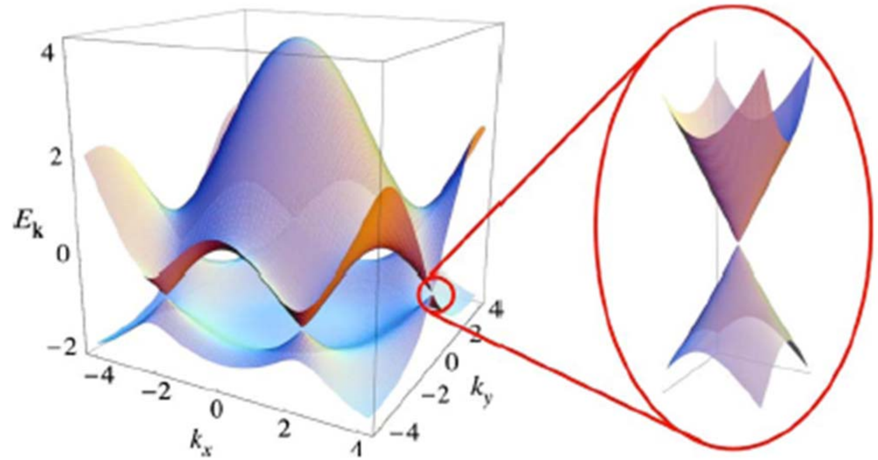
Note two identical sublattices A and B

Hamiltonian can be written as 2x2 matrix $H_{X'X}(p)$, where X',X = A,B

One can associate pseudospin with choice of sublattice and write H with Pauli matrices

Graphene structure





A single layer of carbon atoms tightly packed into a honeycomb lattice

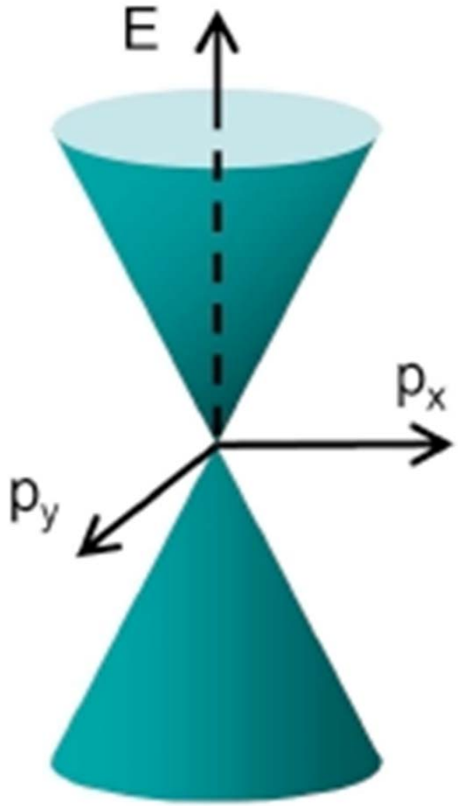
Castro Neto et al. 2009

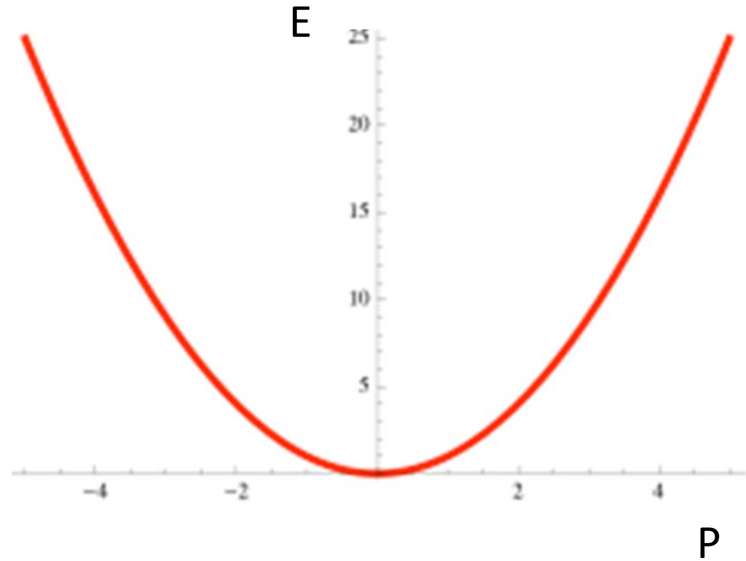
Electron dispersion (dependence of electron energy from its momentum)

Conduction and valence bands touch at E = 0 K,K' symmetry points (gapless semiconductor)

Note linear dependence E(p) near E = 0!!
Where does it come from?
What does it mean?

Linear dispersion: like neutrinos!





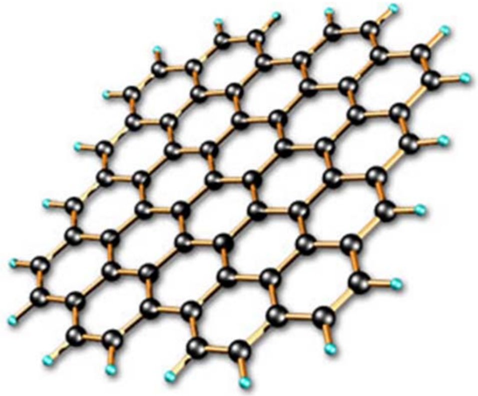
Compare with "normal" particles:

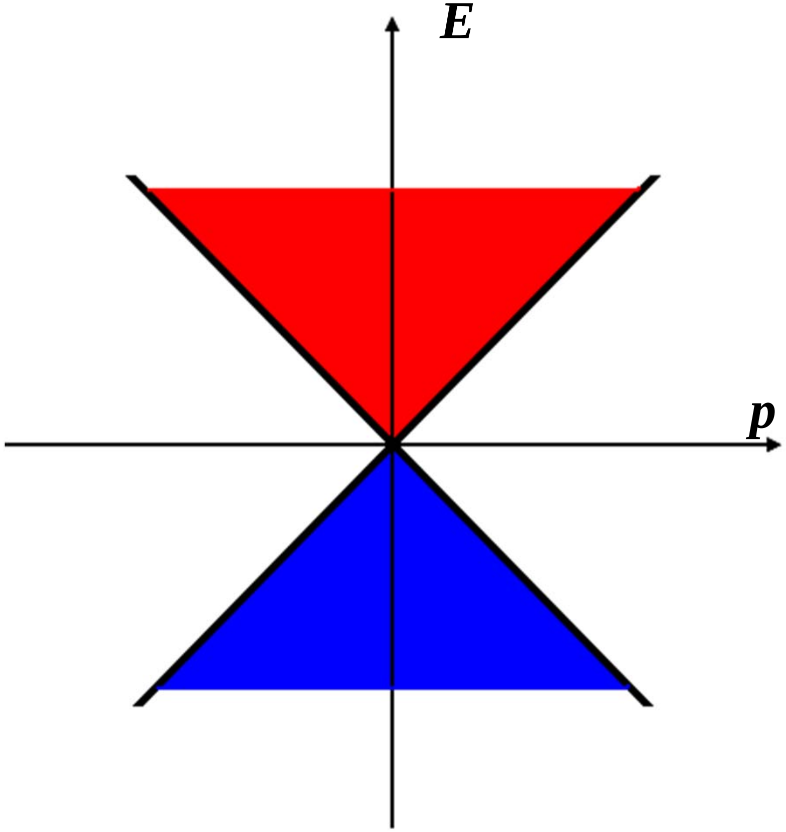
$$E = \frac{p^2}{2m}$$

Photons: $E = pc$

Electrons in graphene: $E = pV; \quad V \approx c/300$

Electron Dynamics in Graphene

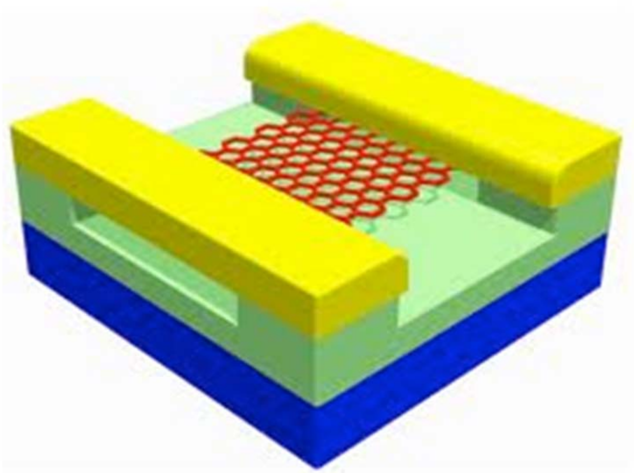


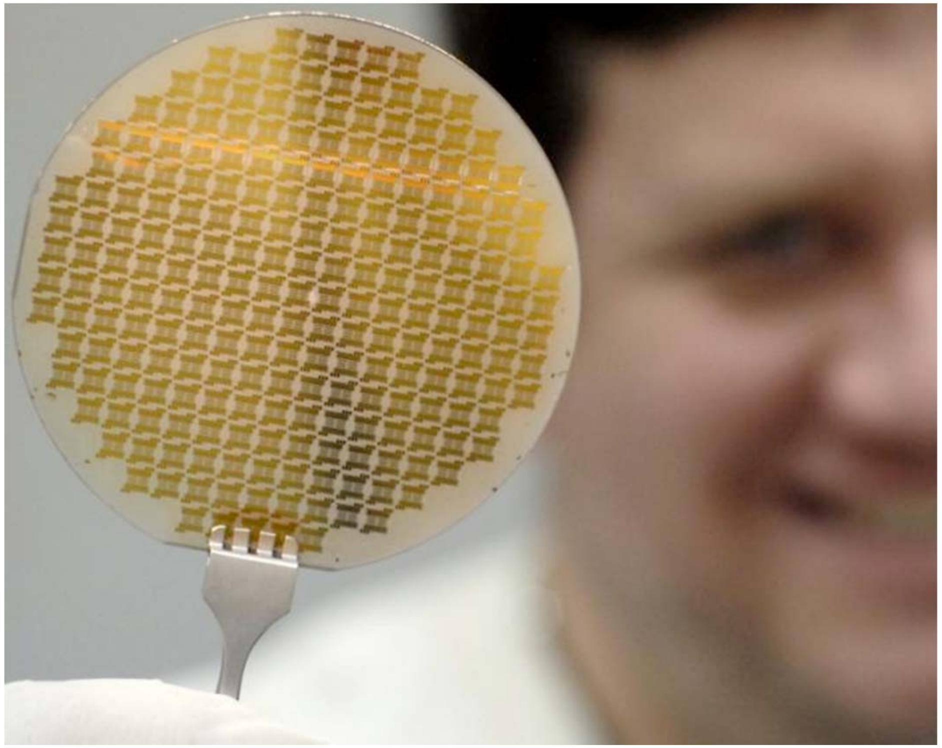


- Ultrahigh mobility, low resistance (like in copper!)
- Unique optical properties (absorption independent on wavelength)
- Unique magnetic properties
- Penetration through energy barriers
- Huge optical nonlinearity
- Highly tunable plasma frequency

Potential applications

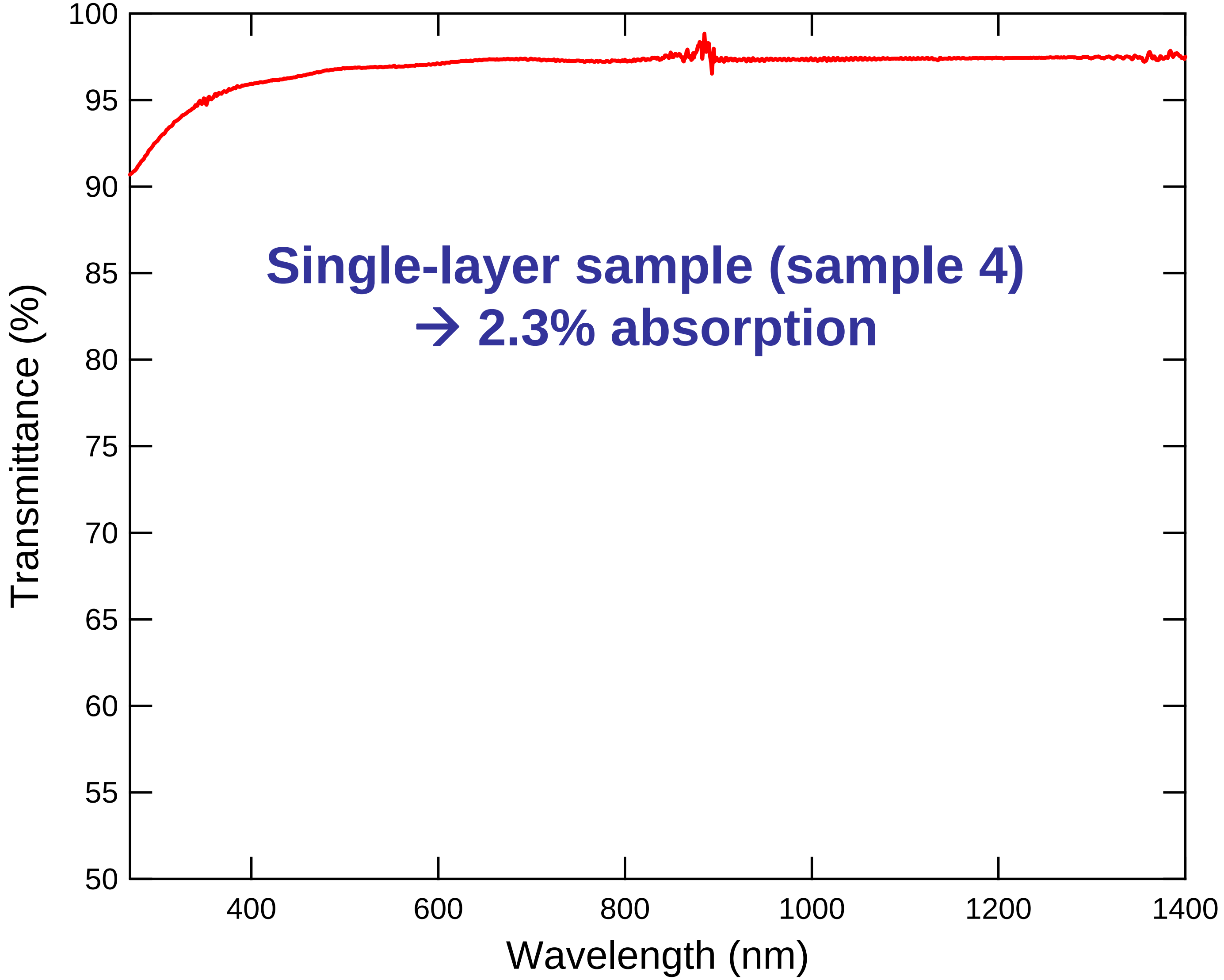
- Transistors
- Integrated circuits
- Lasers
- Detectors
- memory





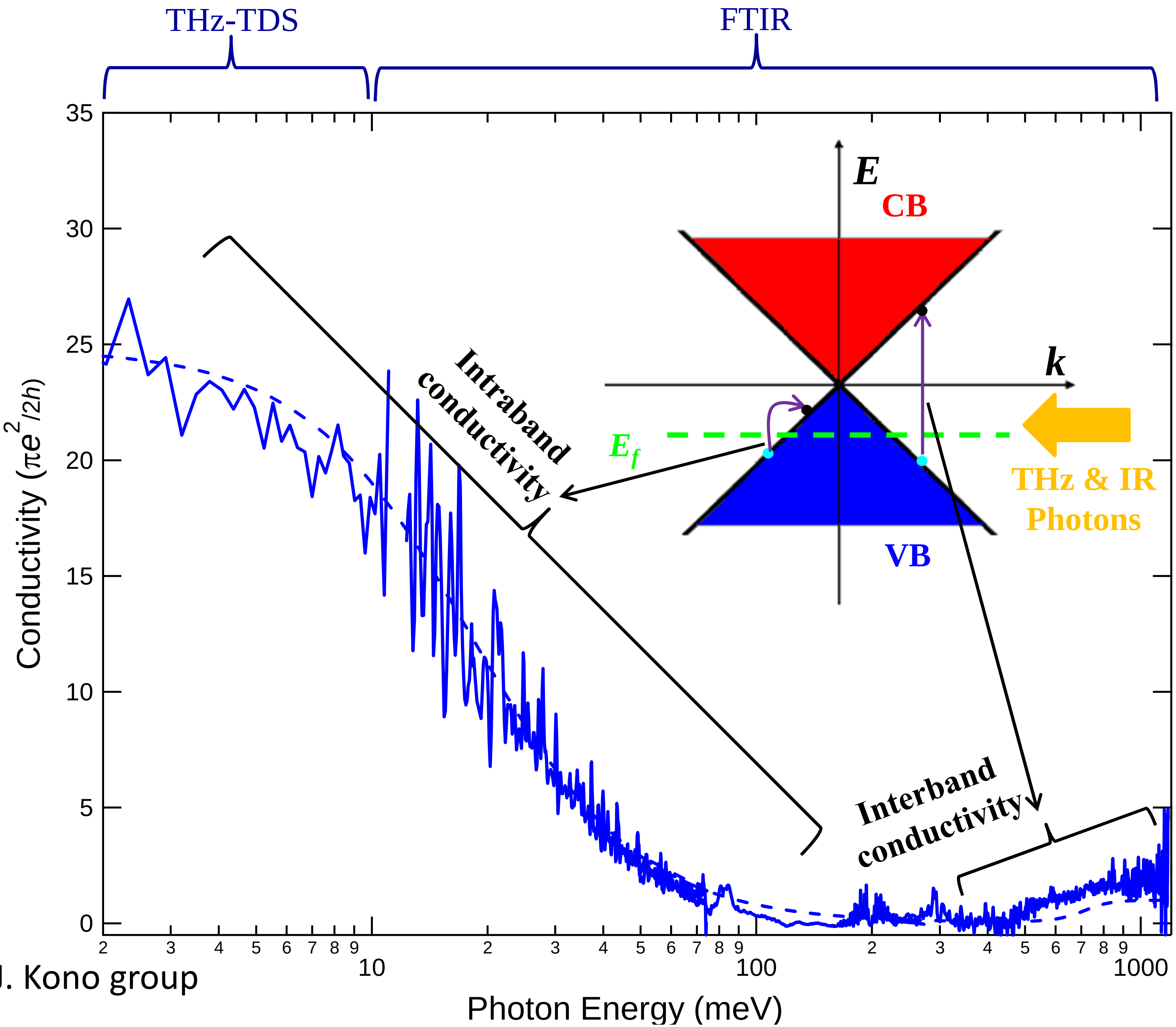
NIR-Visible Absorption

Blackboard derivation



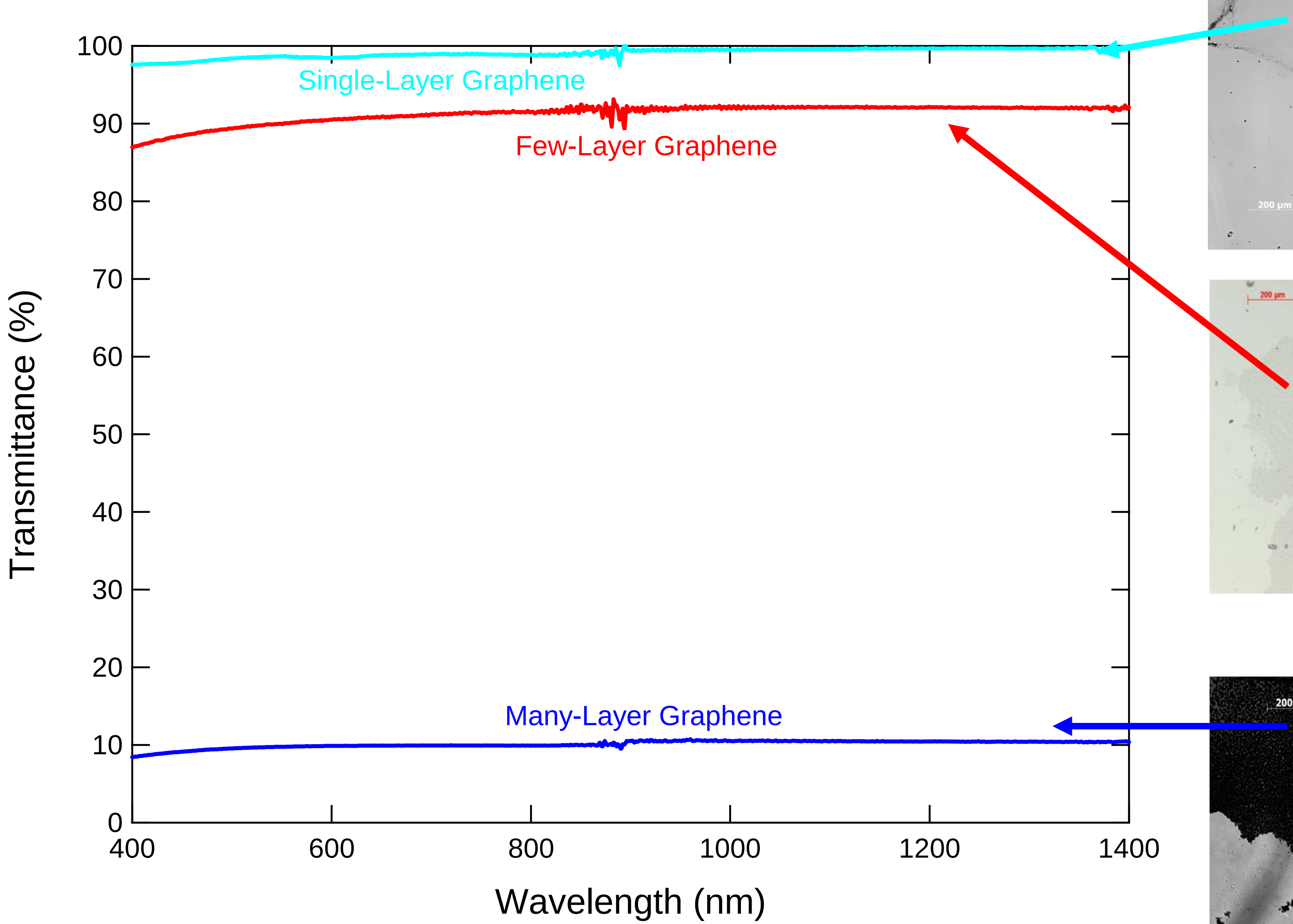
J. Kono, Rice Univ.

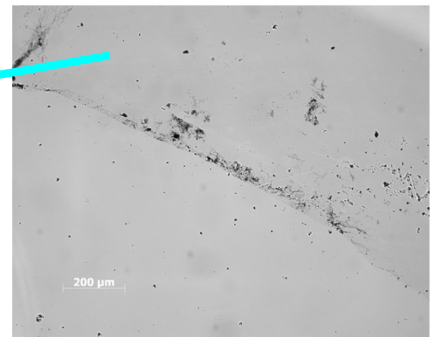
Intraband and Interband Conductivities of Graphene

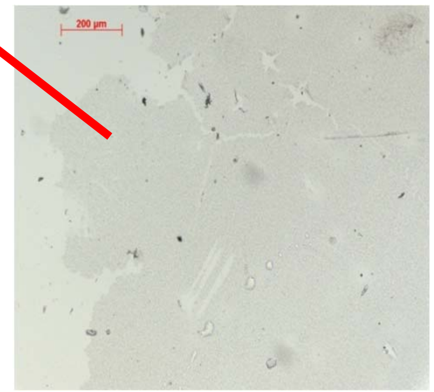


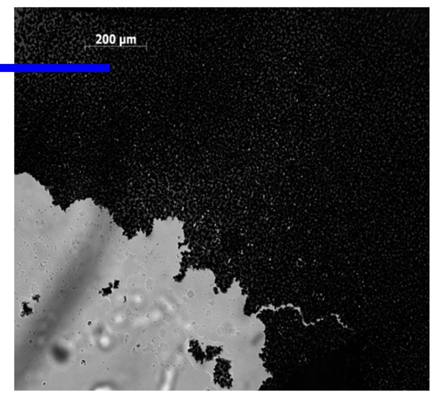
J. Kono group

NIR-Visible Absorption





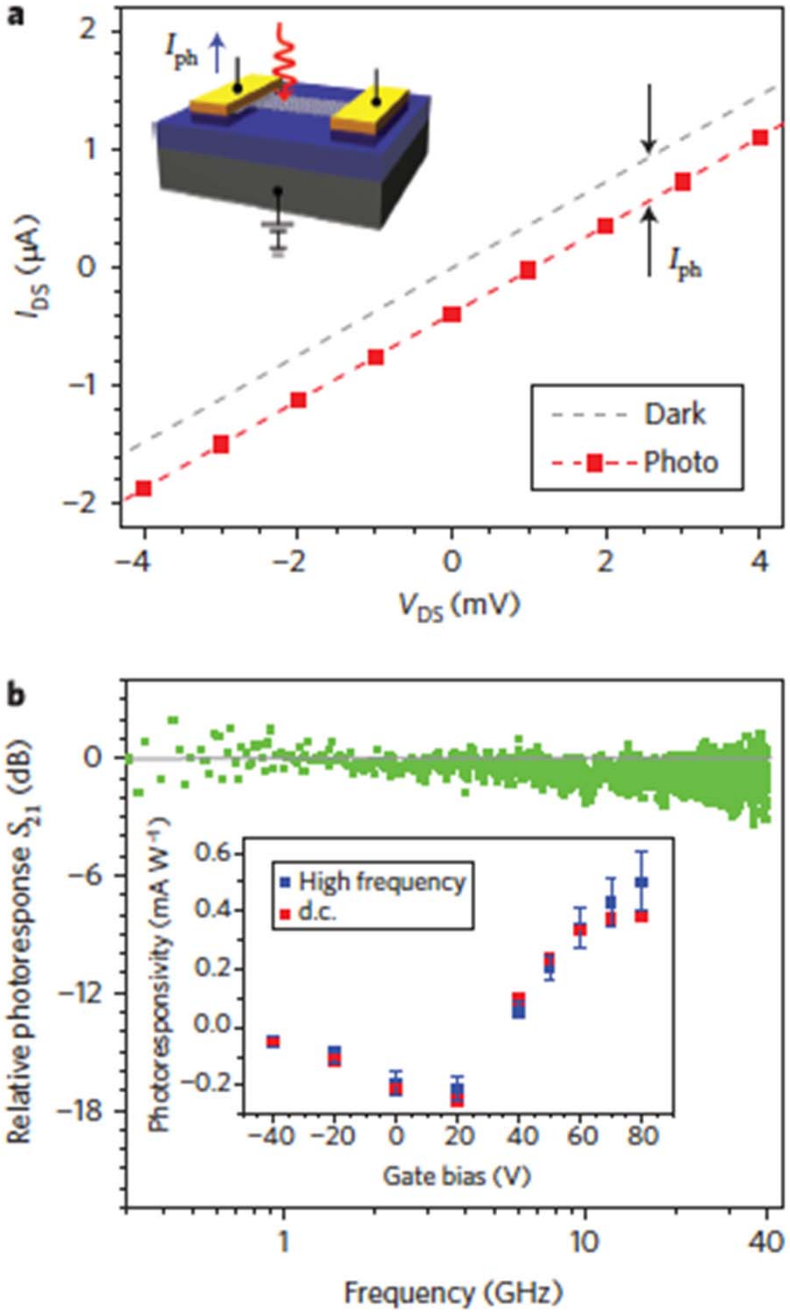


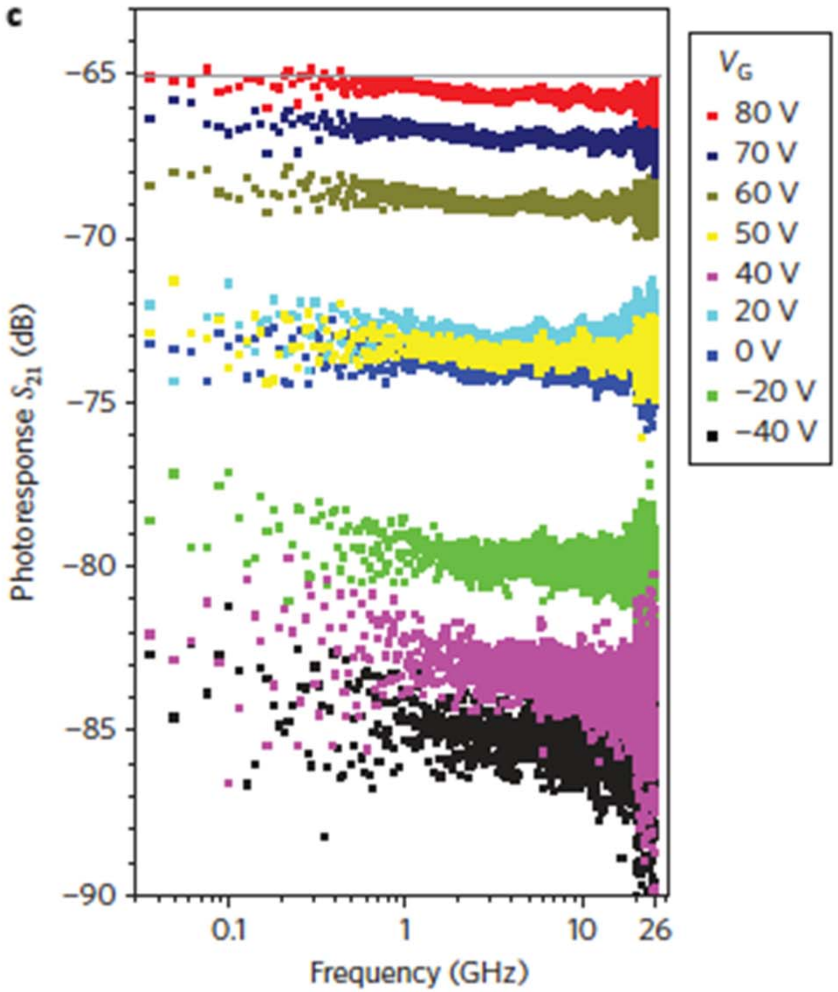


2.3% absorption per layer

J. Kono, Rice Univ.

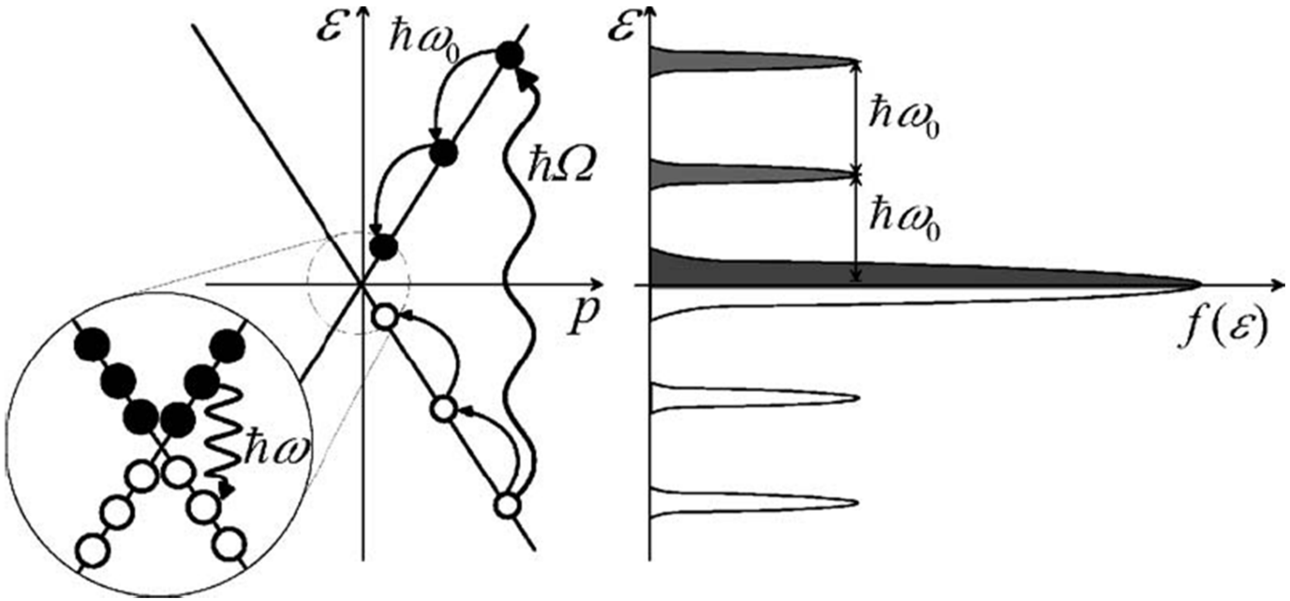
Ultrafast graphene photodetector





Mueller et al. Nature Nanotech. 2009

THz Gain in Graphene under Optical Pumping



- Population inversion readily achievable

V. Ryzhii *et al*., J. Appl. Phys. 101, 083114 (2007)

- Negative THz conductivity (positive gain)

A. Satou *et al*., Phys. Rev. B 78, 115431 (2008)

- Optically-pumped THz laser

A. Dubinov *et al*., Appl. Phys. Exp. 2, 092301 (2009)

THz Dynamics: GaAs 2DEG vs. Graphene

Linear bands lead to highly nonlinear dynamics

S. A. Mikhailov, Europhys. Lett. 79, 27002 (2007); J. Phys.: Condens. Matter 20, 384204 (2008)

Parabolic Dispersion (GaAs):

$$\varepsilon(\vec{p}) = \frac{|\vec{p}|^2}{2m^*}$$

Current Response:

$$j_x(t) = \frac{n_s e^2 E_0}{m^* \omega} \sin \omega t$$

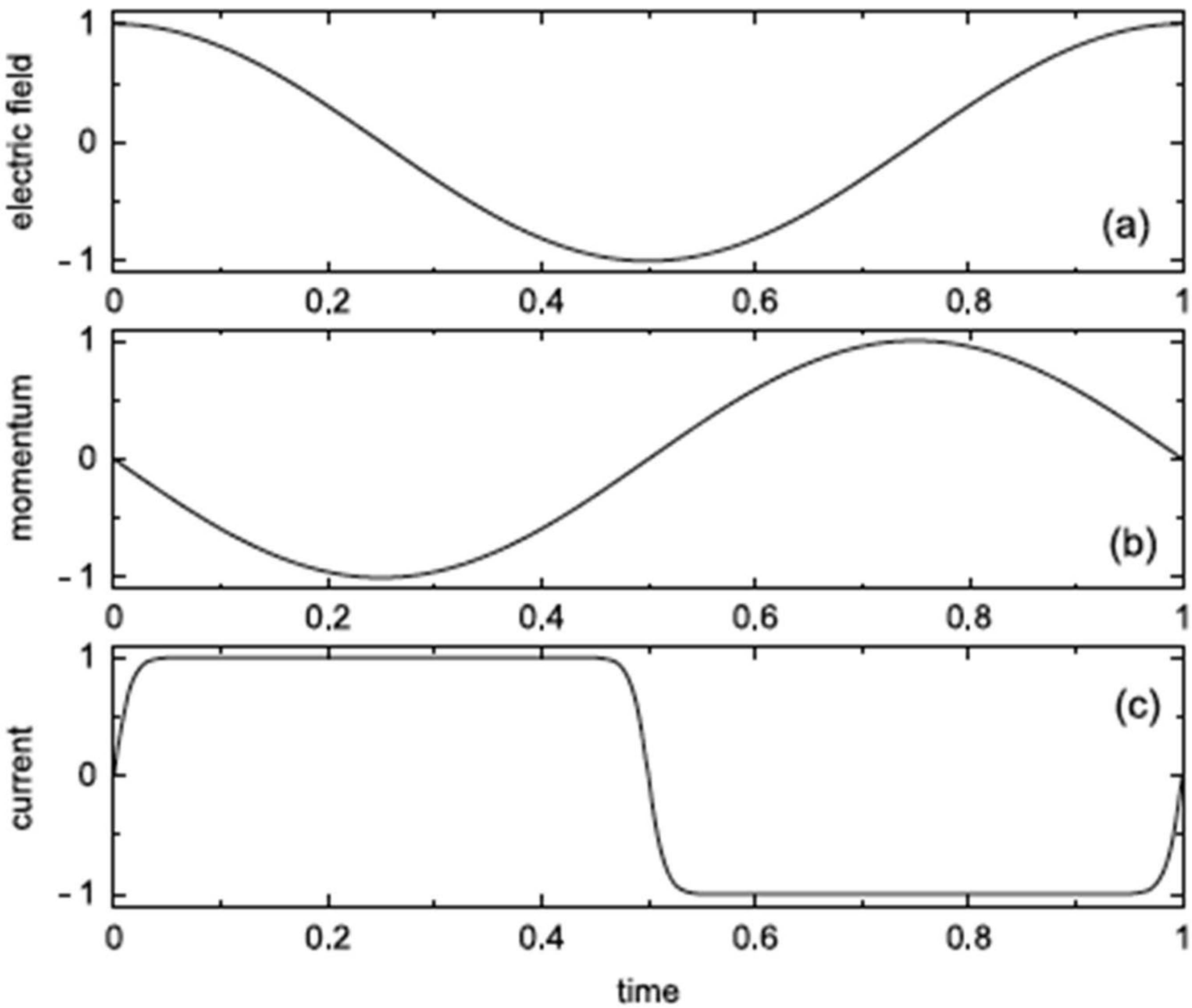
Linear Dispersion (graphene):

$$\varepsilon(\vec{p}) = V|\vec{p}|$$

Current Response:

$$j_x(t) = e n_s V \frac{4}{\pi} (\sin \omega t + \frac{1}{3} \sin 3\omega t + \frac{1}{5} \sin 5\omega t + \ldots)$$

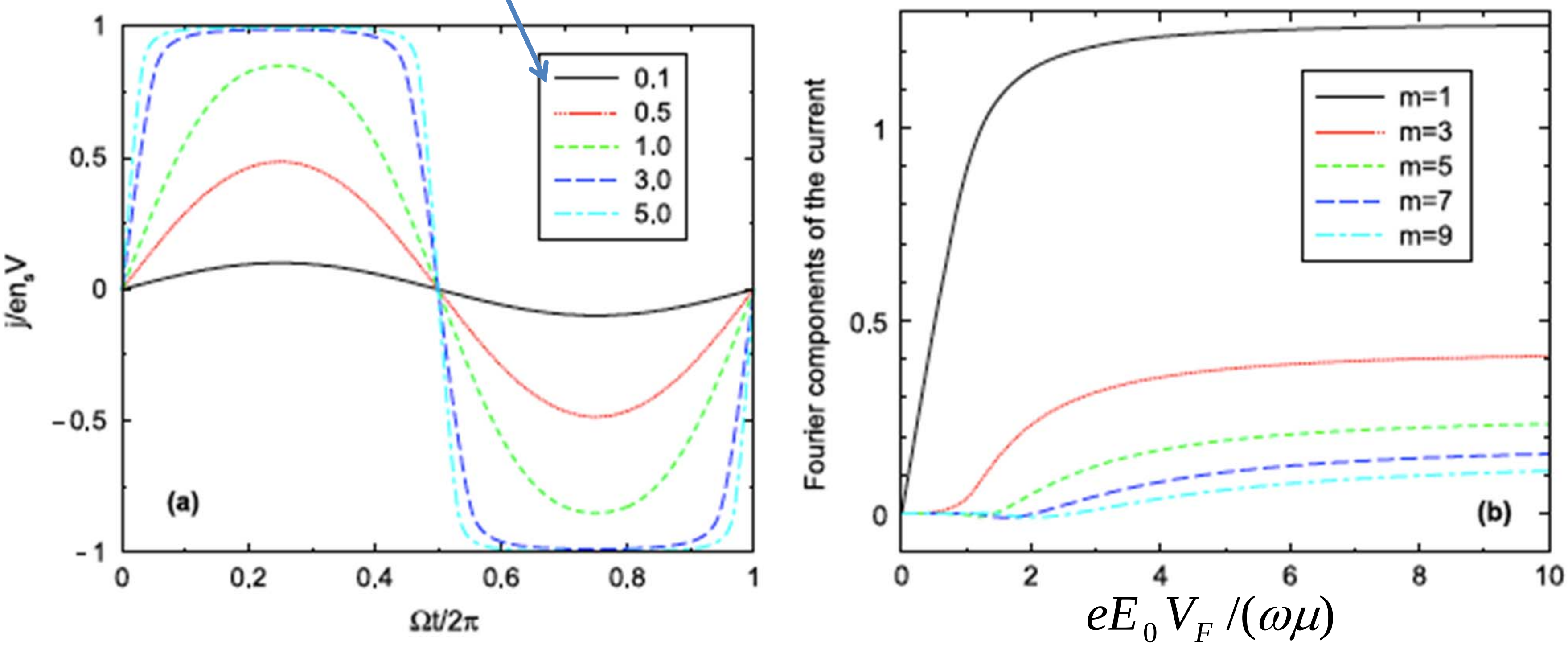
Blackboard derivation of current



Mikhailov 2008

Blackboard derivation of current

$eE_0 V_F/(\omega\mu)$



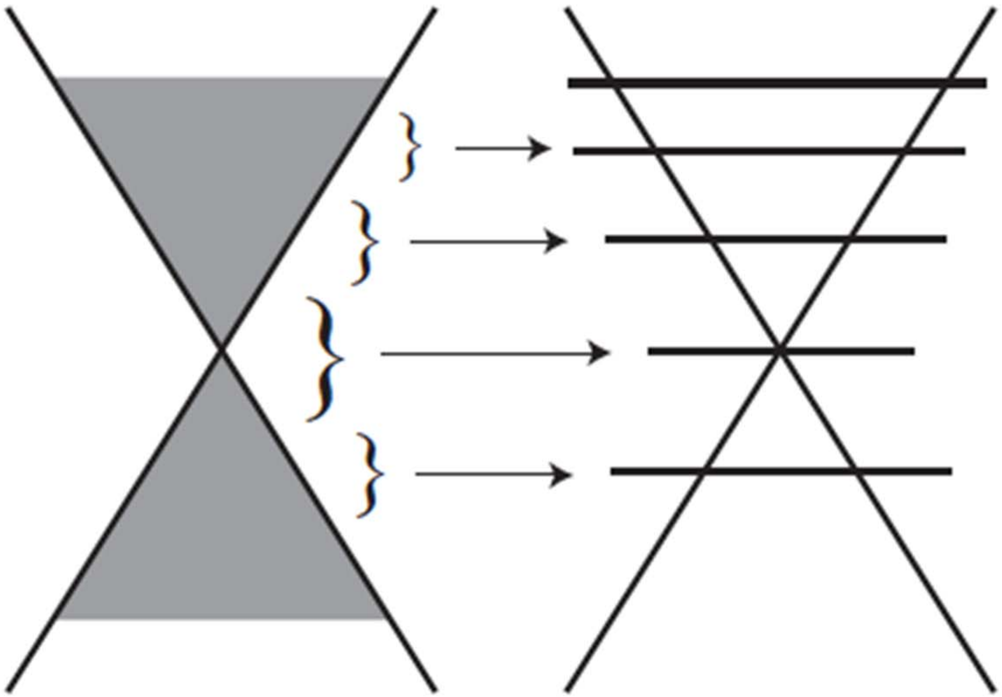
$eE_0 V_F/(\omega\mu)$

Strongly nonlinear response when $eE_0 V_F/(\omega\mu) > 1$

Mikhailov 2008

See also Wallace for DC conductivity

Graphene in the magnetic field

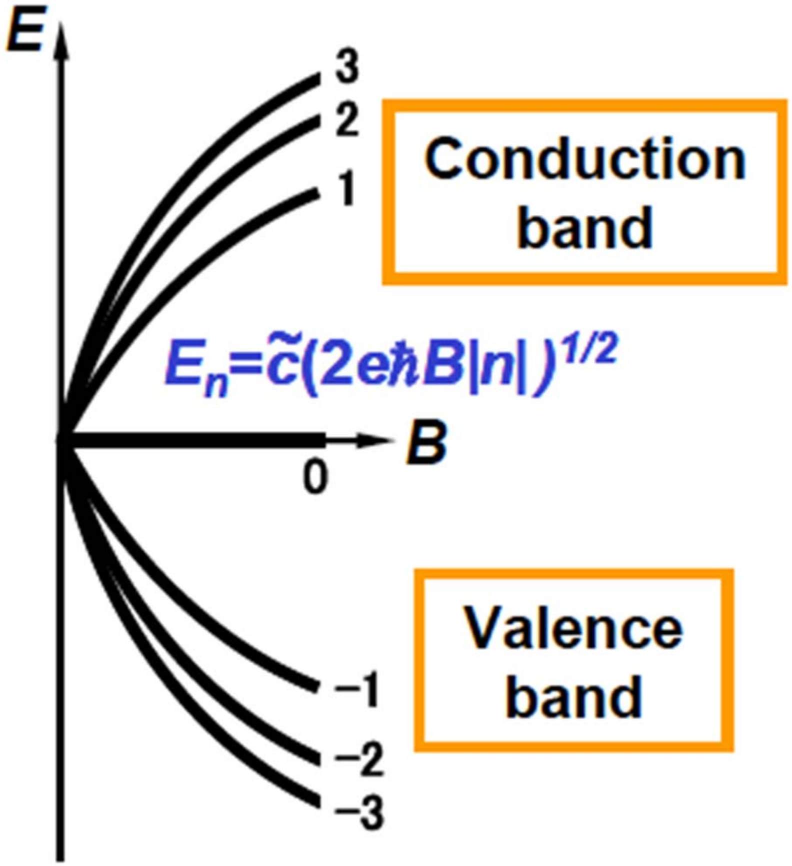


$$E_n = \mathrm{sgn}(n) V_F * \sqrt{2e\hbar B|n|},$$
$$n = 0, \pm 1, \pm 2, \ldots$$

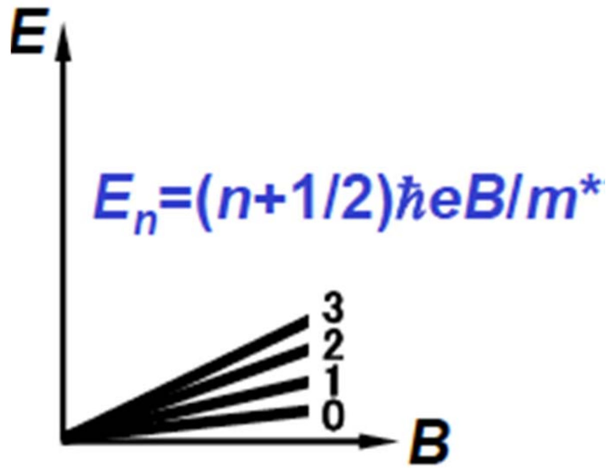
Leggett lectures

Landau levels

In graphene



In GaAs quantum well



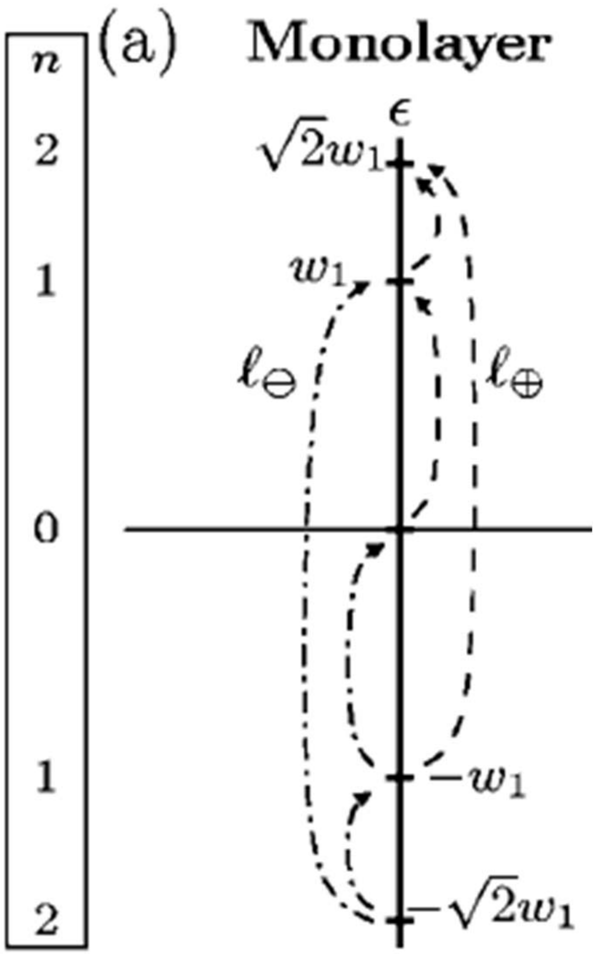
Graphene in the magnetic field

Selection rules:
Normal matter

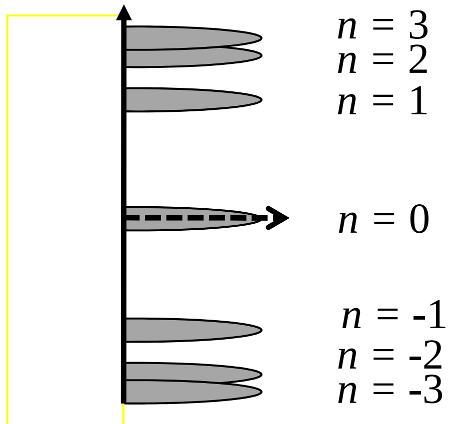
$$\Delta n = \pm 1$$

Selection rules:
graphene

$$\Delta |n| = \pm 1$$

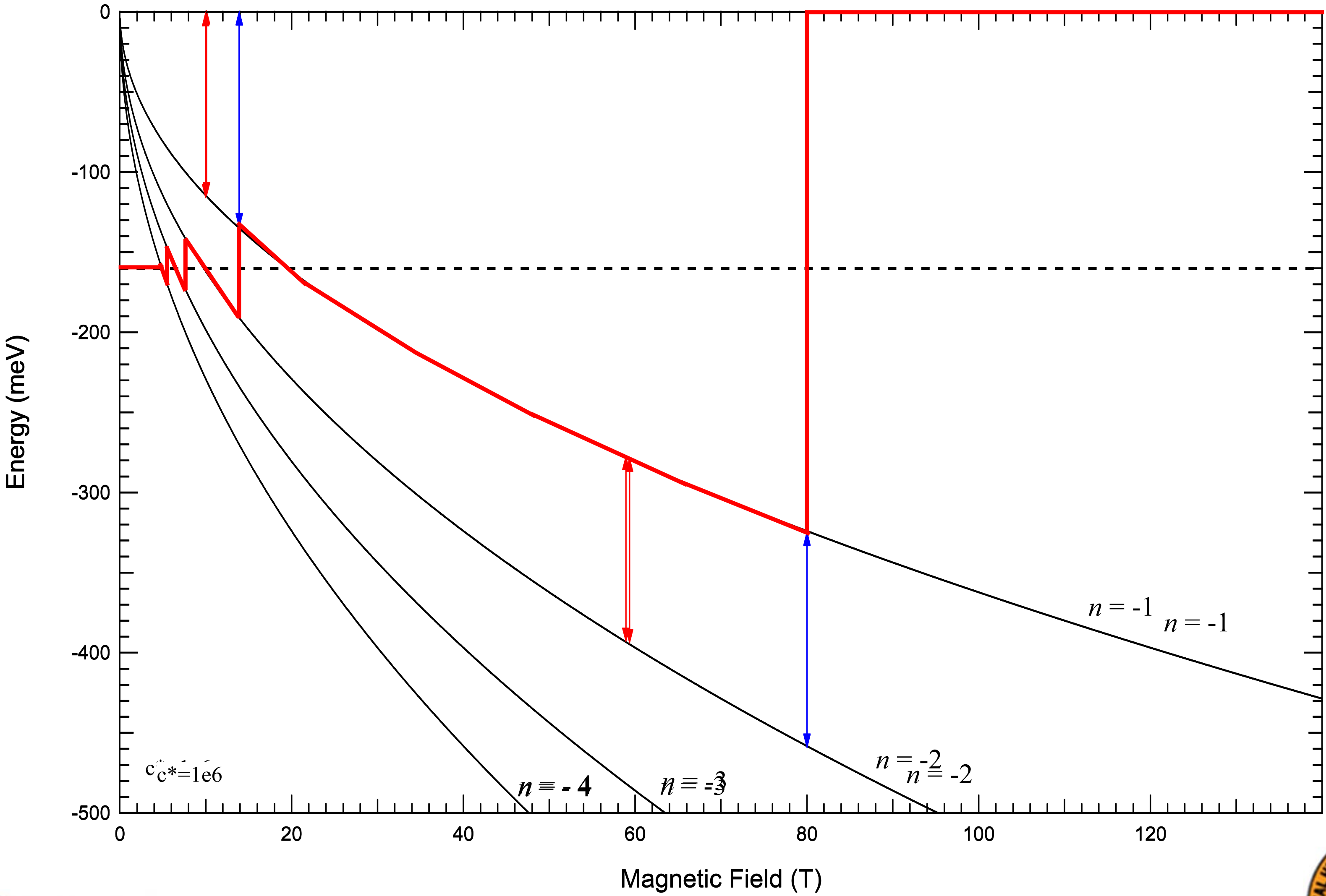


Abergel & Falko 2007



$$E_n = \mathrm{sgn}(n) V_F * \sqrt{2e\hbar B|n|}$$

Landau Levels vs. B

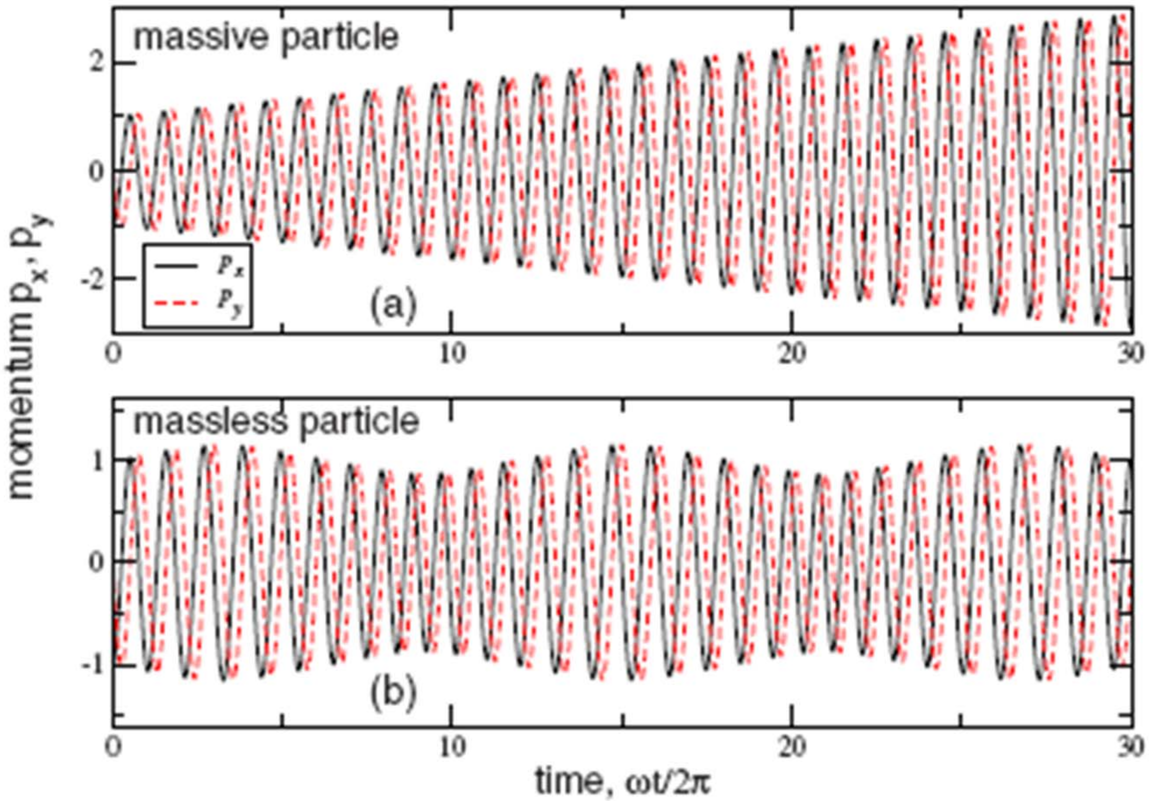


Nonlinear THz Dynamics in *B*

PHYSICAL REVIEW B **79**, 241309(R) (2009)

Nonlinear cyclotron resonance of a massless quasiparticle in graphene

S. A. Mikhailov*
Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany

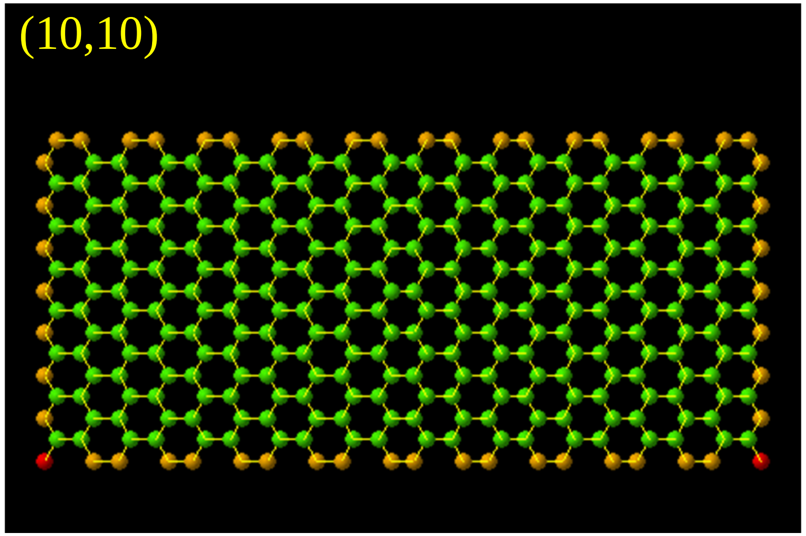


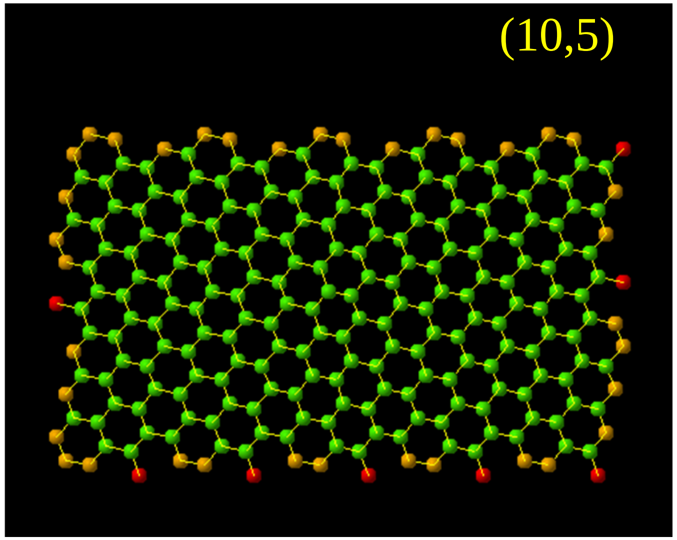
GaAs

$$\frac{d\mathbf{p}}{dt} = -\frac{e}{c}\mathbf{v}\times\mathbf{B} - e\mathbf{E}(t), \quad \mathbf{v} = V\frac{\mathbf{p}}{p}$$

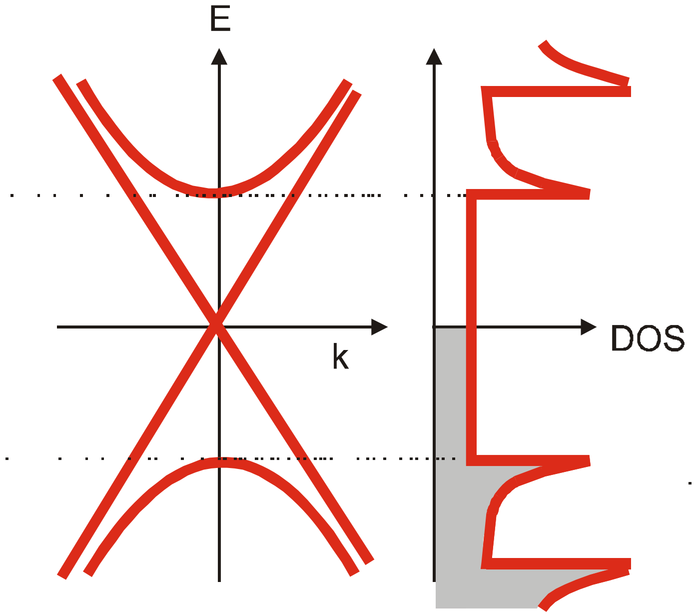
Graphene

Single-Walled Carbon Nanotubes

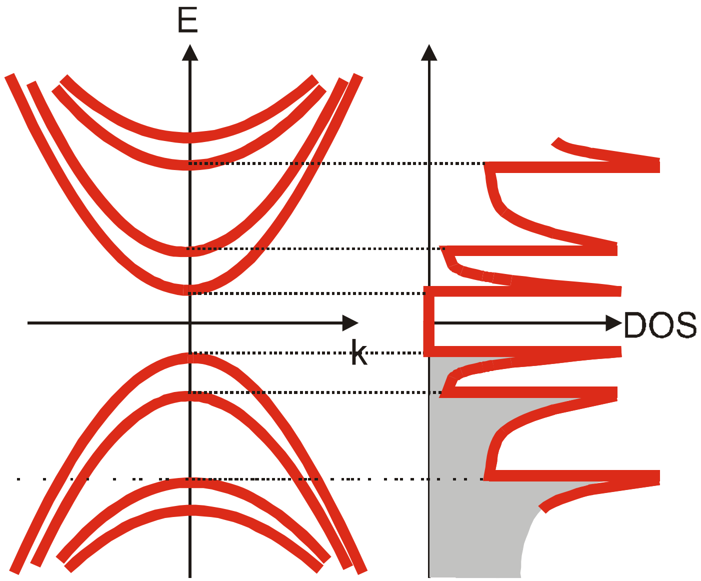




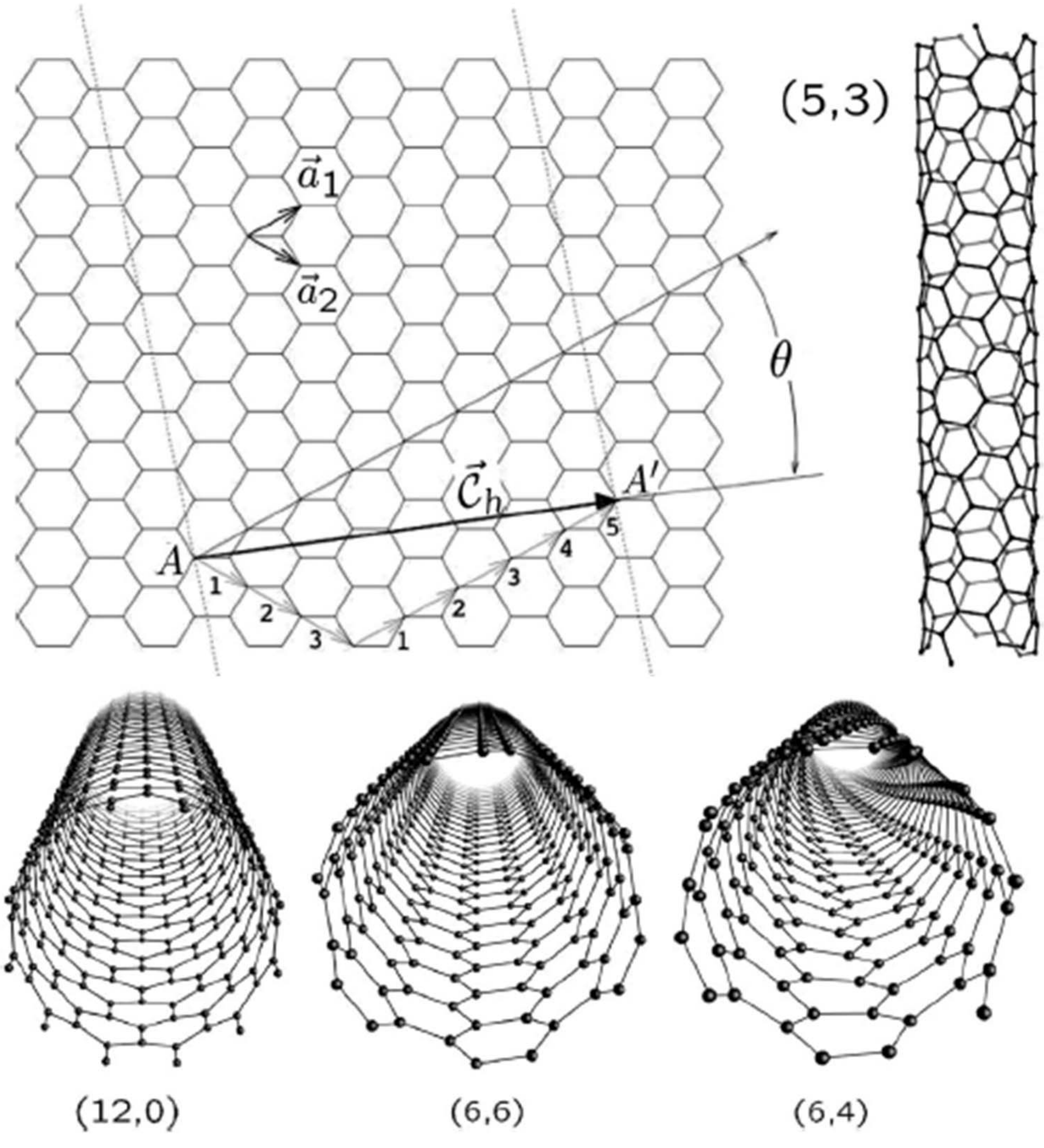
Animation by Prof. S. Maruyama (Univ. of Tokyo)



Metallic

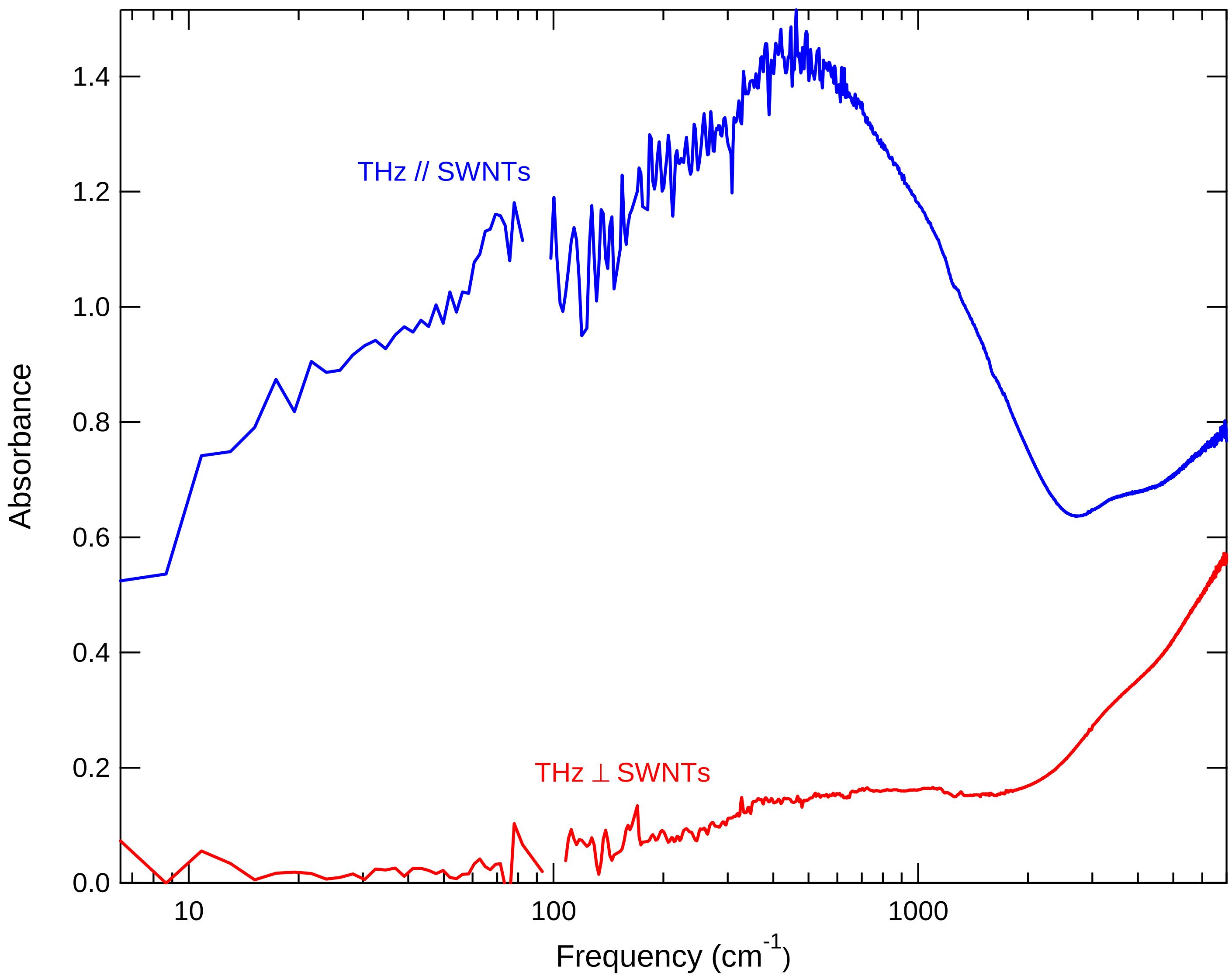


Semiconducting



(5,3)
$\vec{a}_1$
$\vec{a}_2$
θ
$\vec{C}_h$
A
A′
1
2
3
1
2
3
4
5
(12,0)
(6,6)
(6,4)

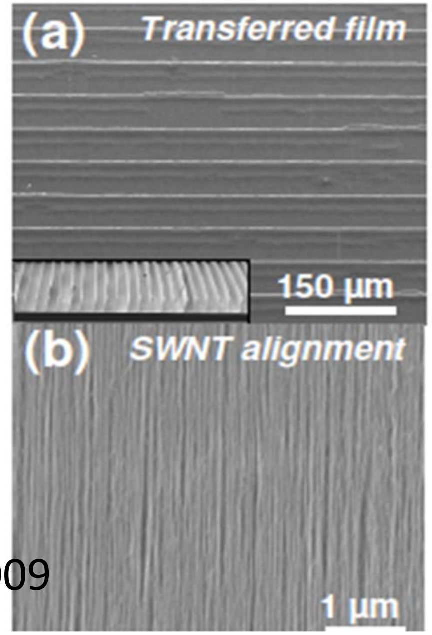
THz & IR Dynamics of Single-Walled Carbon Nanotubes (SWNTs)



Kono group 2011

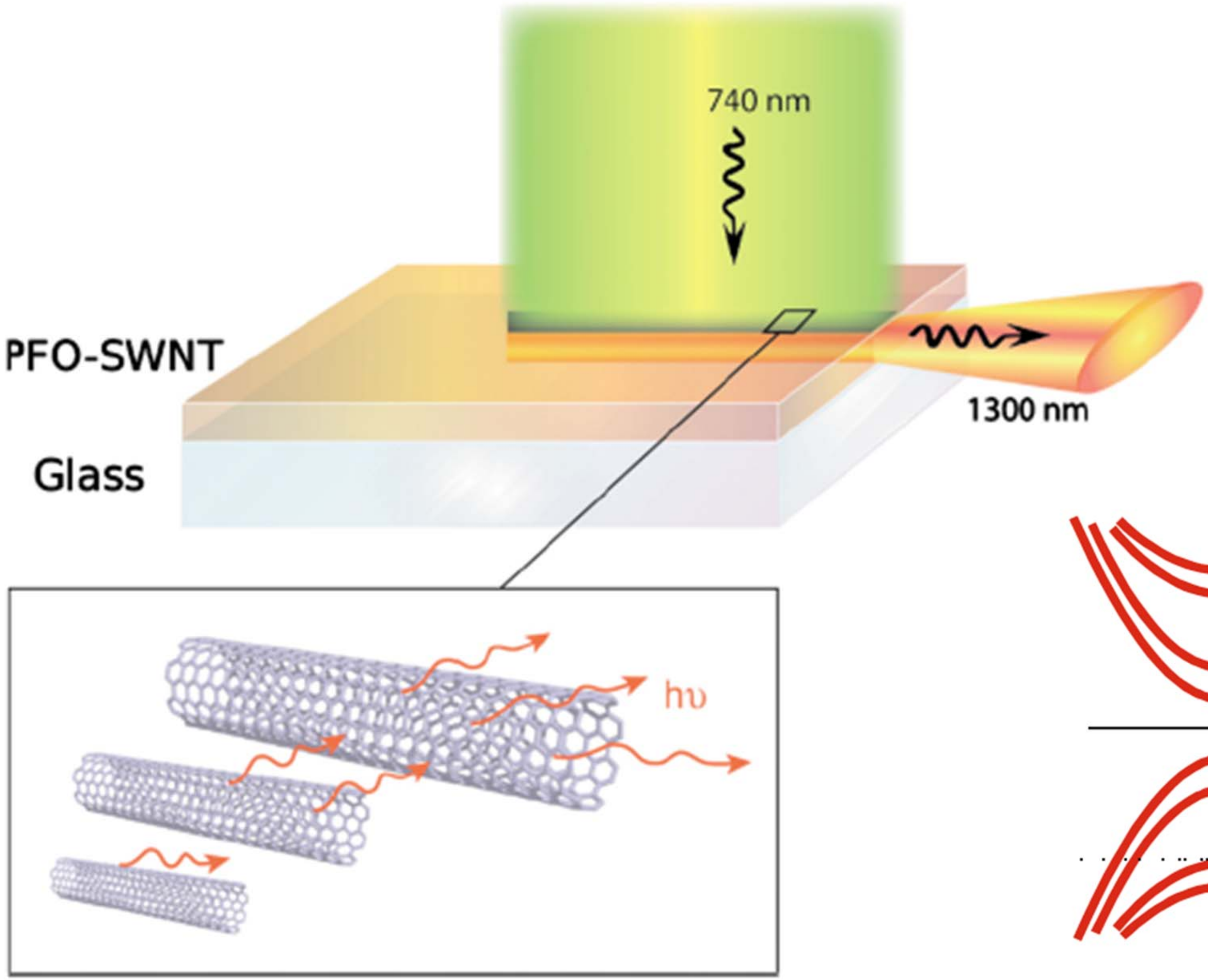
Strong Anisotropy!

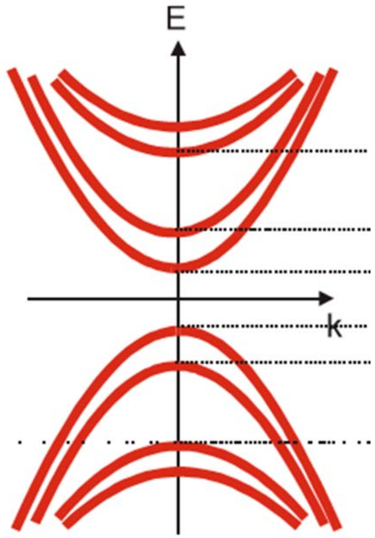
- A broad FIR peak
- Peak position shifts as the SWNTs sample changes.
- Peak origin is still under debate and being seeked.



Pint et al. 2009

Gain in semiconducting CNTs





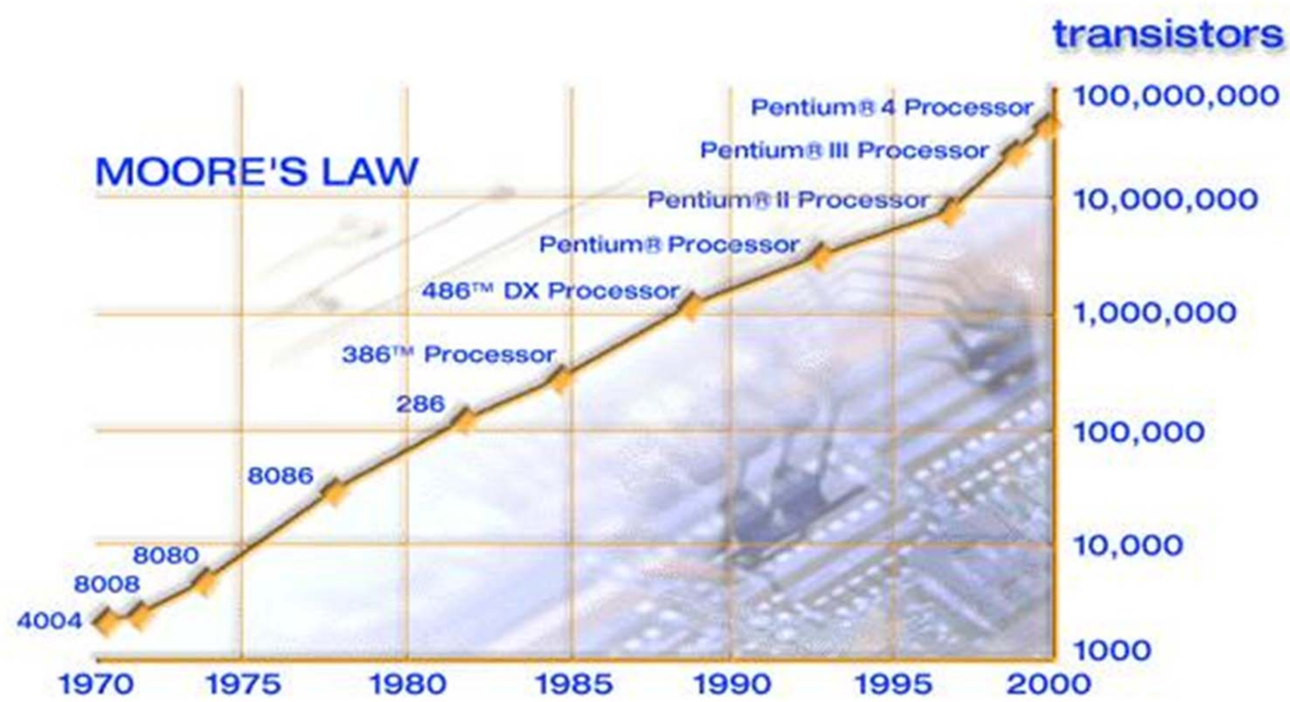
Gain 190 cm^{-1}

Vivien APL 2010

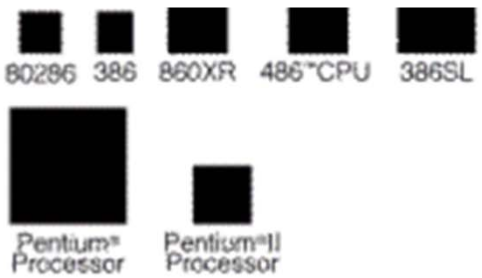
Common problem: small interaction volume

- Increase interaction by plasmonic effects?
- Plasmonics has been developed in parallel for sensing, communications, and computing applications

Smaller, Denser, Cheaper

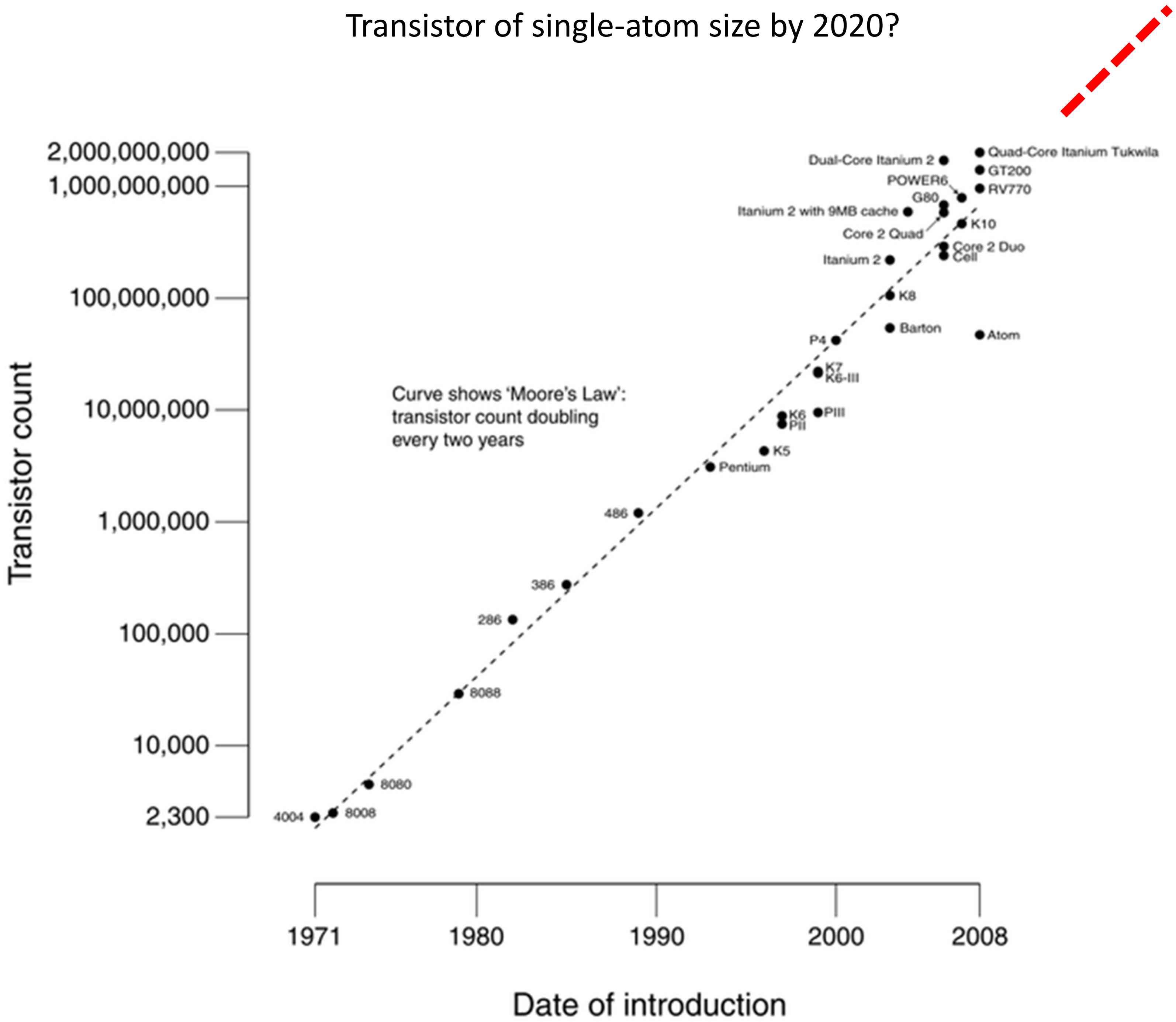


Gordon Moore, Intel co-founder



Moore's Law (1965): every 1.5 years
the number of transistors on a chip is doubled

Transistor of single-atom size by 2020?

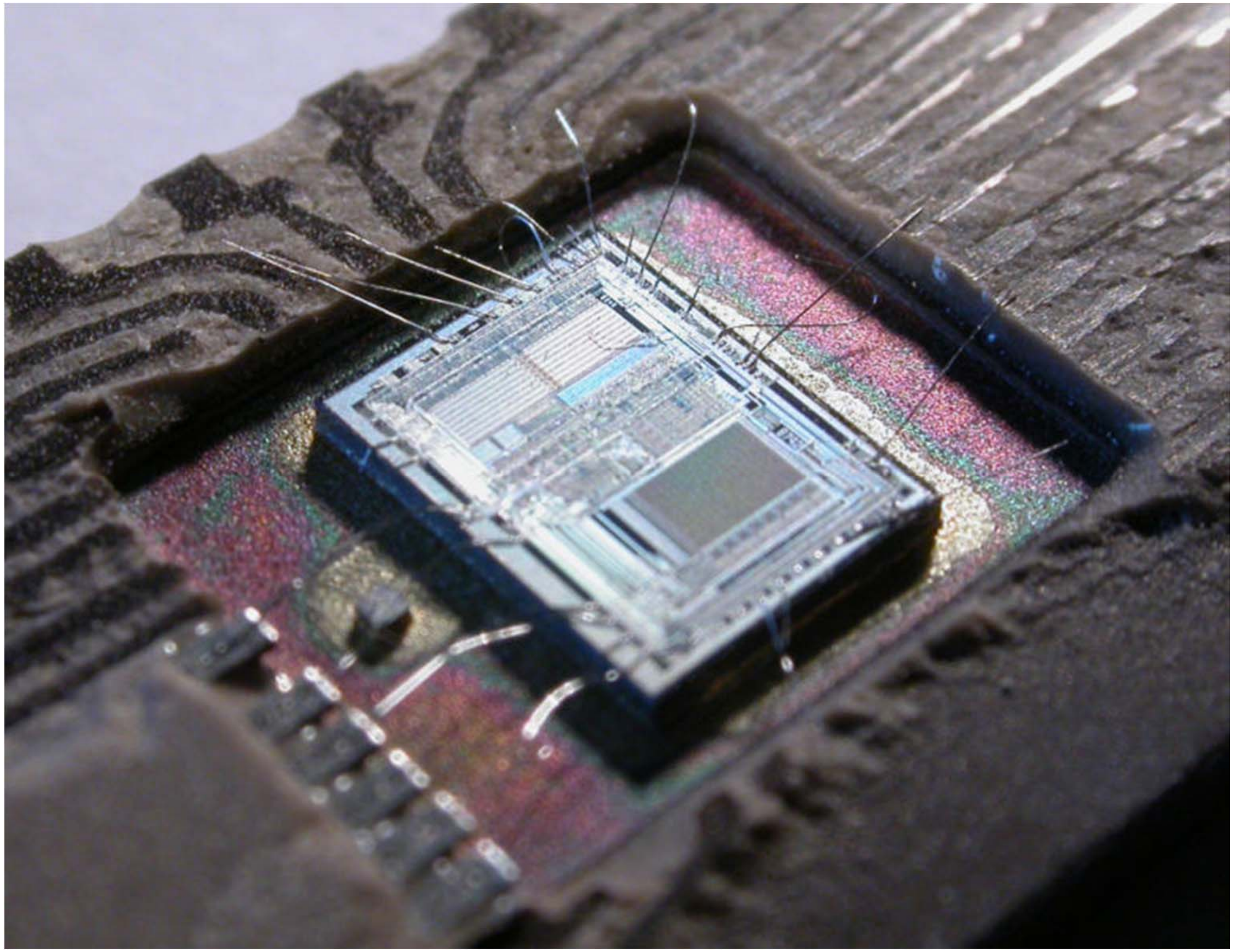


Number of transistors grows, but this does not improve the performance as much.

Reason?

We use 21-century semiconductor devices and 19-century copper wires connecting them!

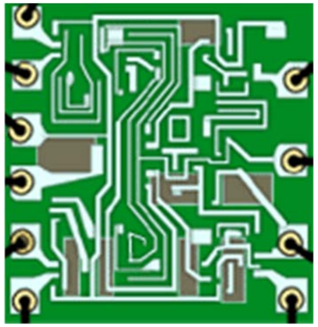
Electronic circuits: 45 nm wires, 1 million transistors per mm^2

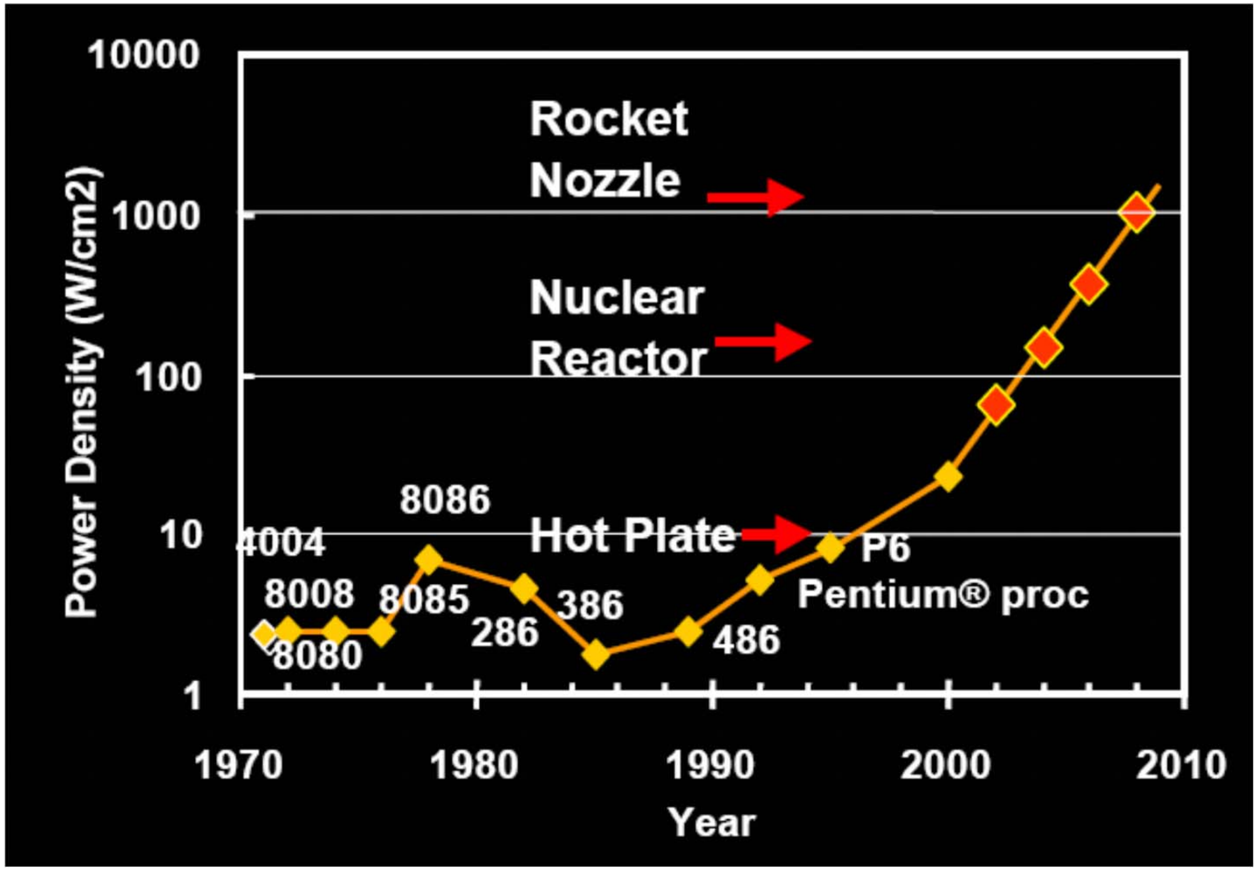


Computing speed is limited by inertia of electrons

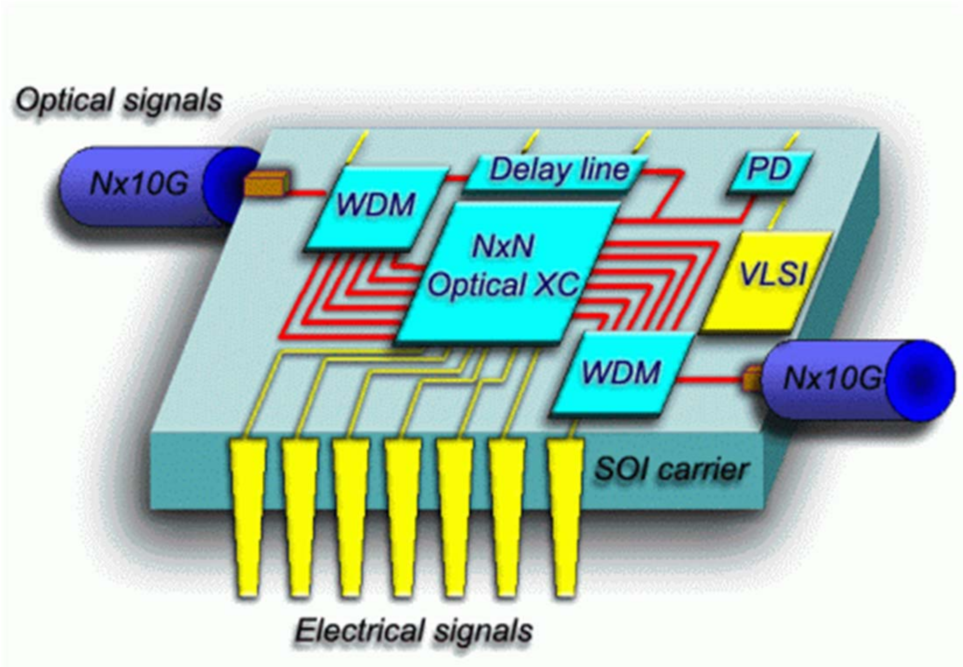
The interconnect bottleneck

- 10^9 devices per chip
- Closely spaced metal wires slow down computation
- Huge heat generated due to electric resistance





THE DREAM: could we replace electrons with photons, and electric circuits with all-optical circuits?



IBM website

Futuristic silicon chip with monolithically integrated photonic and electronic circuits

wires → waveguides

Can electronic circuits be replaced by photonic ones?!

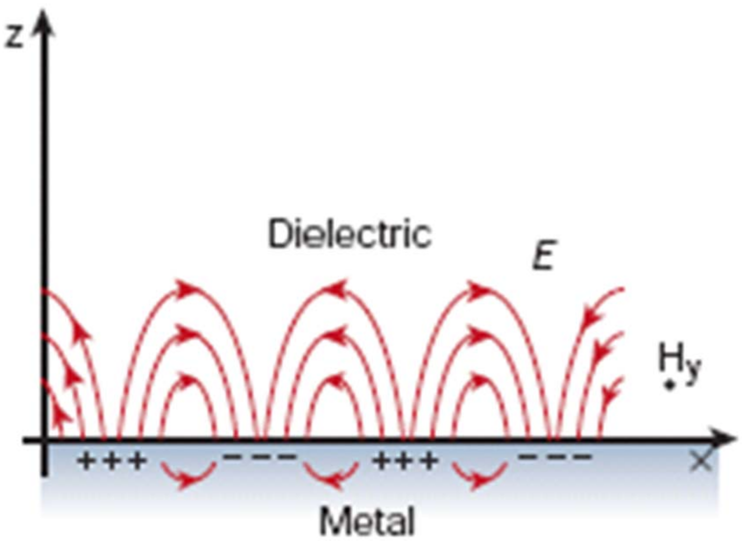
Using photons as bits of information instead of electrons would speed up the computing

Photons travel much faster and don’t dissipate as much power

However, large size of a photon would make computers 1000 times larger!

Optical computer is still a dream.

What is a surface plasmon polariton?

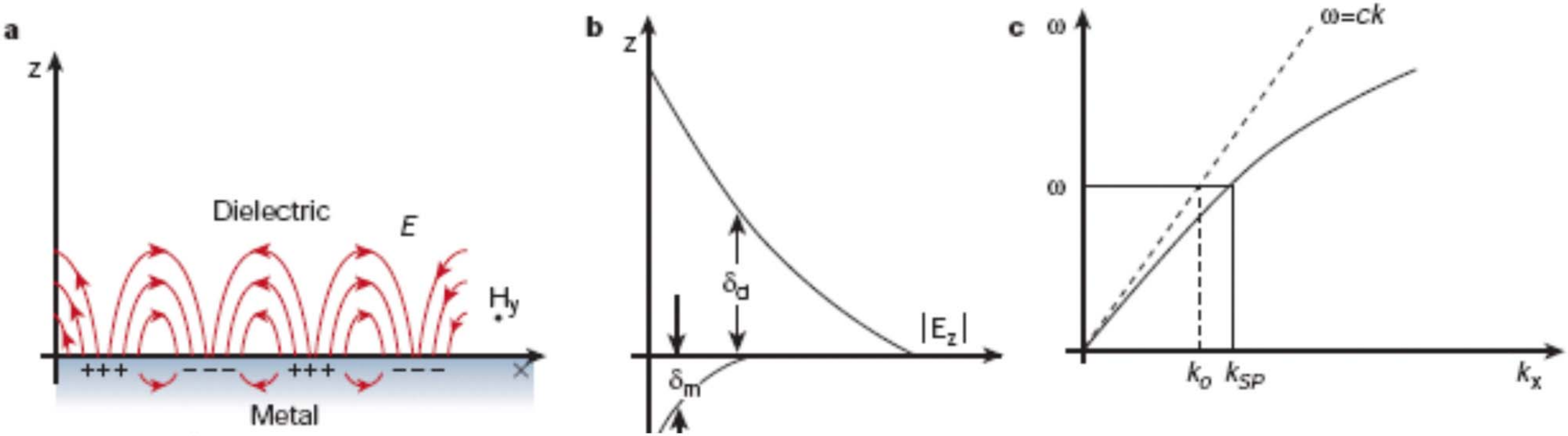


Barnes et al. Nature 2003

Transverse EM wave coupled to a plasmon (wave of charges on a metal/dielectric interface) = SPP (surface plasmon polariton)

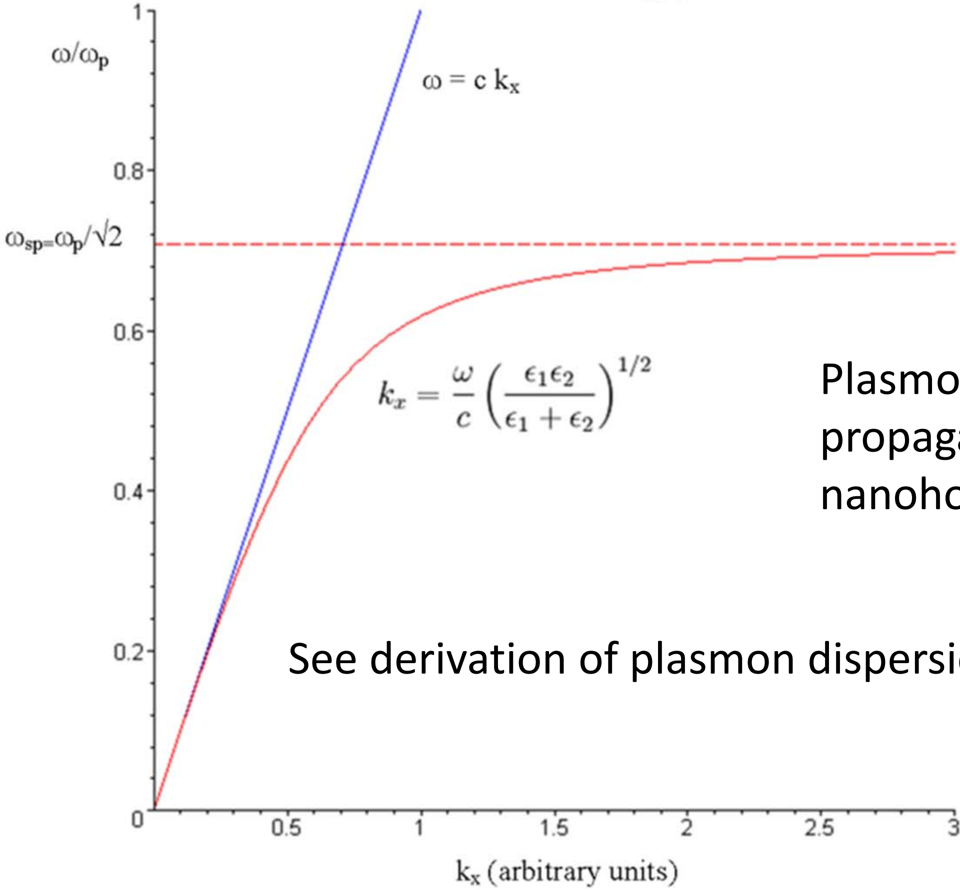
Note: the wave has to have the component of E transverse to the surface (be TM-polarized).

Polariton – any coupled oscillation of photons and dipoles in a medium



Barnes et al. Nature 2003

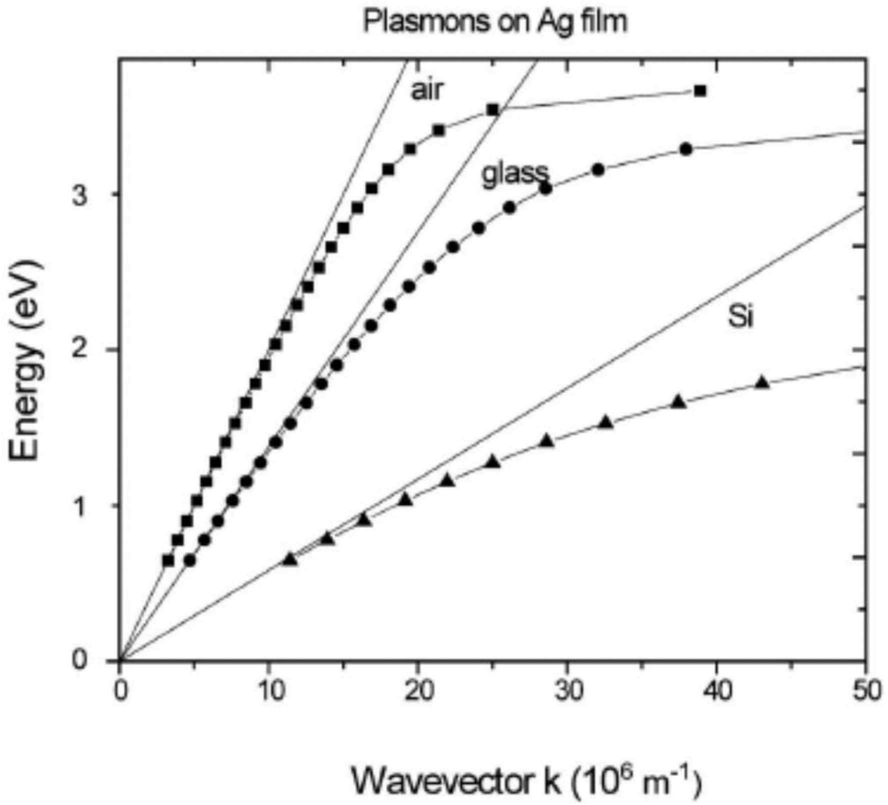
Surface plasmons

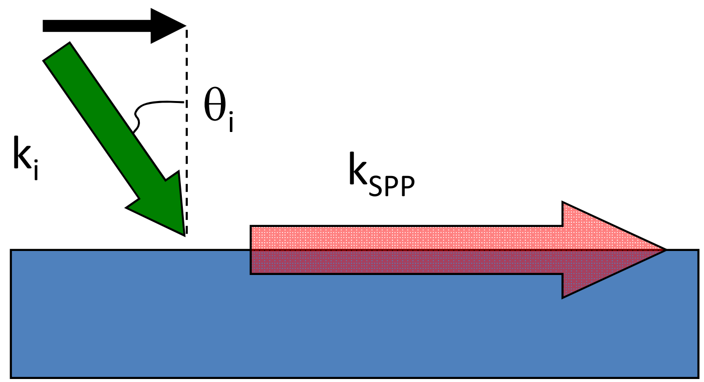


Plasmons can be confined to nanoscale and propagate along nanostrips, through nanoholes, etc.

See derivation of plasmon dispersion on white board

Note: we cannot excite SPP by simply illuminating the surface!





Excitation condition

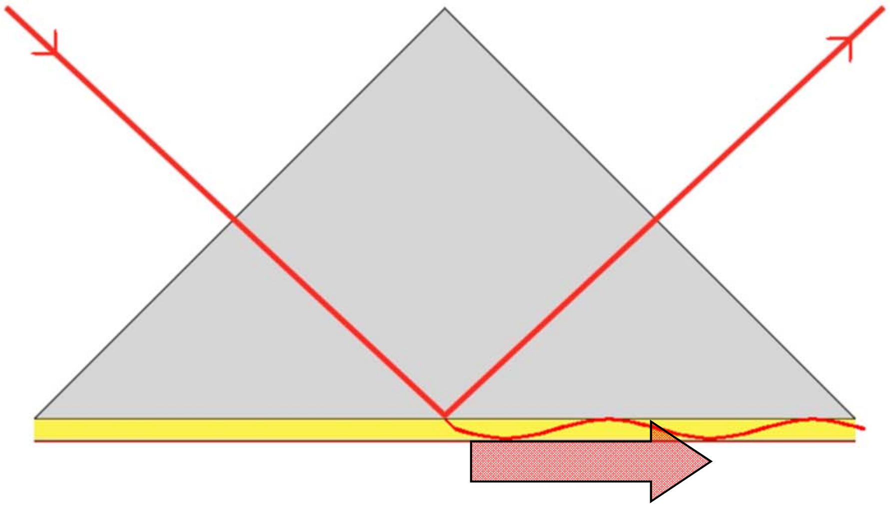
$$k_i \sin\theta_i = k_{SPP}$$

Impossible to satisfy!
k_i is always less than k_{SPP}

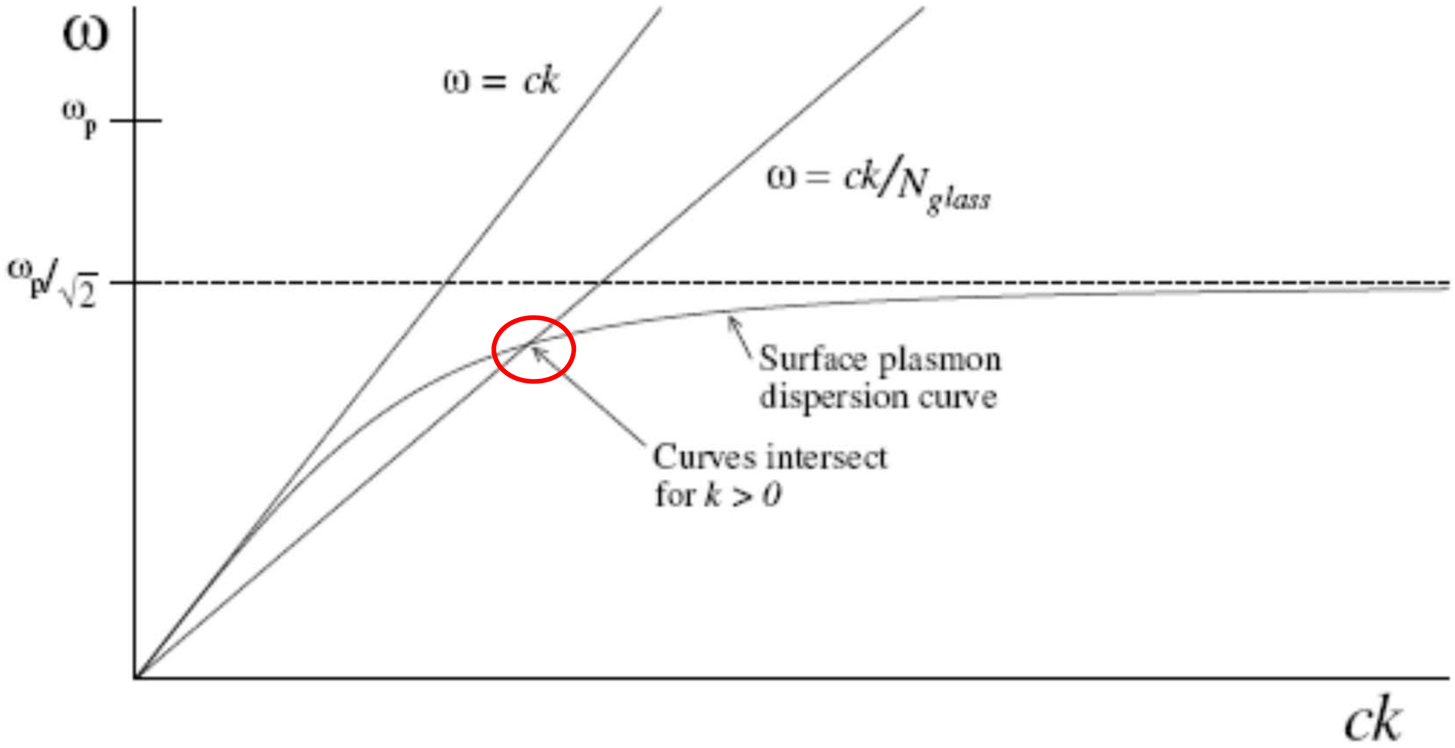
Calculated dispersion of surface plasmon-polaritons propagating at a Ag/air, Ag/glass, and Ag/Si interface, respectively.

Maier & Atwater, JAP 2005

Excitation of SPP:
Kretschmann configuration

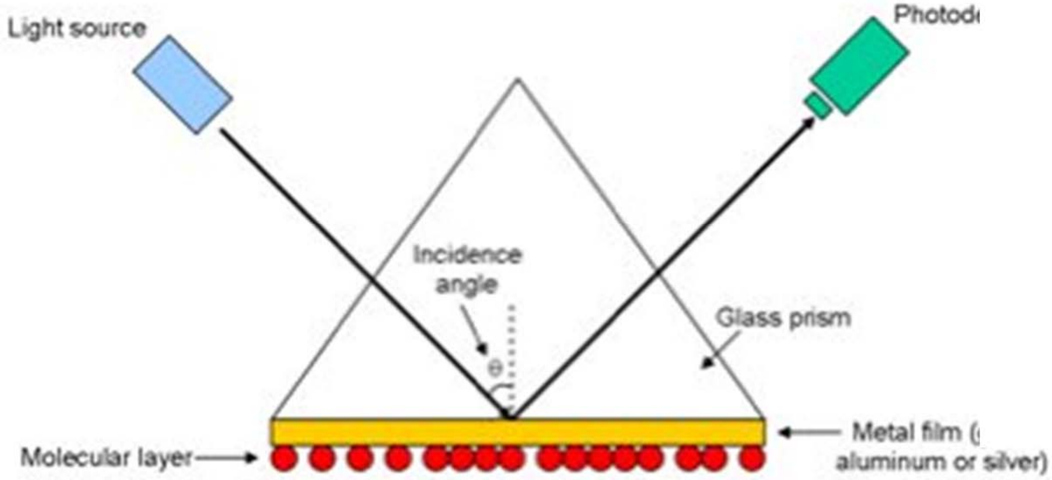


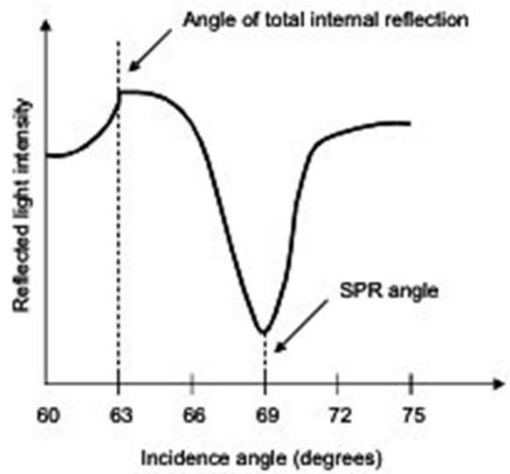
Note: these SPP are not particularly small-size



Nevertheless, this technique is simple and can be used when we don't care about having short SPP wavelength

Chem-Bio Sensing in the Kretschmann configuration

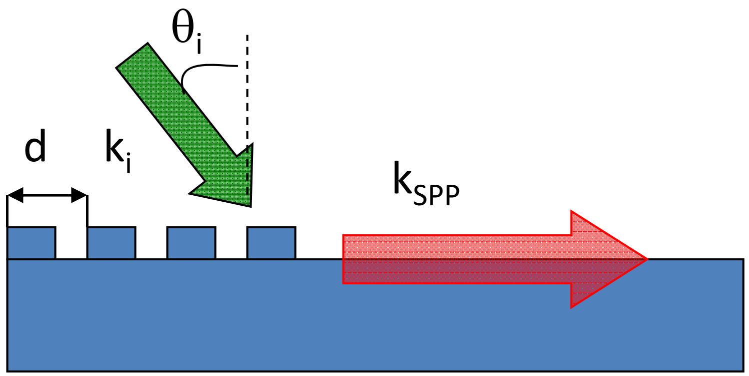




Example of SPR spectrum

Note: the angle is in the TIR range!

Exciting SPP (or any mode of your choice) by scattering light off grating



This is effectively a (quasi-)momentum conservation

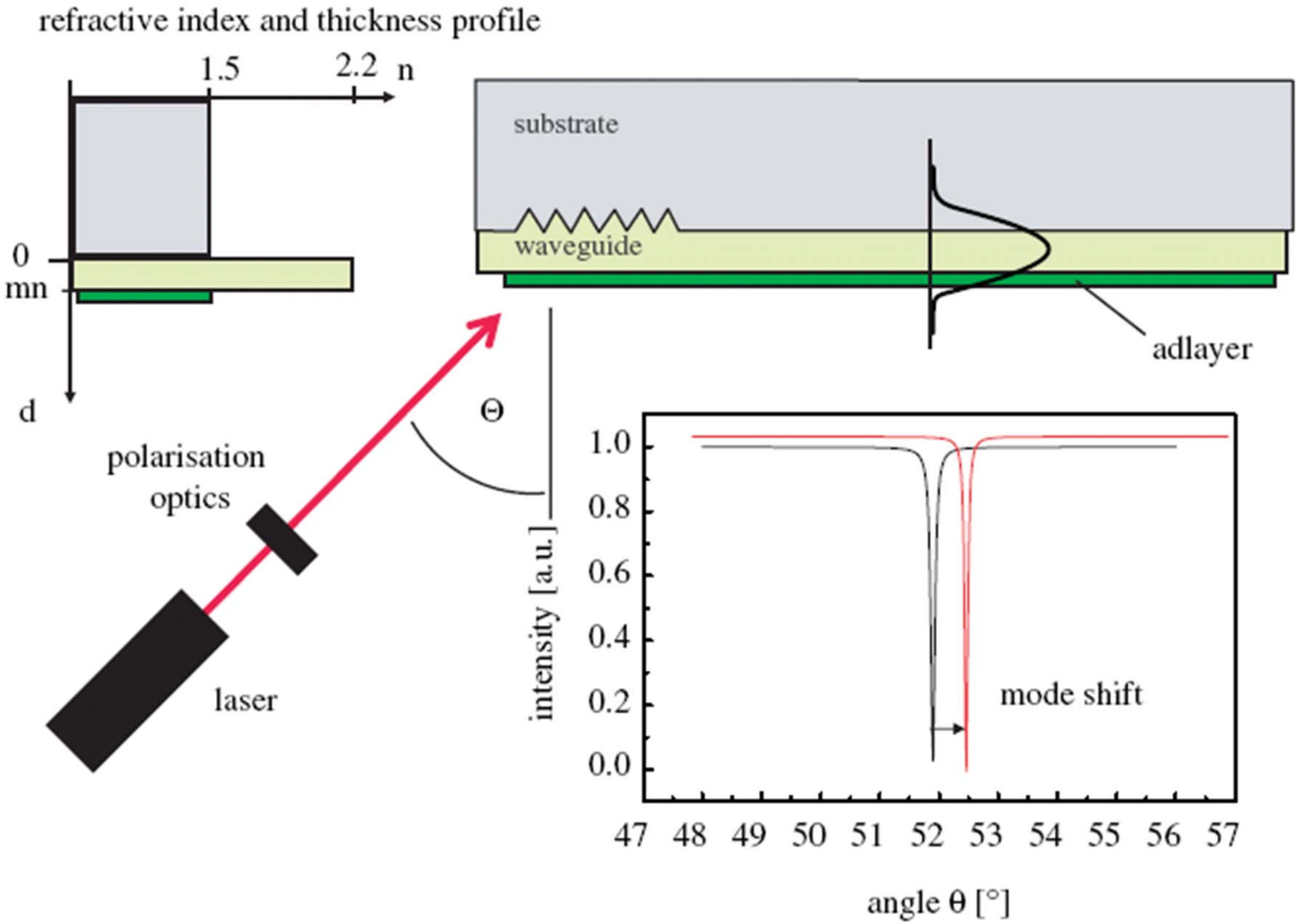
Grating changes longitudinal wave vector of a photon by

$$K_g = \pm m \frac{2\pi}{d}; \; m = 1,2,\ldots$$

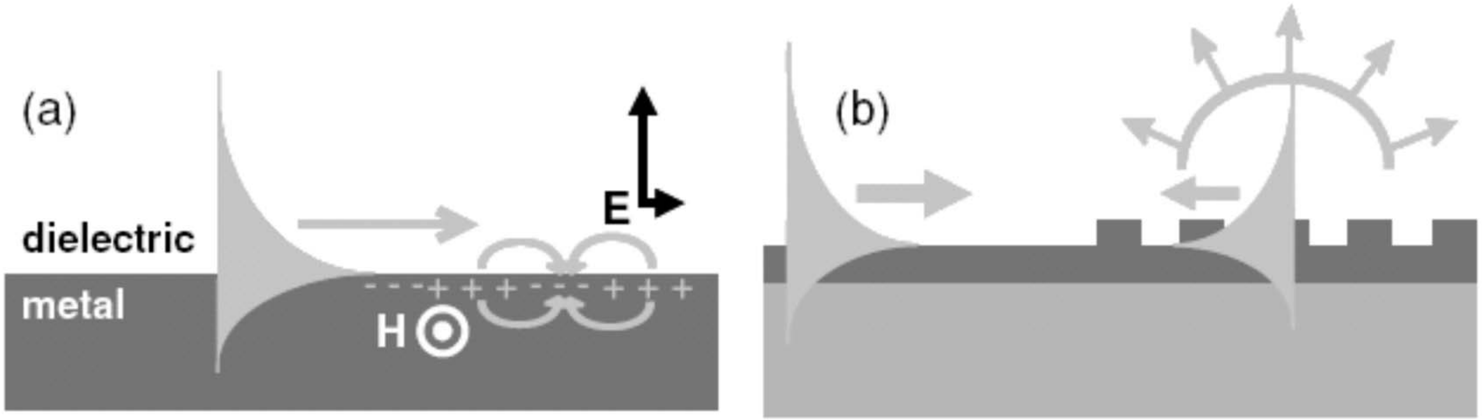
Coupling to SPP is achieved when

$$k_i \sin\theta_i + K_g = k_{SPP}$$

Adsorbed molecules change the excitation angle of EM mode

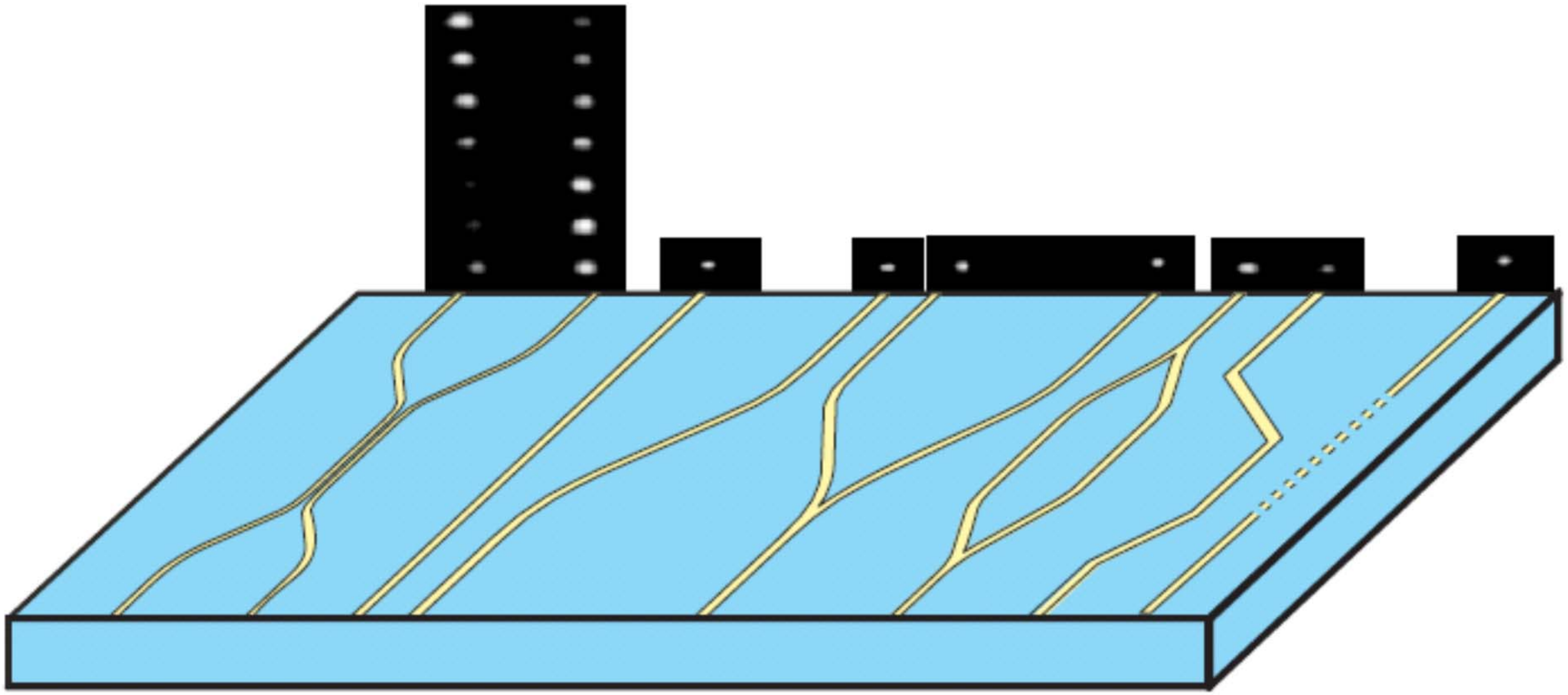


Grating can be also used to <u>extract</u> SPPs:



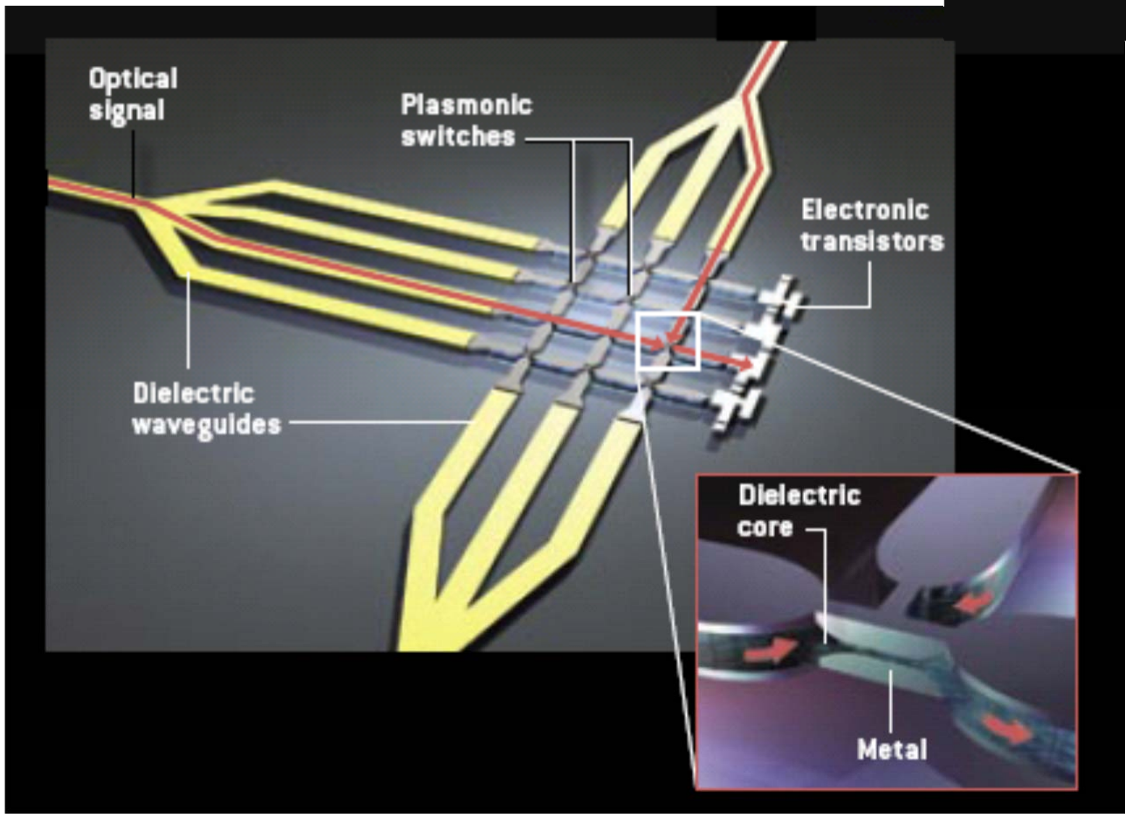
Bozhevolnyi 2007

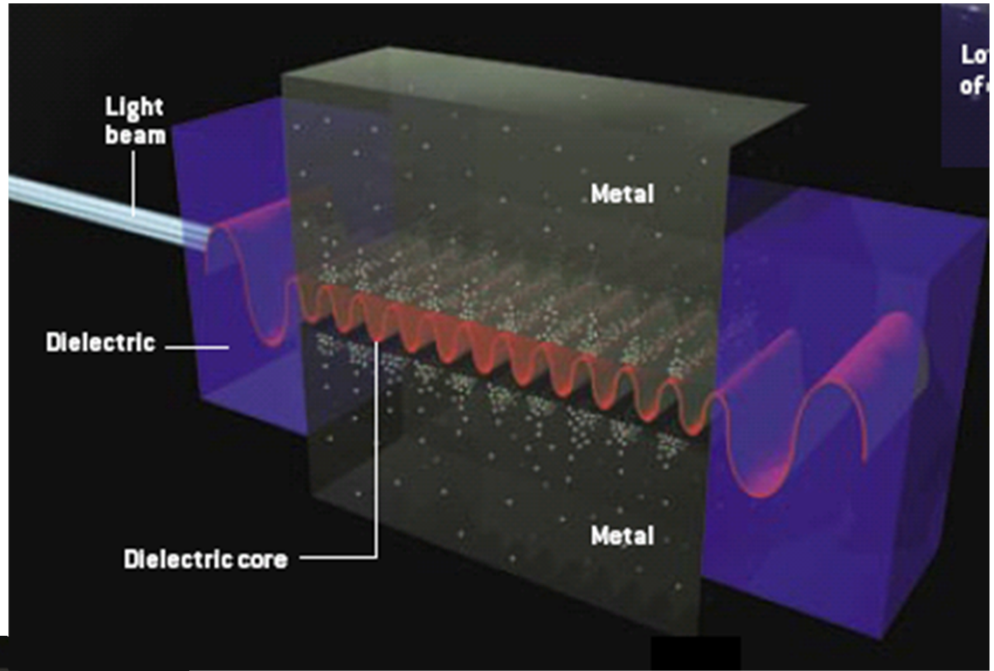
Elements of integrated photonic chips based on SPP



THE DREAM: Plasmonic chips

Plasmonic switches (“plasmonsters”)

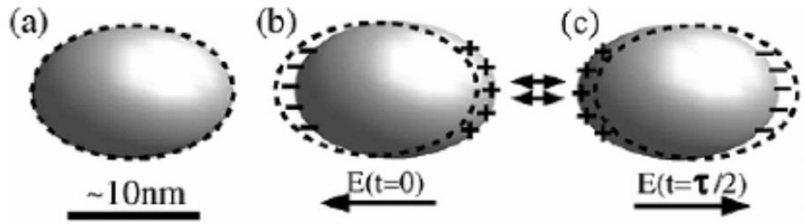


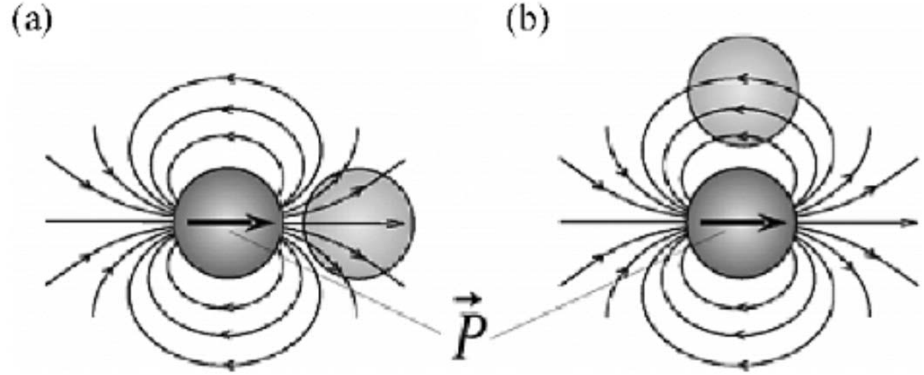


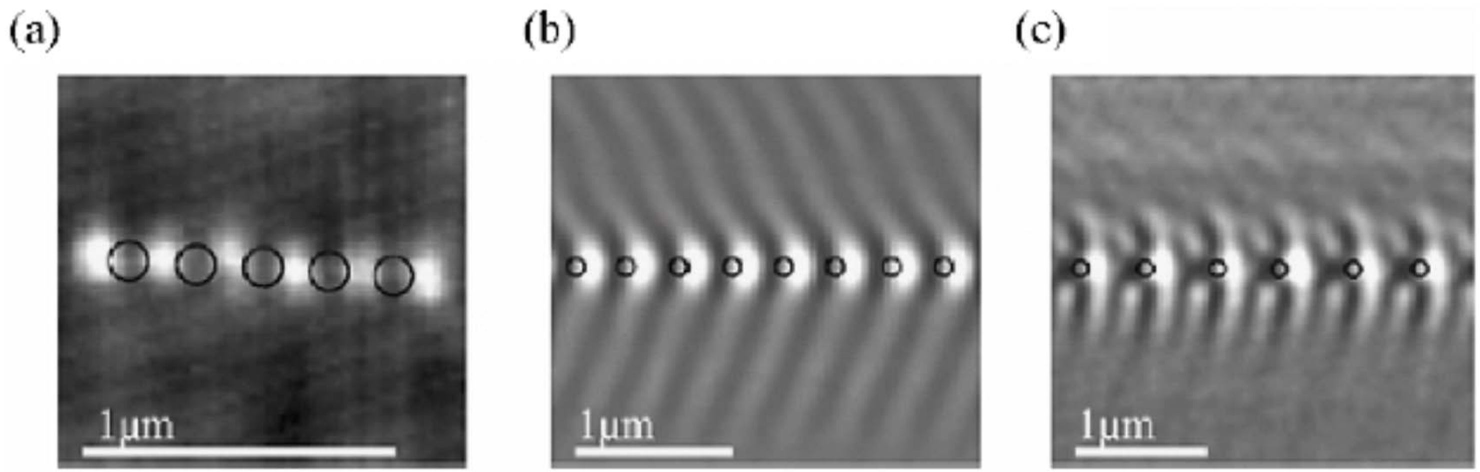
Slot waveguide

H. Atwater, Sci. Am. 2007

Plasmon waveguides made from chains of nanoparticles







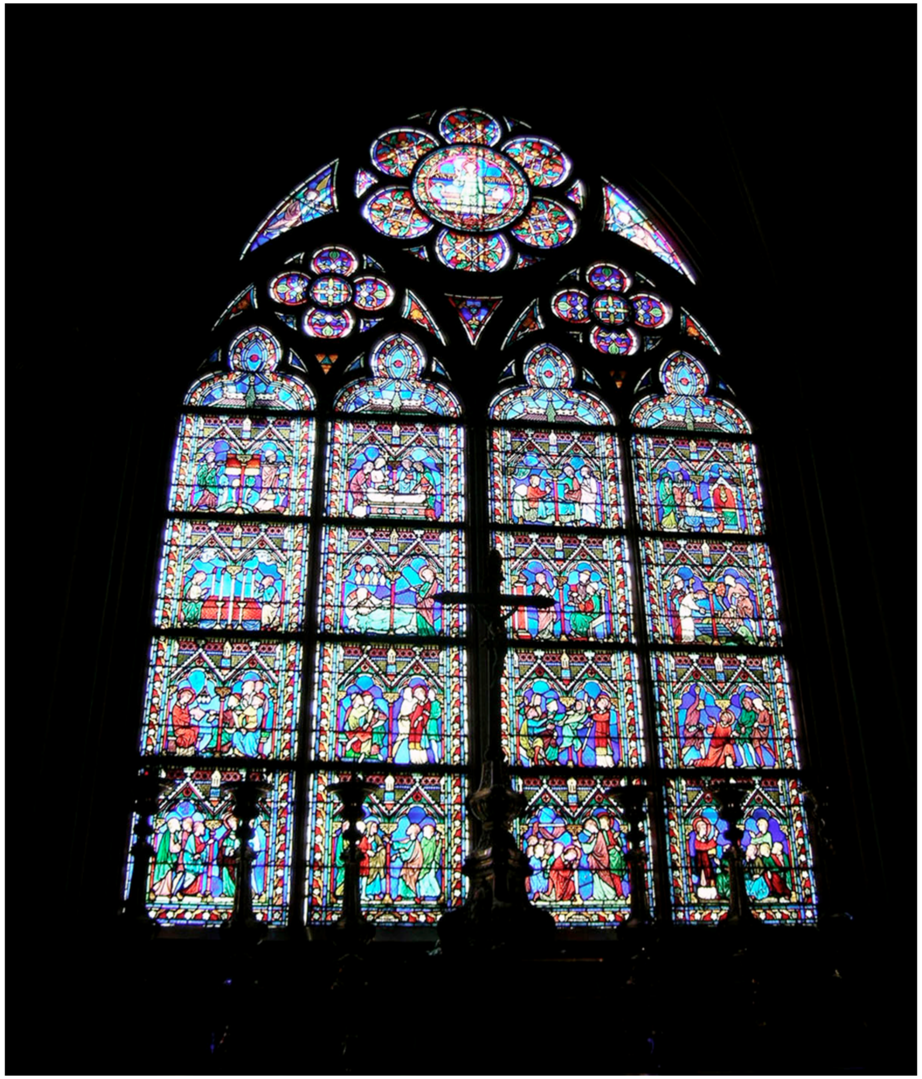
Hohenau et al. 2007

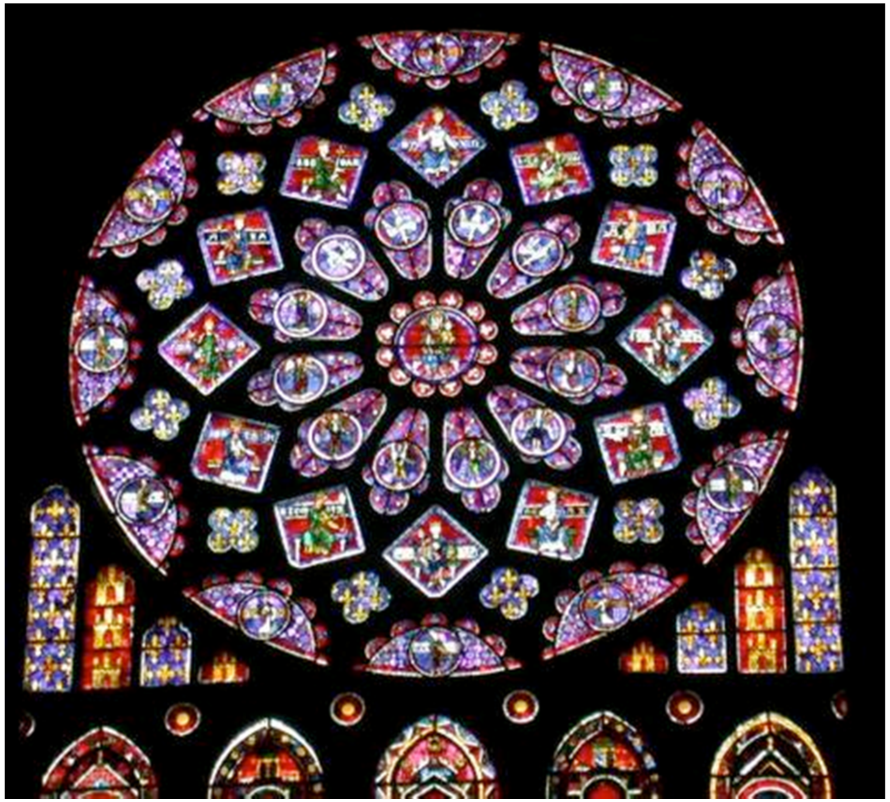
LYCURGUS CUP, a Roman goblet dating from the fourth century A.D., changes color because of the plasmonic excitation of metallic particles within the glass matrix. When a light source is placed inside the normally greenish goblet, it looks red.

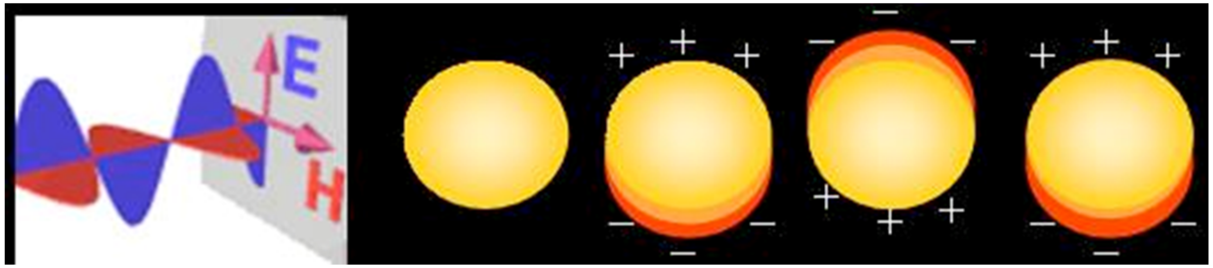
Plasmon absorption by metallic nanoparticles in stained glass windows, glass cups, ceramic pots

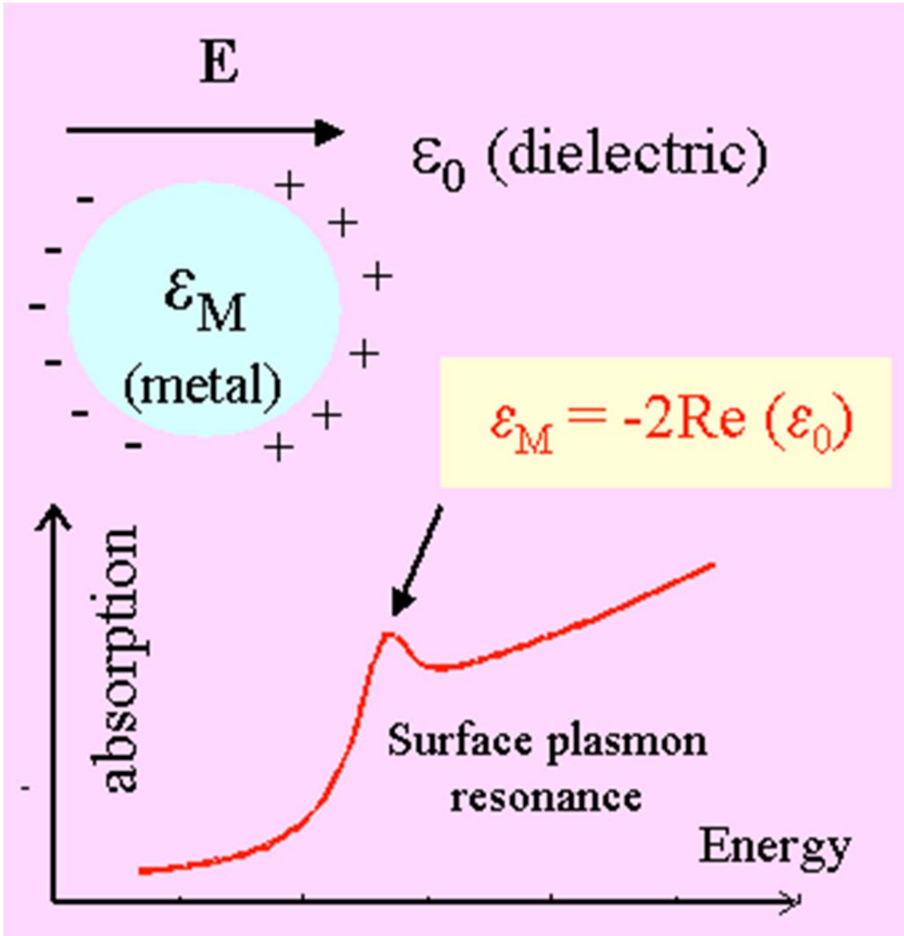
Lycurgus Cup, Romans 450 A.D.

Stained glass windows in Notre Dame

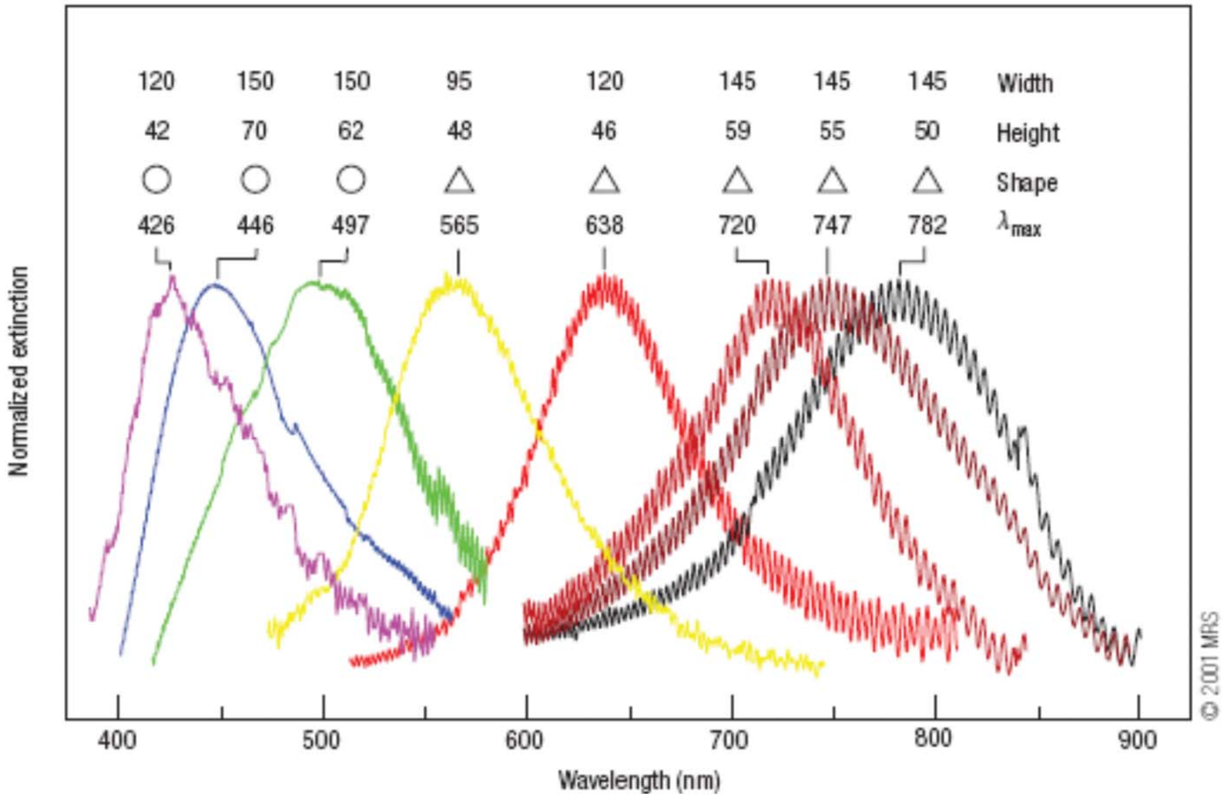





E
H


E
ε_0 (dielectric)
ε_M
(metal)
$\varepsilon_M = -2\mathrm{Re}\,(\varepsilon_0)$
absorption
Surface plasmon
resonance
Energy

The shape of the nanoparticle extinction and scattering spectra, and in particular the peak wavelength λ_{max}, depends on nanoparticle composition, size, shape, orientation and local dielectric environment.

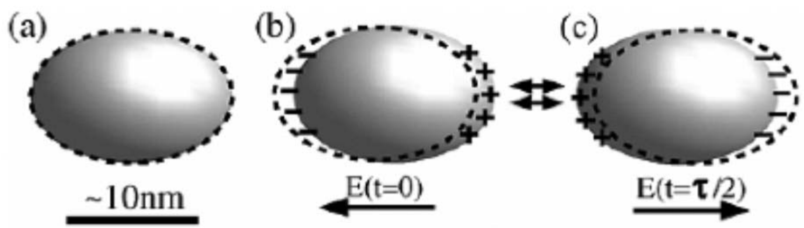


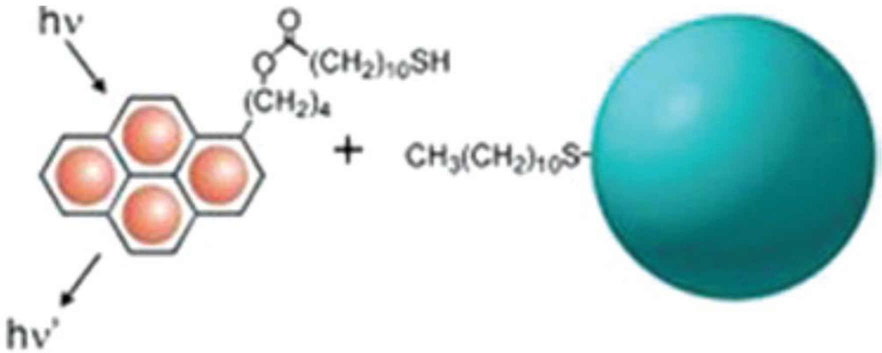
Effect of size and shape on LS PR extinction spectrum for silver nanoprisms and nanodiscs formed by nanosphere lithography. The high-frequency signal on the spectra is an interference pattern from the reflection at the front and back surfaces of the mica.

Anker et al., Nature Mat. 2008

Light incident on the nanoparticles induces the conduction electrons in them to oscillate collectively with a resonant frequency that depends on the nanoparticles' size, shape and composition. As a result of these LSPR modes, the nanoparticles absorb and scatter light so intensely that single nanoparticles are easily observed by eye using dark-field (optical scattering) microscopy.

This phenomenon enables noble-metal nanoparticles to serve as extremely intense labels for immunoassays, biochemical sensors and surface-enhanced spectroscopies.





What to observe?? (a) shift of the SPR spectrum

When molecules bind to a nanoparticle, the SPR peak wavelength is shifted:

$$\Delta\lambda \approx m(n_{adsorbate} - n_{medium})(1 - e^{-2d/l_d})$$

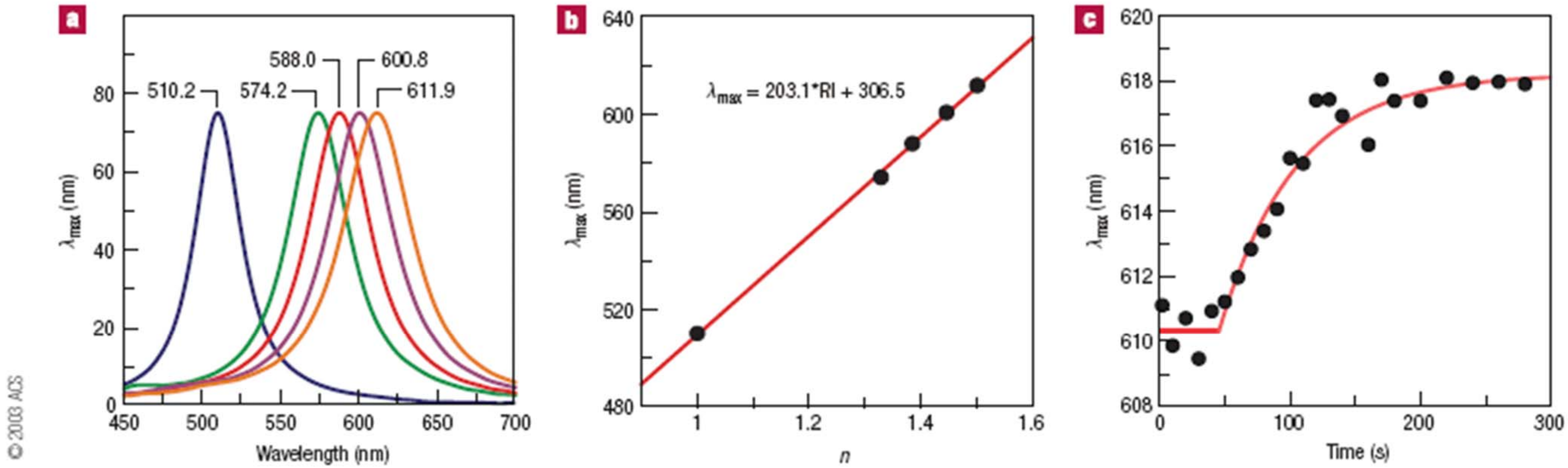


Figure 2 Single-nanoprism LSPR. **a**, Resonant Rayleigh scattering spectrum from a single silver nanoparticle in various solvent environments (left to right): nitrogen, methanol, propan-1-ol, chloroform and benzene. **b**, Plot depicting the linear relationship between the solvent refractive index n and the LSPR λ_{max}; the regression equation is $\lambda = 203.1n + 306.5$. **c**, Monitoring the real-time adsorption of octanethiol (1 mM) onto a single nanoparticle. At this concentration, the rate constant is estimated to be 0.017 s^{-1}. Reprinted with permission from ref. 11.

Anker et al., Nature Mat. 2008

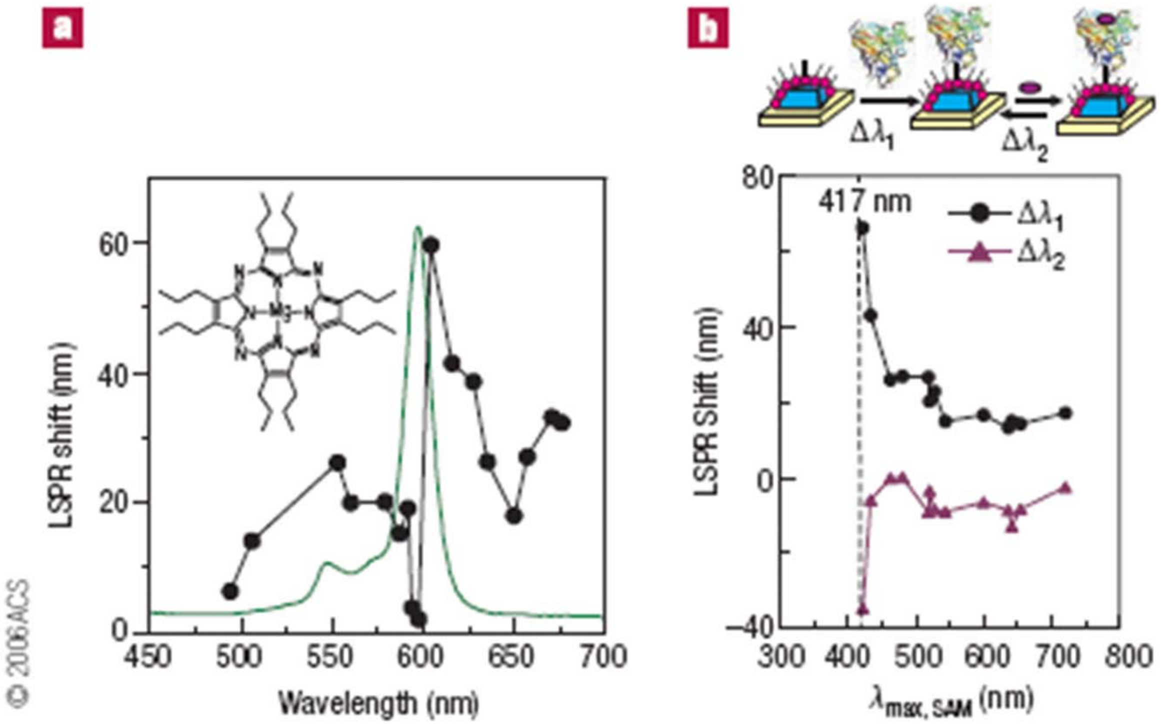
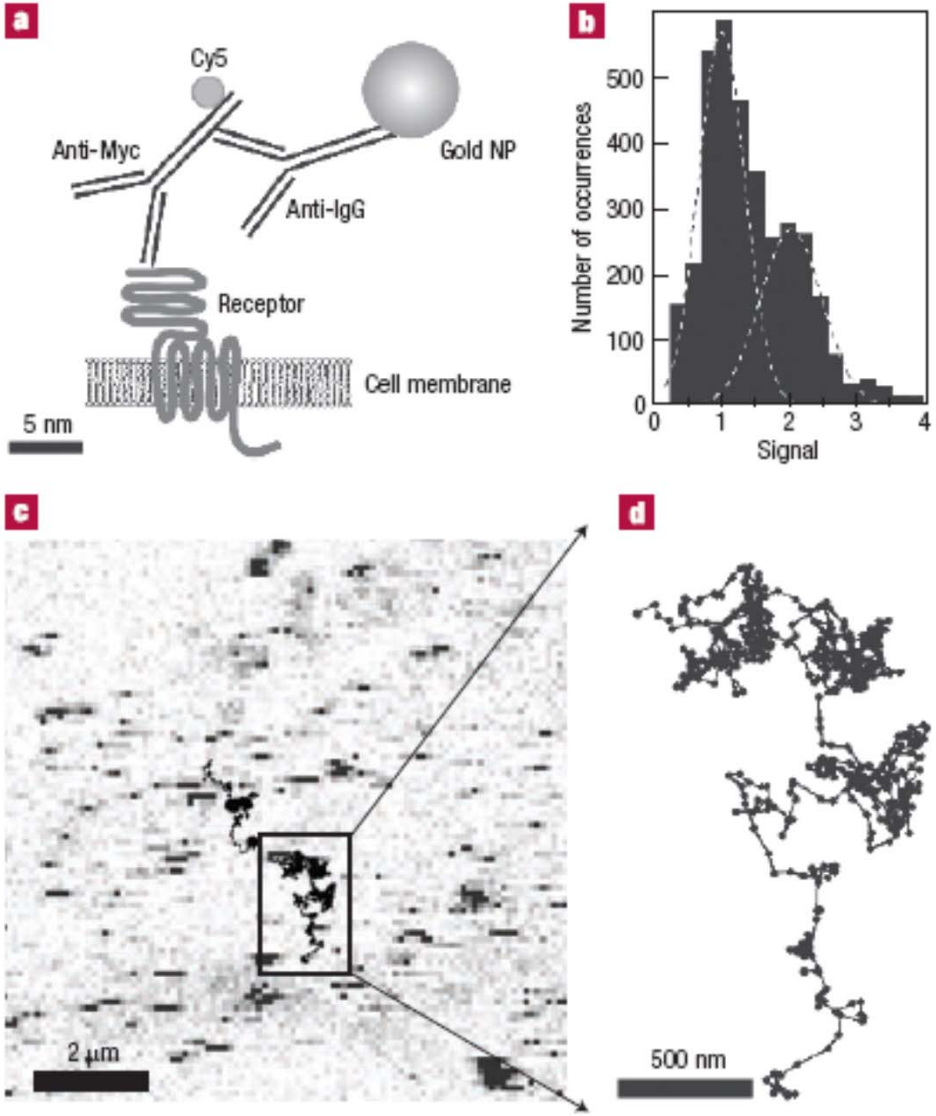


Figure 4 Wavelength-dependent LSPR shifts induced by resonant molecules. **a**, Comparison of LSPR shifts induced by a monolayer of MgPz adsorption on silver nanoparticles with the LSPR of bare silver nanoparticles (black line with dots). Inset: molecular structure of MgPz. Reprinted with permission from ref. 70. The green line is the solution absorption spectrum of MgPz. **b**, Schematic representation of CYP101 immobilized on a silver nanobiosensor followed by binding of camphor, and plots of LSPR shifts against $\lambda_{max,SAM}$ (LSPR of SAM-functionalized nanoparticles), where $\Delta\lambda_1$ is the shift on binding of CYP101 and $\Delta\lambda_2$ is the shift on binding of camphor. The vertical black dotted line denotes the molecular resonance of substrate-free CYP101. Reprinted with permission from ref. 72.

Anker et al., Nature Mat. 2008

What to observe?? (b) increase in temperature caused by optically heating the nanoparticle and its environment



You can track these particles by scattering the probe beam off a thermally induced change in the refractive index!

Anker et al., Nature Mat. 2008