Surfaces, Interfaces, and Thin Films: Characterisation at the Nanometre Scale

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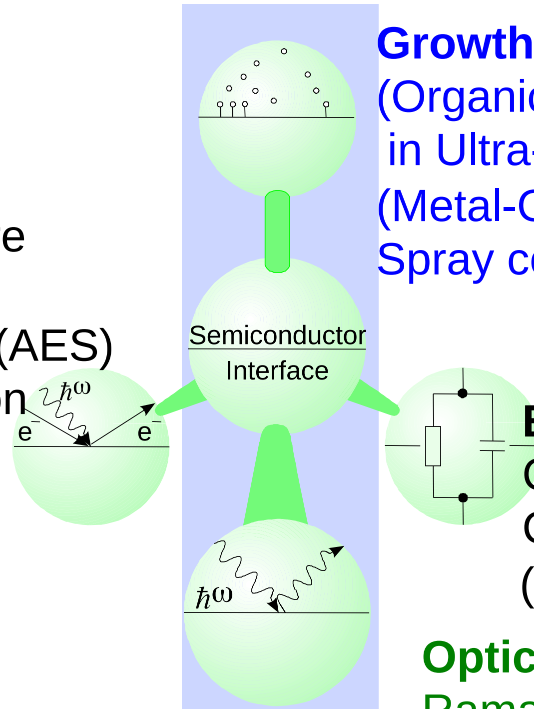
1. Photons vs. electrons: Basic considerations for achieving surface/interface sensitivity
2. Extending the photon energies towards the vacuum ultraviolet region: Ellipsometry using synchrotron radiation
3. Special ways of achieving surface/interface sensitivity in Raman and reflectance anisotropy spectroscopy
4. High resolution photoemission and X-ray absorption fine structure measurements

Semiconductor Physics – Activities in Chemnitz

Surface Science:
Photoemission Spectroscopy (UPS and XPS)
X-ray Absorption Fine Structure (NEXAFS)
Auger Electron Spectroscopy (AES)
Low Energy Electron Diffraction (LEED)
Inverse Photoemission
Kelvin Probe (CPD)



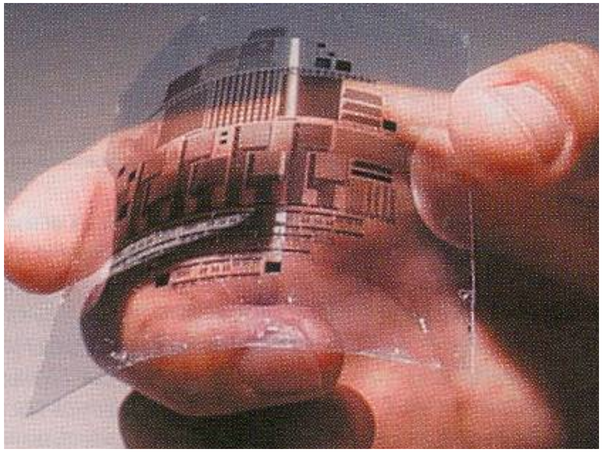
Growth:
(Organic) Molecular Beam Deposition in Ultra-High Vacuum
(Metal-Organic) Vapour Phase Deposition
Spray coating

Electrical Measurements:
Current-Voltage (IV)
Capacitance-Voltage (CV)
(Deep Level) Transient Spectroscopy

Nanoscale Characterization:
- Micro-Raman spectroscopy and imaging
- Atomic force microscopy
- Kelvin probe force microscopy, current sensing AFM
  Tip- and surface-enhanced Raman spectroscopy (TERS and SERS)
- ANSYS: finite element simulation package Matlab

Optical Spectroscopy:
Raman Spectroscopy (RS)
Spectroscopic Ellipsometry (SE)
Infrared Spectroscopy (IR)
Reflection Anisotropy Spectroscopy (RAS)
Photoluminescence and UV-vis

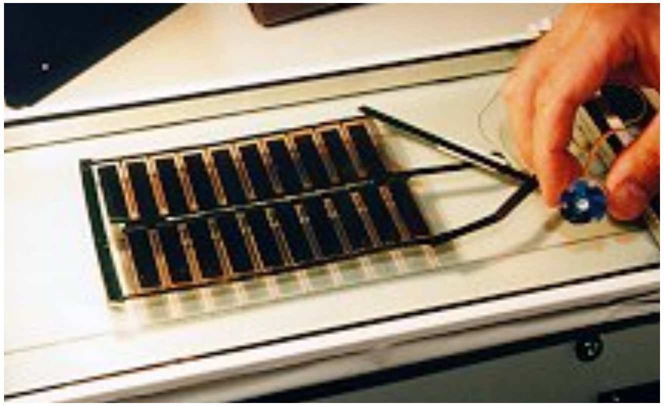
Organic field-effect transistors



Displays (Kodak)

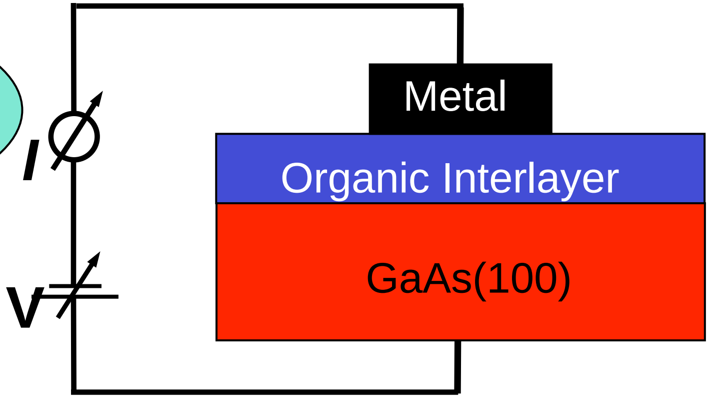
Electrically driven organic lasers

Organic semiconductors



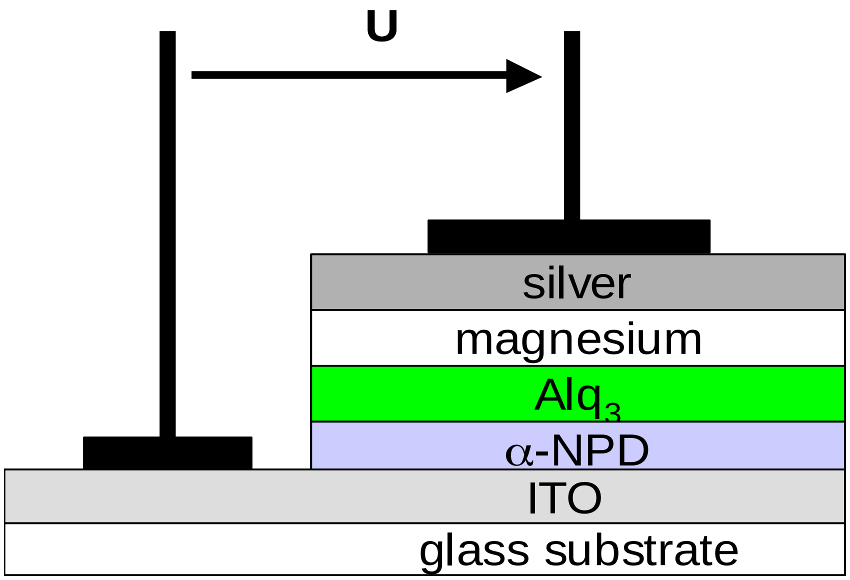
Plastic solar cells

Organic/Inorganic Microwave Diodes



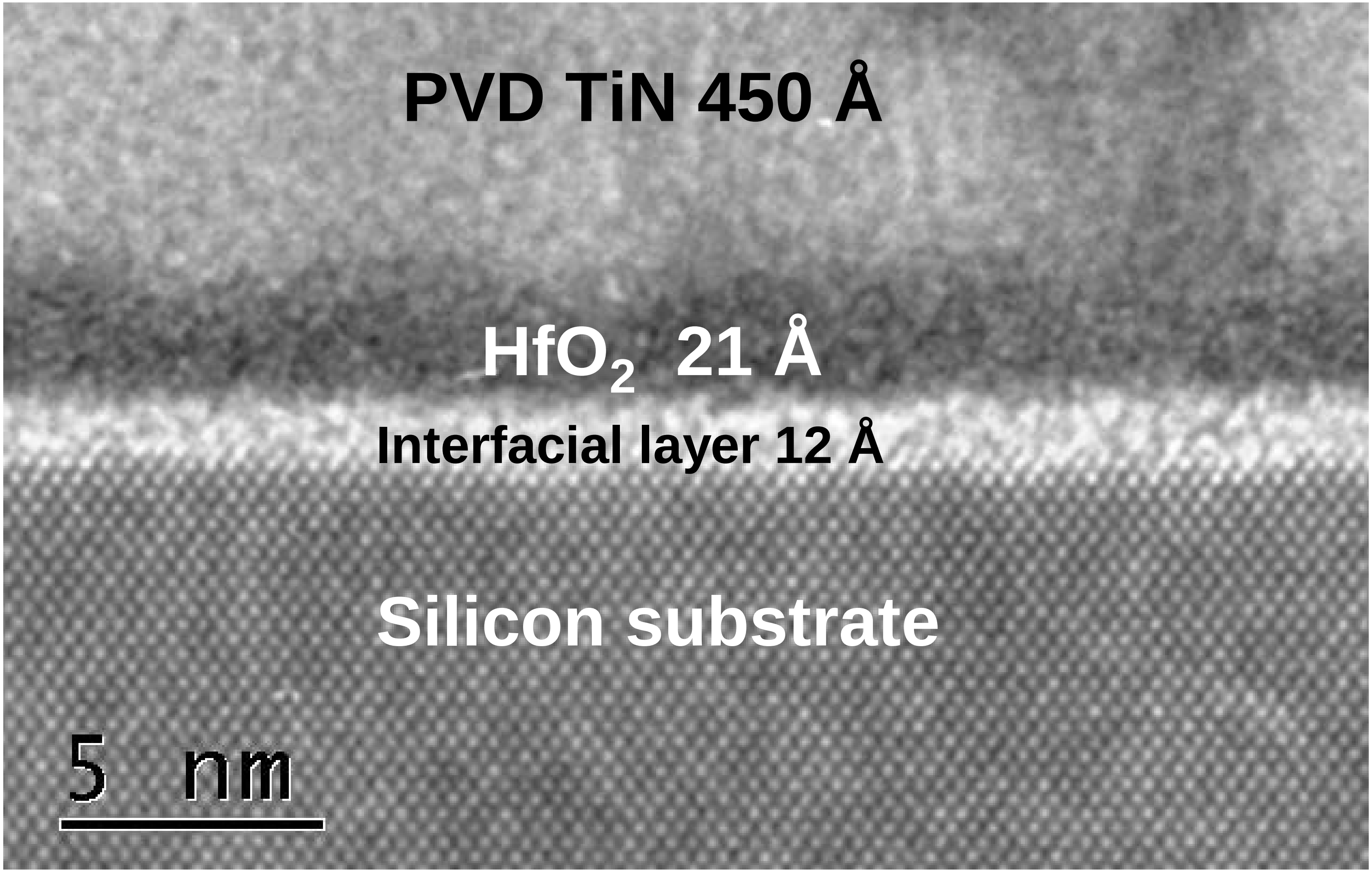
Organic-modified Schottky Diodes

First OVPD-OLED



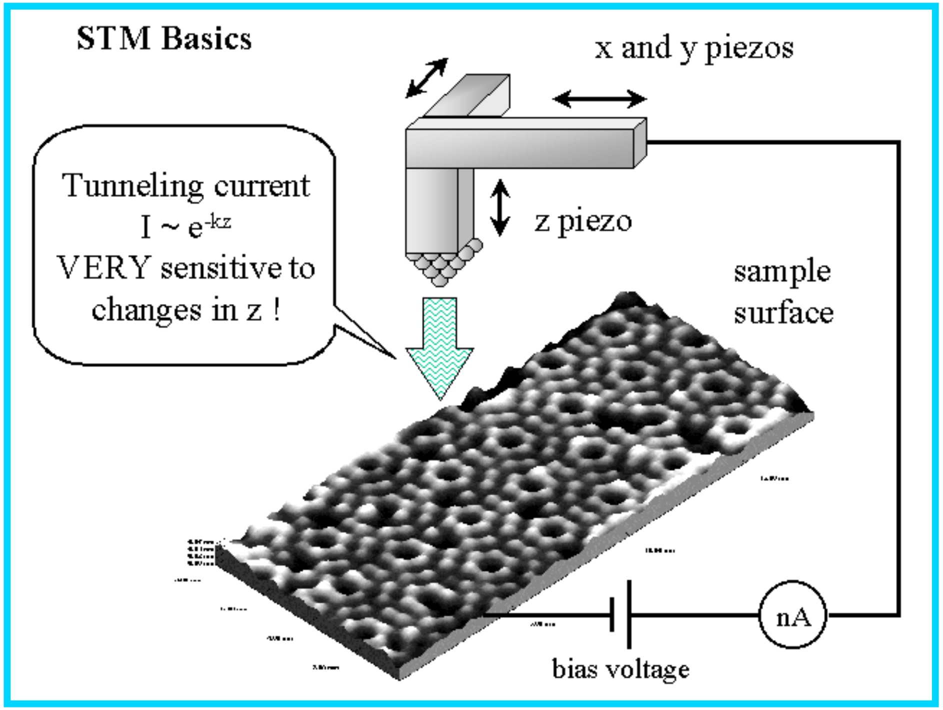
Structure of the large area OVPD-OLED device

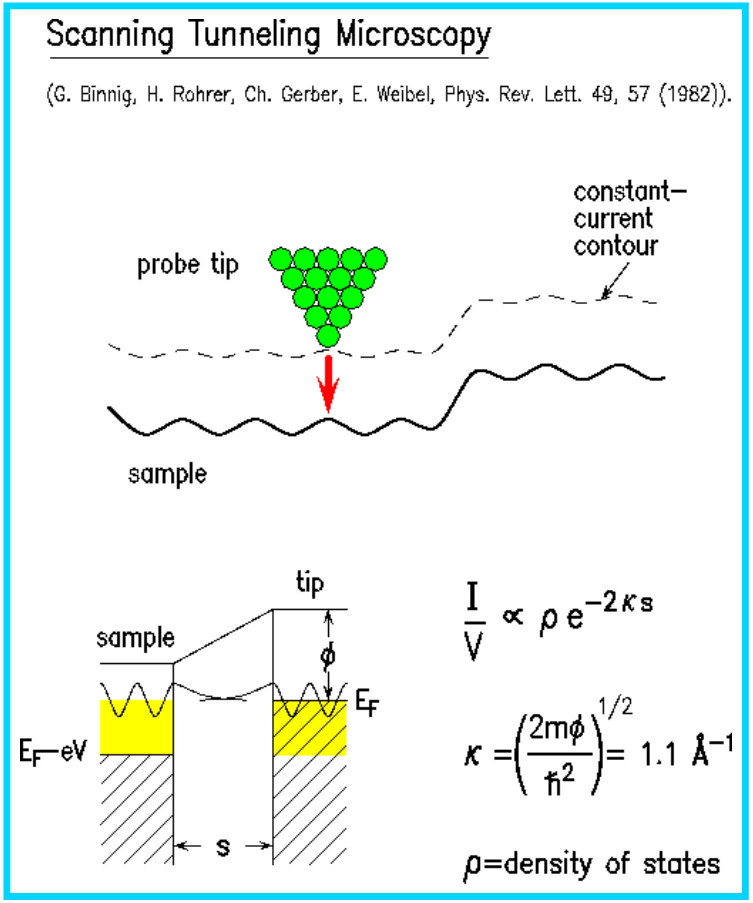
First large area *OVPD-OLED* displaying the Logo of TU Braunschweig processed on a substrate size of 35 x 50 mm².



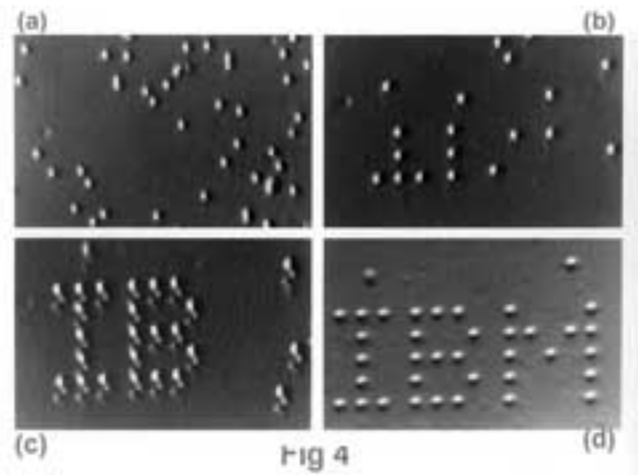
Avinash Agarwal *et al.*, Alternatives to SiO_2 as Gate Dielectrics for Future Si-Based Microelectronics, 2001 MRS Workshop Series (2001)

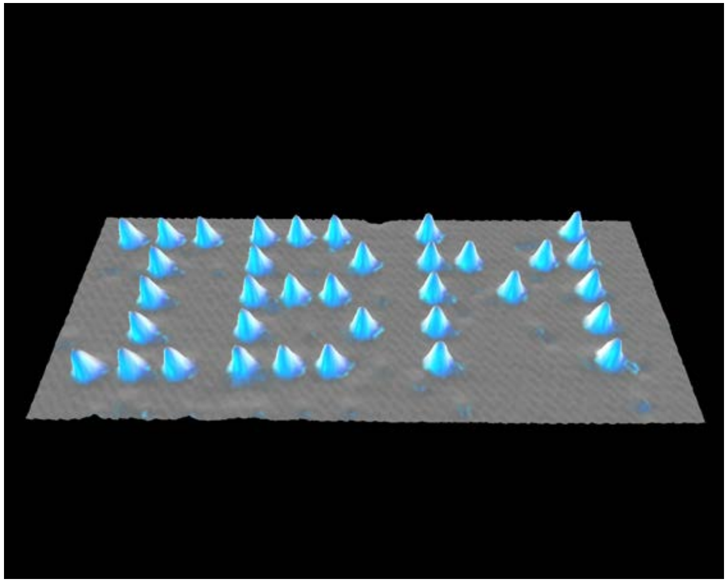
Scanning Tunneling Microscopy

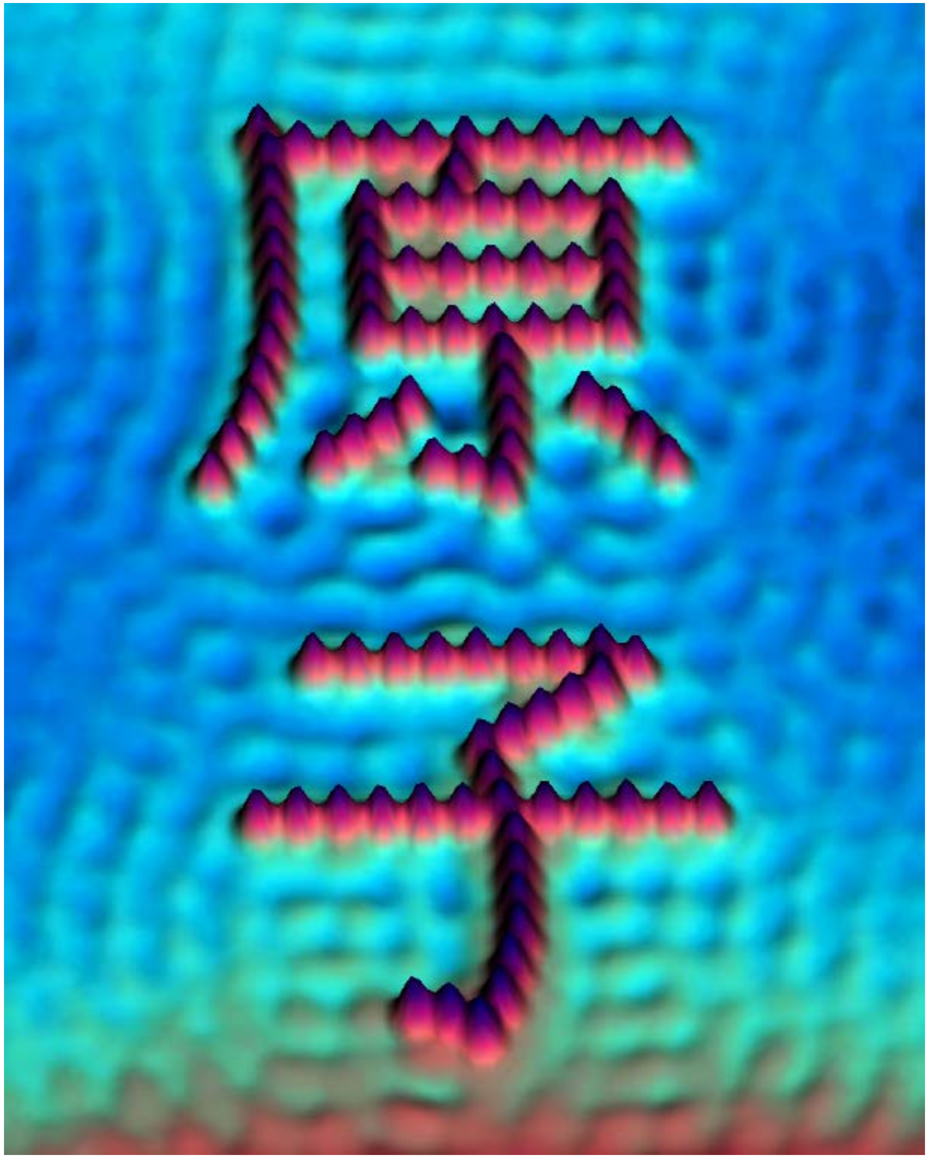




Moving atoms one at a time…

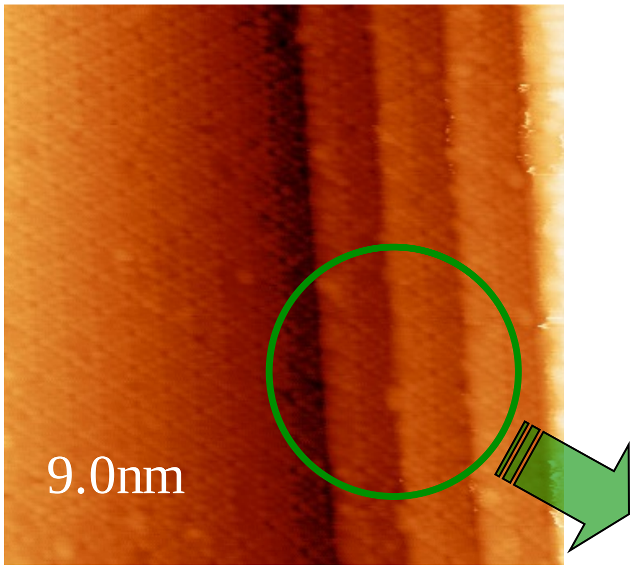


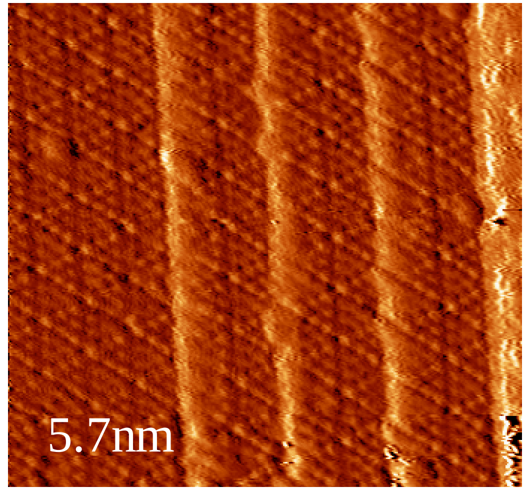


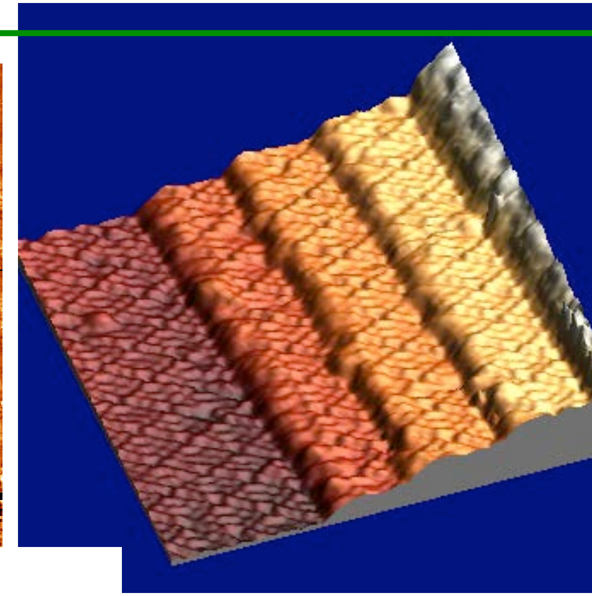


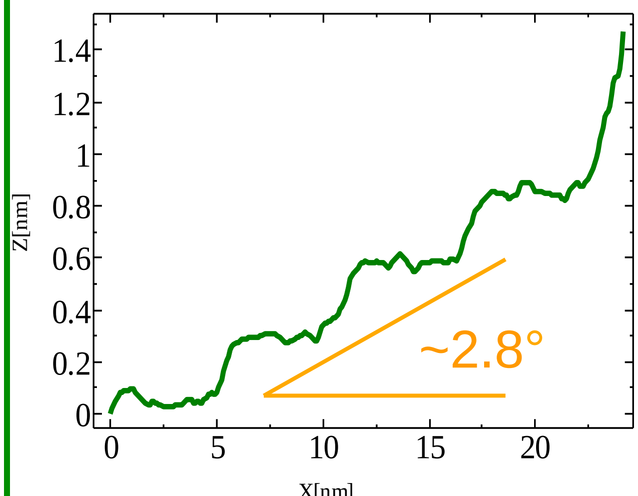
Monatomic Regular Steps on Si(111)-3°

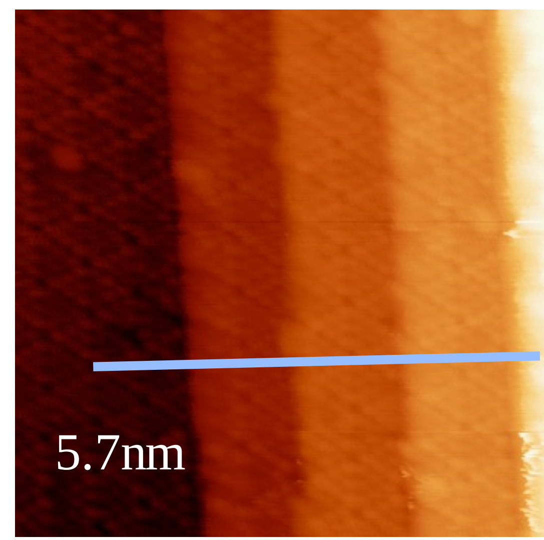
After 30sec. x 2times of flash











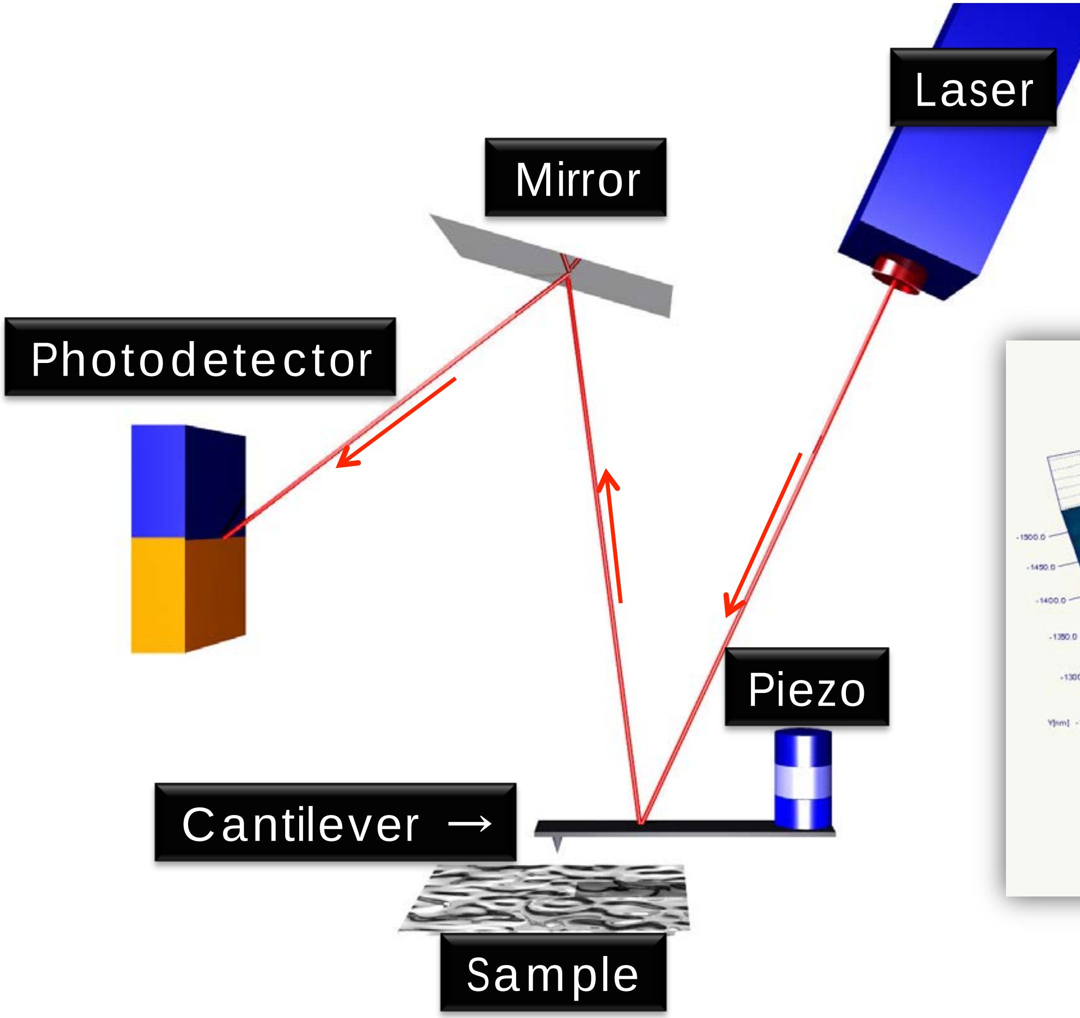
Monatomic layer on each step (0.3 nm/layer)

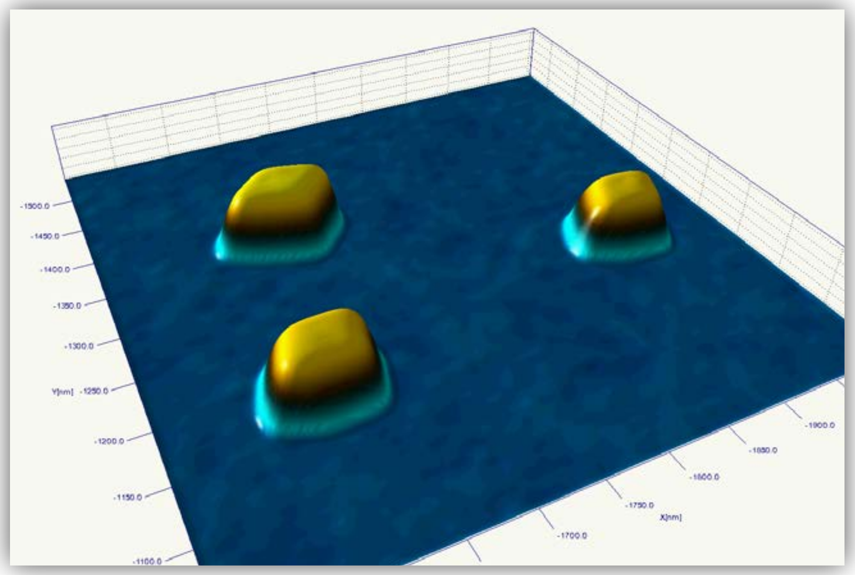
Equidistant terraces

Atomically straight edges

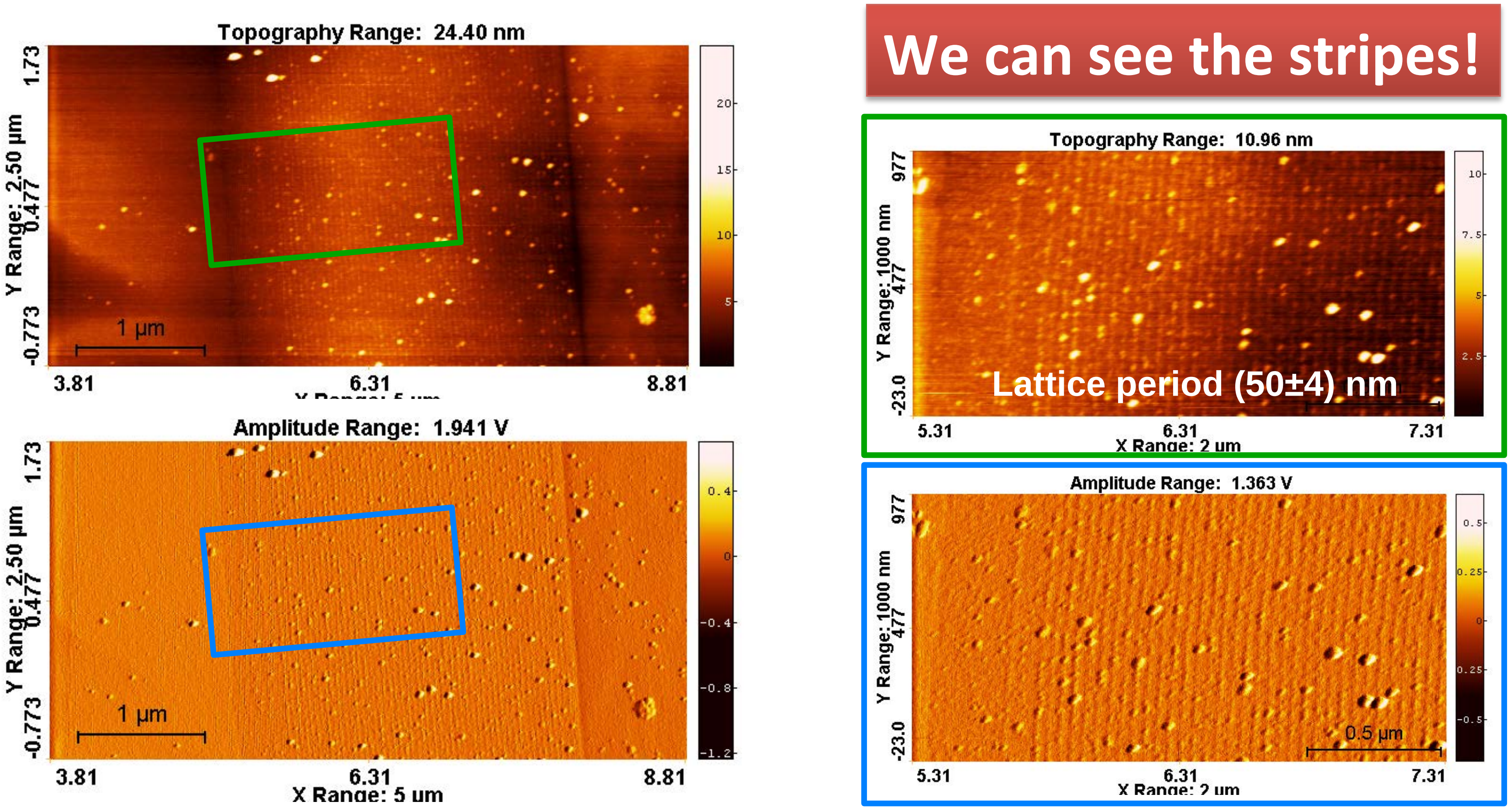
Experimental slope ~ Nominal value of wafer

Atomic force microscopy (AFM)

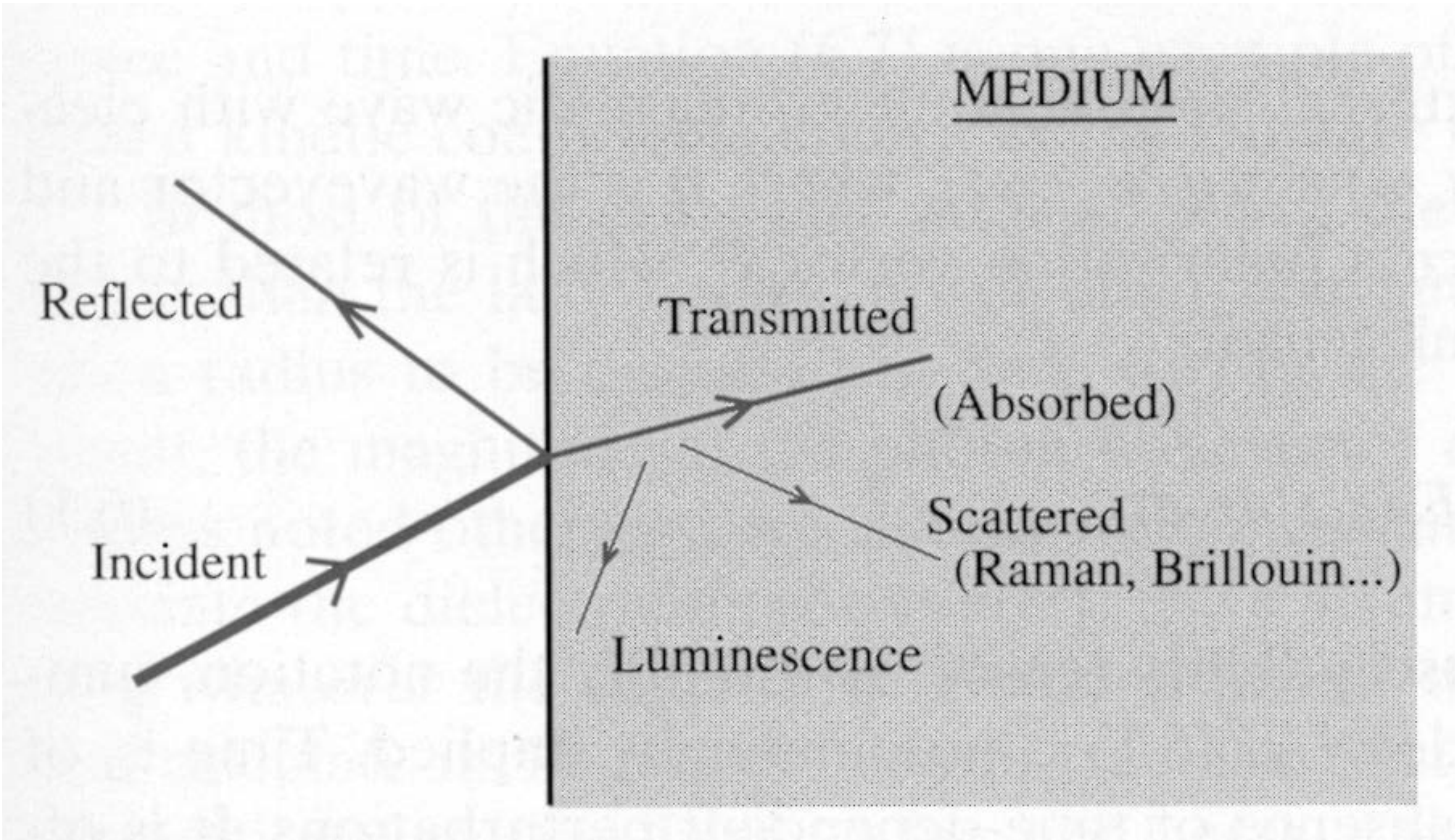




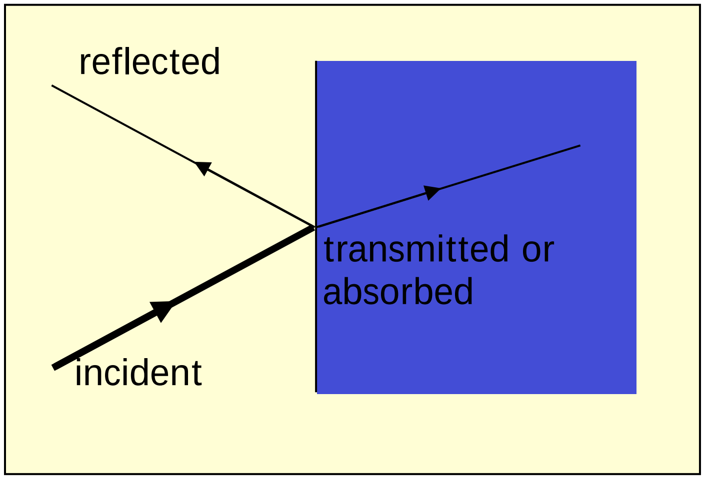
AlAs QDs in InAs matrix.
Ion milling with cooling.



Optical Spectroscopy



Light – Matter Interaction



Dielectric Function

$$\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$$

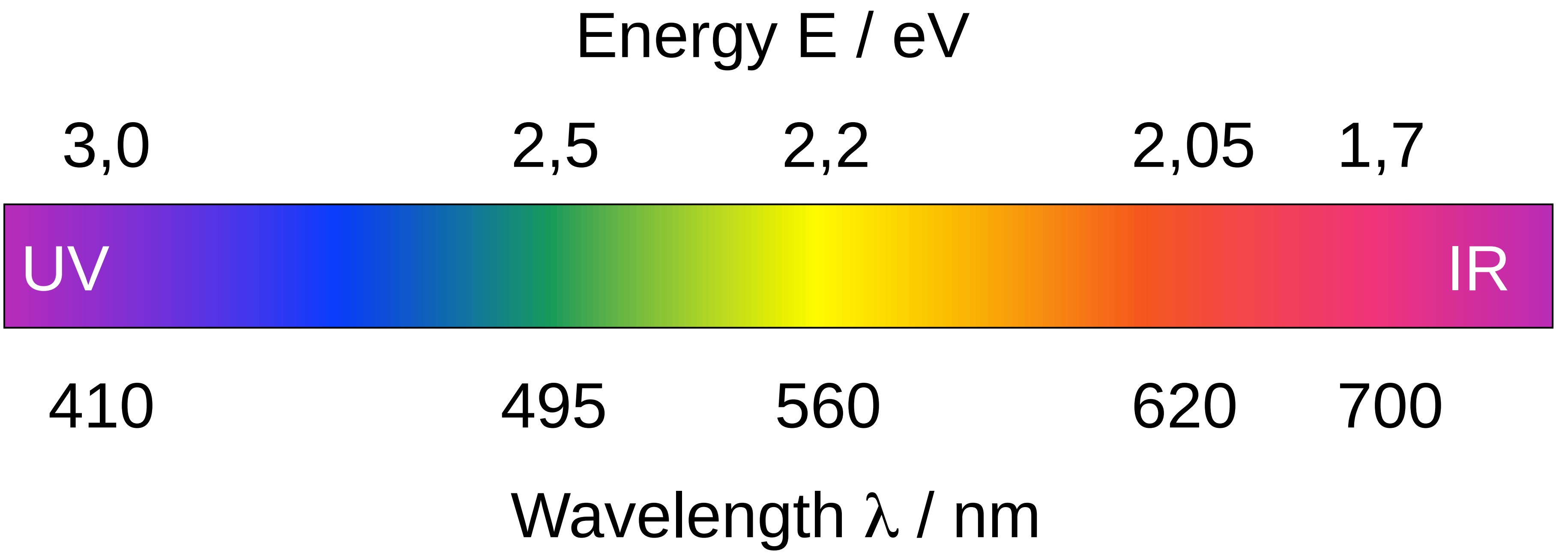
describes light – matter interaction

Refractive index: $\tilde{n}(\omega) = \sqrt{\varepsilon(\omega)} = n + i\kappa$

with n real part of refractive index (refraction !) and κ the so-called extinction coefficient (absorption).

Absorption coefficient: $\alpha = \dfrac{2\omega\kappa}{c}$

Light intensity as function of distance x travelled in a medium: $I(x) = I_0 \exp(-\alpha x)$



$1\ \text{eV} = 1{,}602\times10^{-19}\ \text{J}$

$1\ \text{nm} = 10^{-9}\ \text{m} = 10\ \text{Å}$

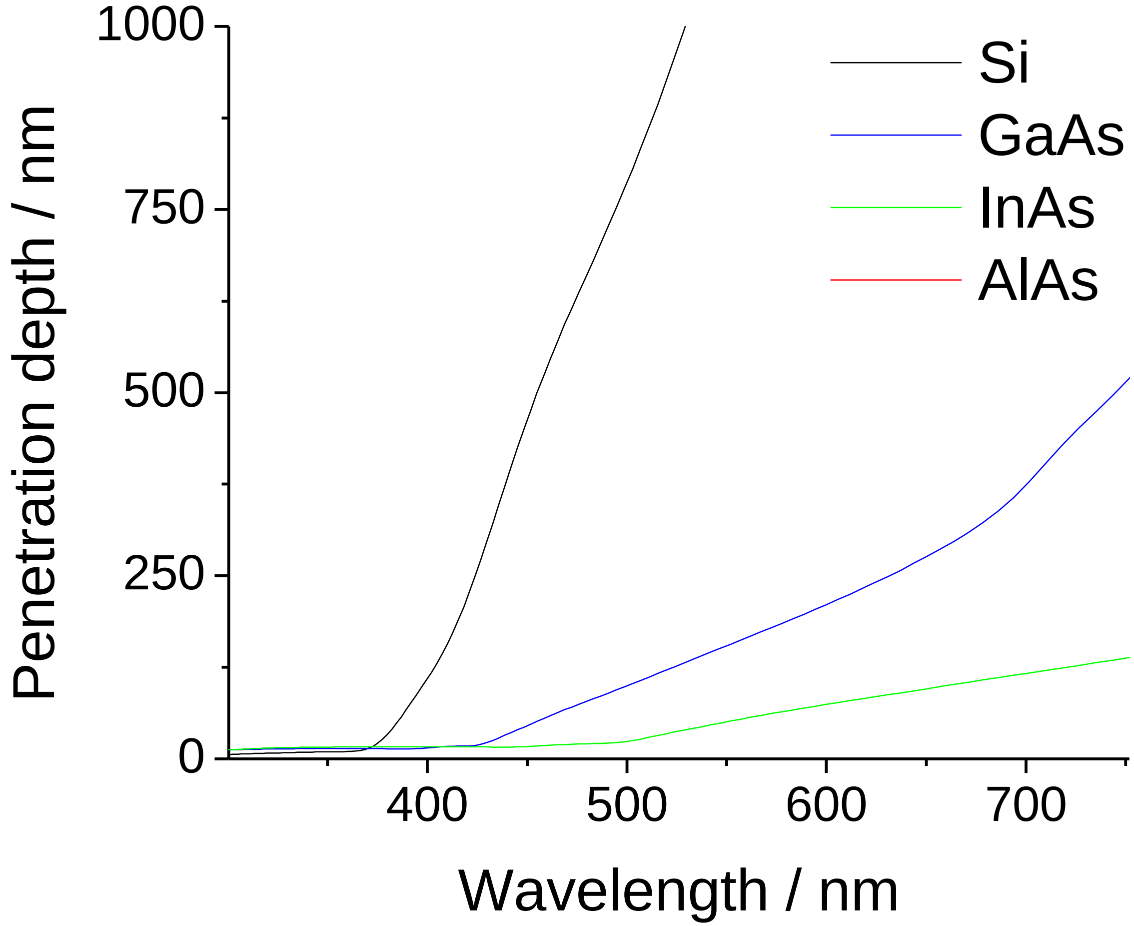
Penetration depth

$$I(z) = I_0 e^{-\frac{2\pi k}{\lambda} z}$$

$$\delta_p = \frac{\lambda}{4\pi k}$$ - Information depth

k - extinction coefficient

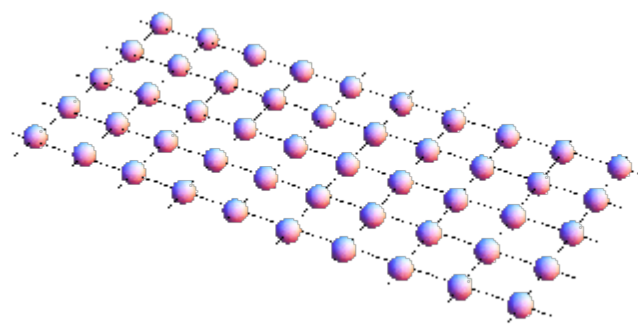
z - depth



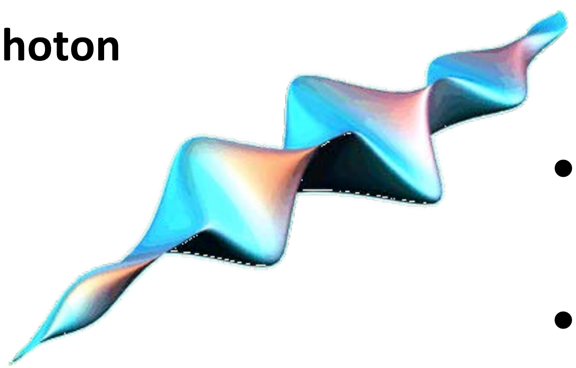
Raman Spectroscopy

- Information about atomic arrangement
  - Chemical/molecular analysis
  - Crystallinity
  - Polymorphism
  - Phase
- Non-destructive

Phonon frequency depends on **elastic constant** of chemical bond and **atom mass**



Photon



- Applied to any optically accessible sample
- Solid, liquid, gas, transparent, non-transparent, bio-applications
- Microscopic spatial resolution
- Confocal analysis

Handheld Raman spectrometer

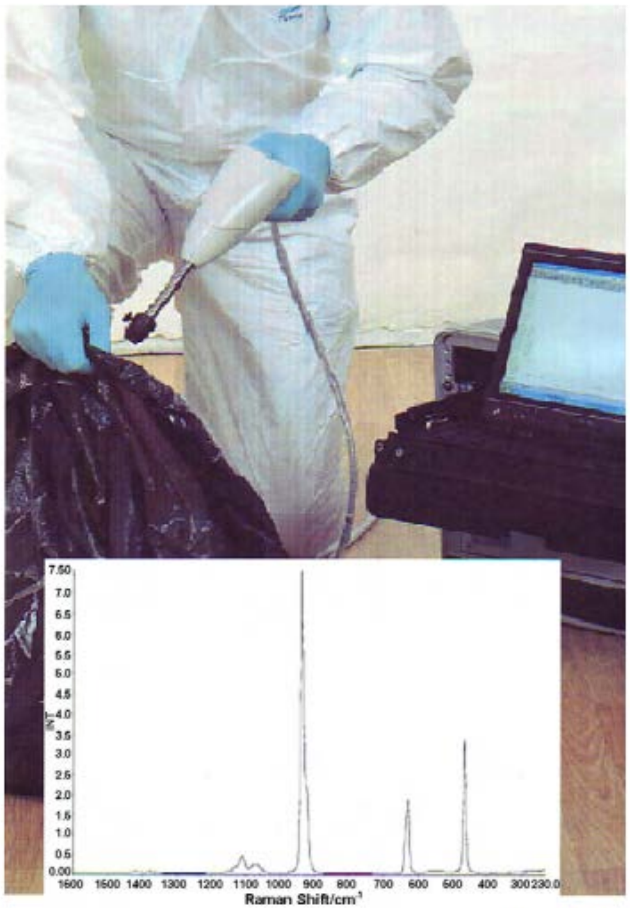


Fig. 2. Raman spectrum of ammonium perchlorate explosive through black plastic bag using a portable Raman station.

Identification and use with:
•Narcotics & illicit street drugs;
•Explosives & chemical warfare agents;
•Hazardous materials & chemical spills;
•Pharmaceutical IQ/OQ/PQ quality;
•Gemstone authentication, etc.

Research Article

Journal of RAMAN SPECTROSCOPY

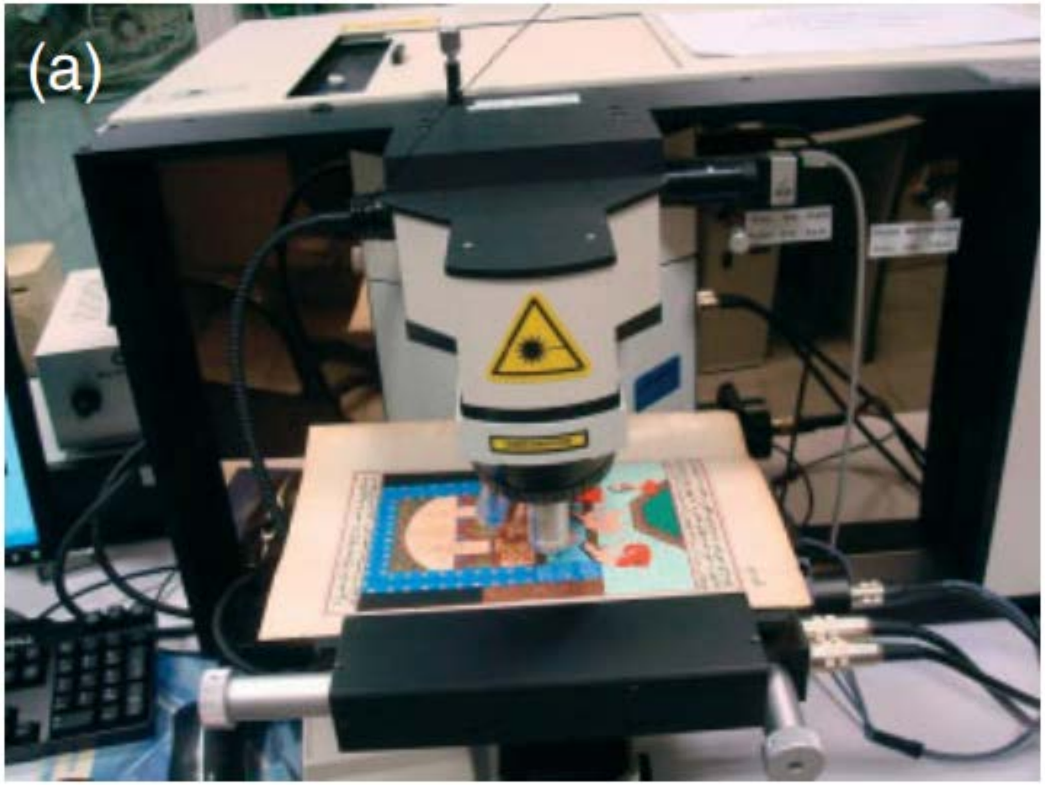
Received: 10 December 2009 Accepted: 3 February 2010 Published online in Wiley Online Library: 30 March 2010

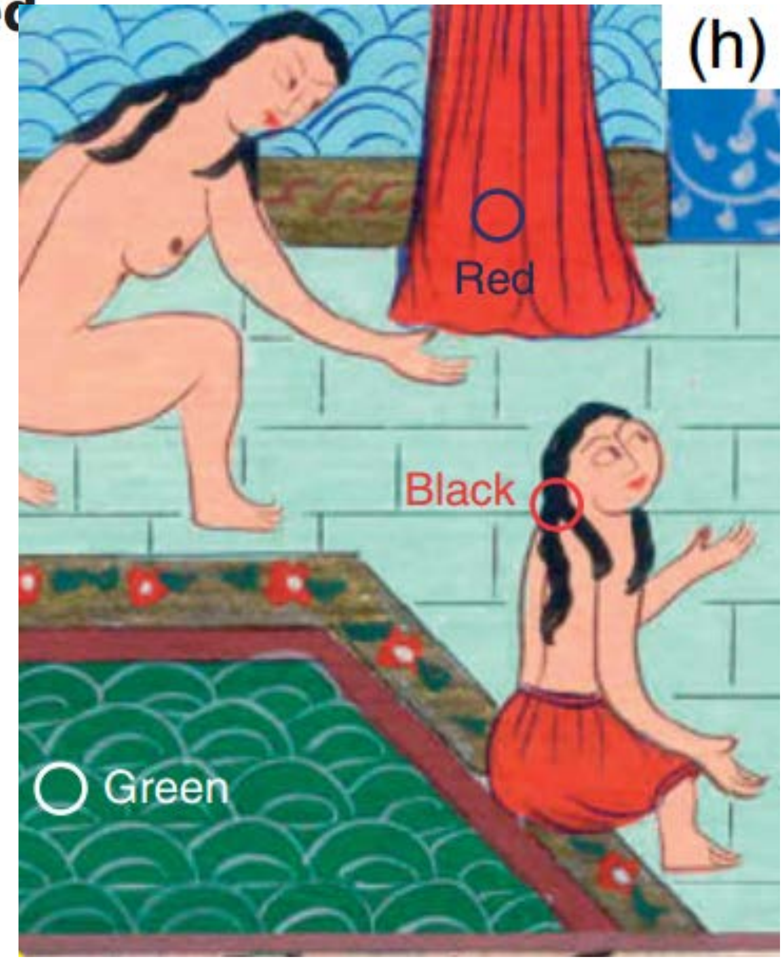
(wileyonlinelibrary.com) DOI 10.1002/jrs.2644

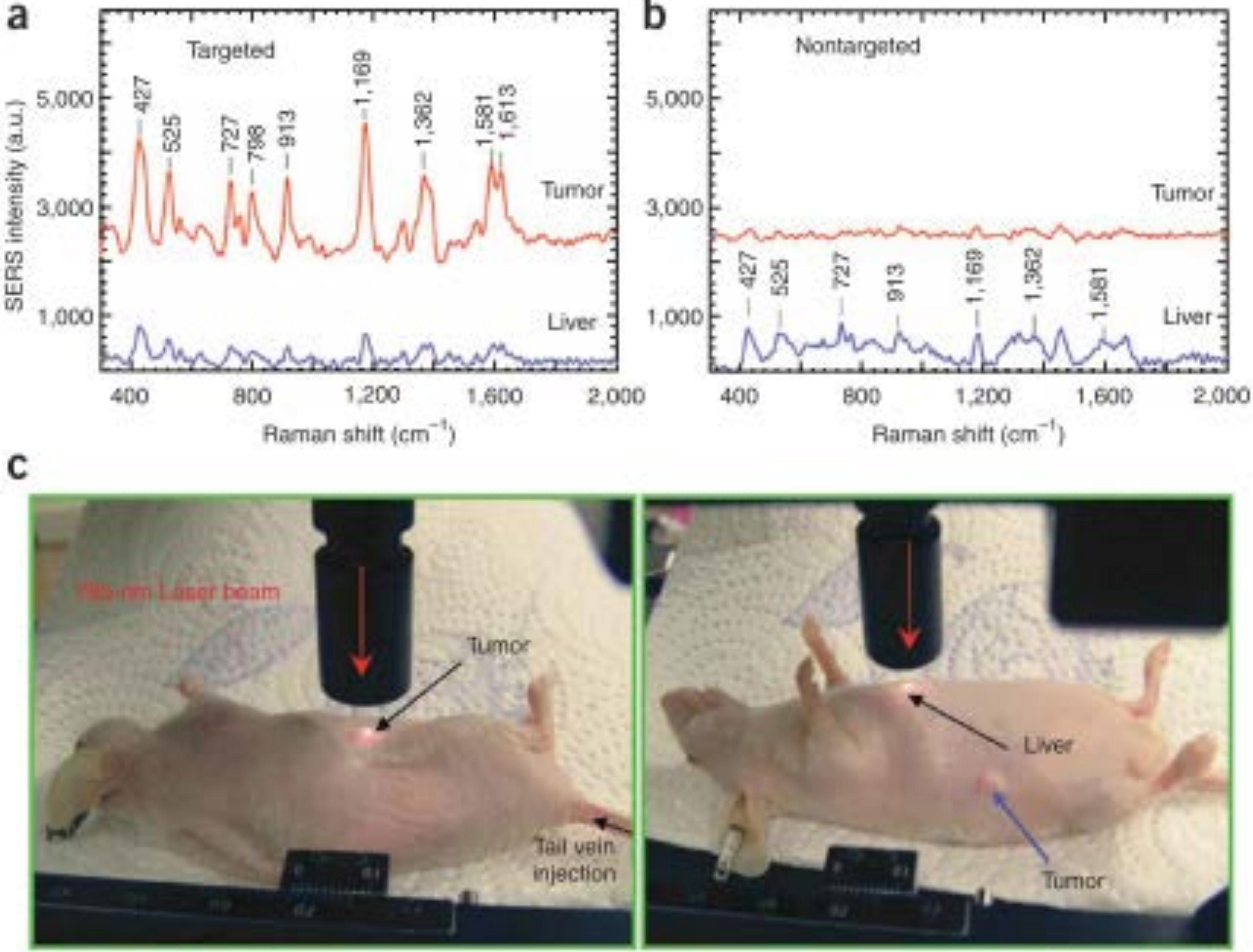
Forgery detection on an Arabic illuminated manuscript by micro-Raman and X-ray fluorescence spectroscopy

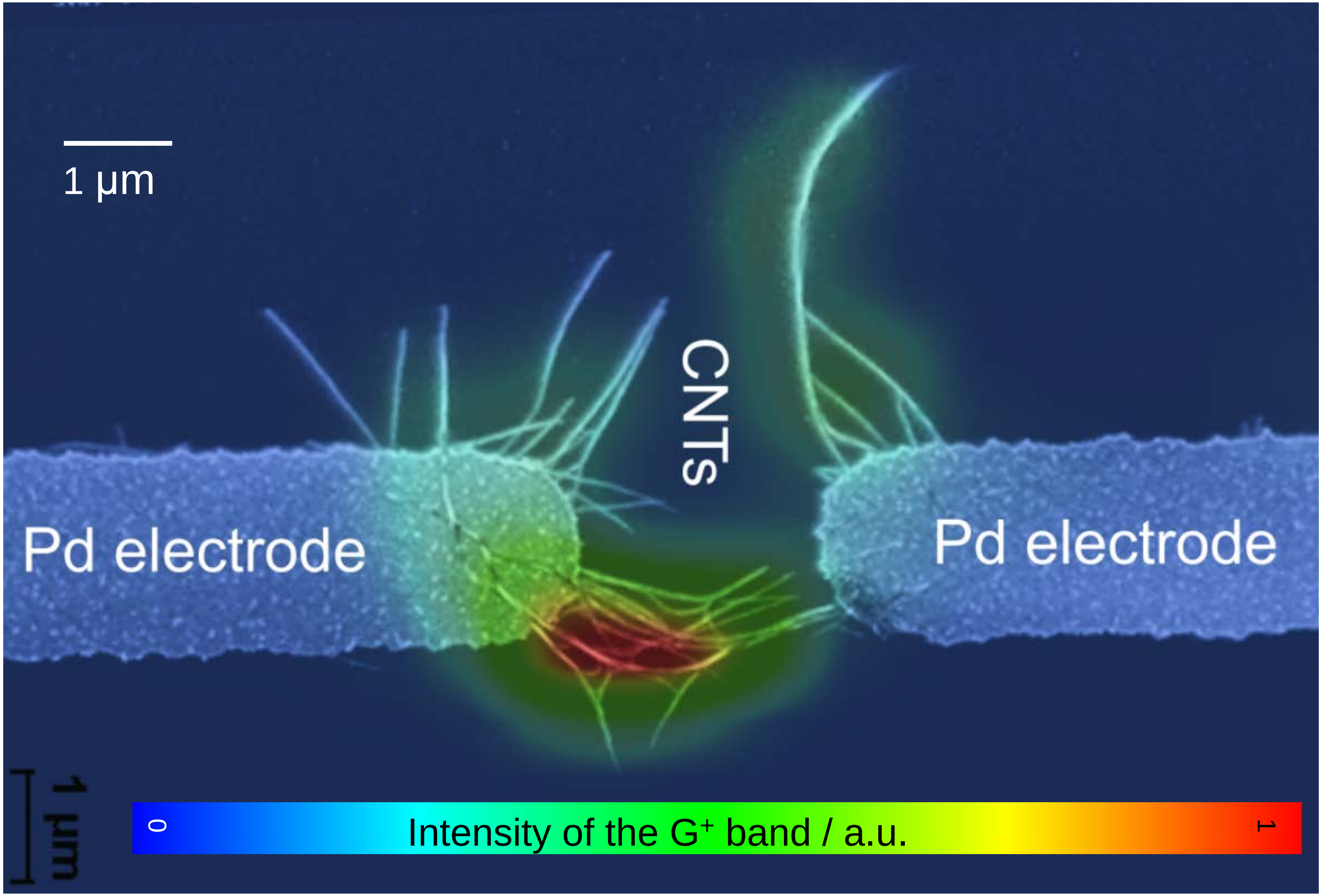
A

ai



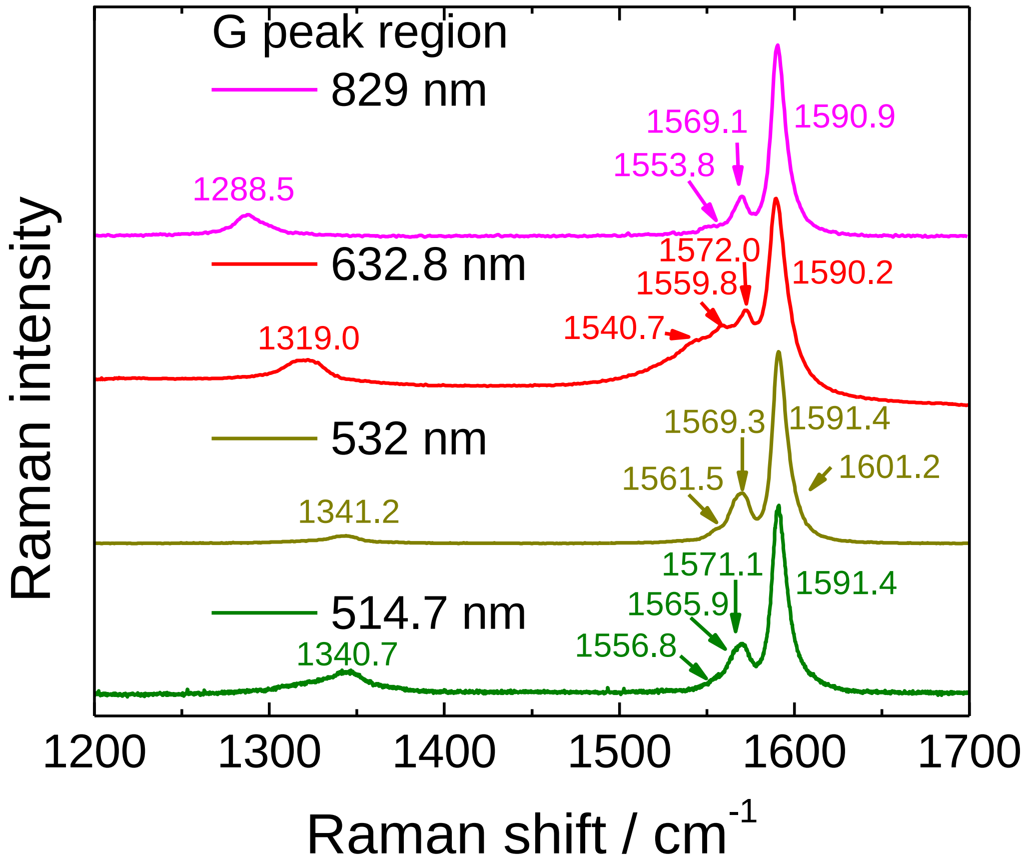



a
Targeted
SERS intensity (a.u.)
5,000
3,000
1,000
427
525
727
798
913
1,169
1,362
1,581
1,613
Tumor
Liver
400
800
1,200
1,600
2,000
Raman shift (cm^{-1})
b
Nontargeted
5,000
3,000
1,000
Tumor
427
525
727
913
1,169
1,362
1,581
Liver
400
800
1,200
1,600
2,000
Raman shift (cm^{-1})
c
Tumor
Tail vein
injection
Liver
Tumor


1 µm
CNTs
Pd electrode
Pd electrode
1 µm
0
Intensity of the G+ band / a.u.
1

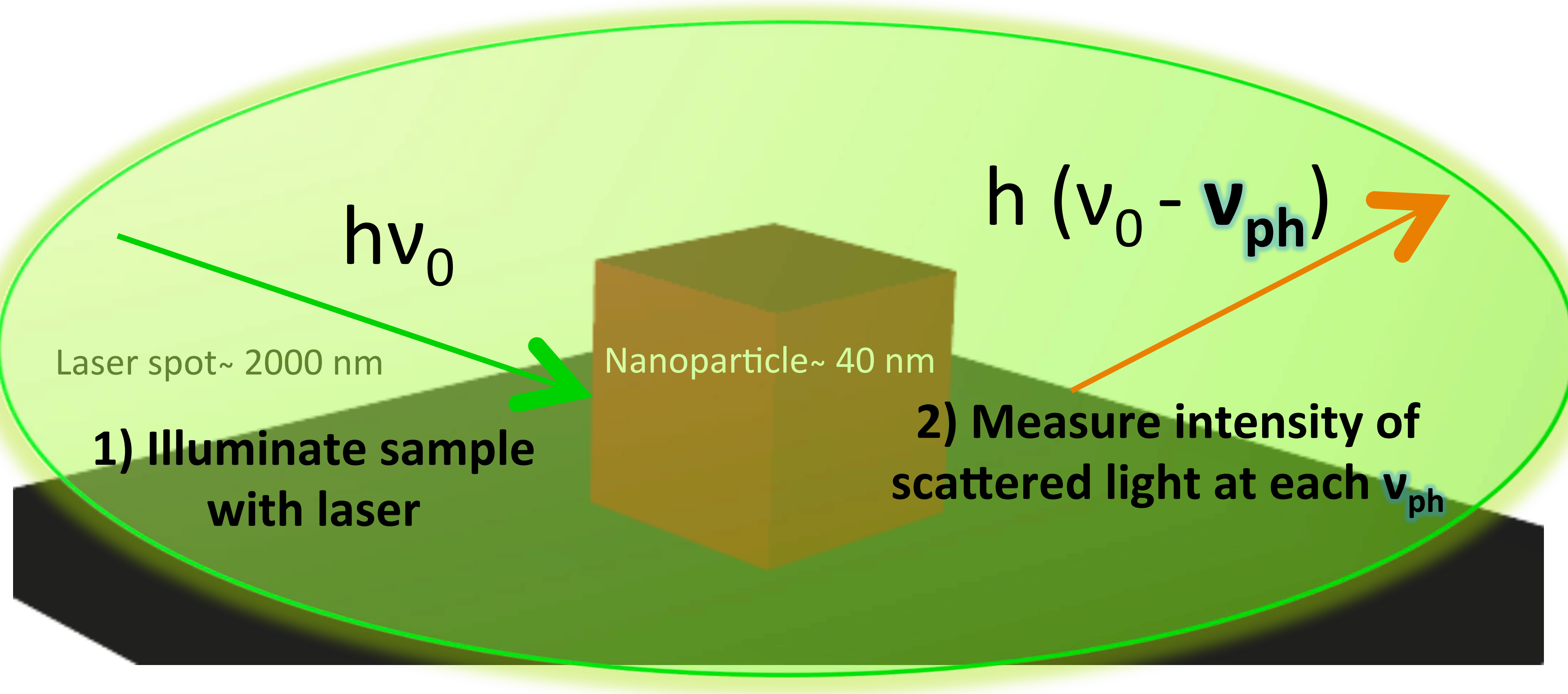
Raman spectroscopy: Key technique for the analysis of CNT

Diameter distribution 1.1 – 1.6 nm

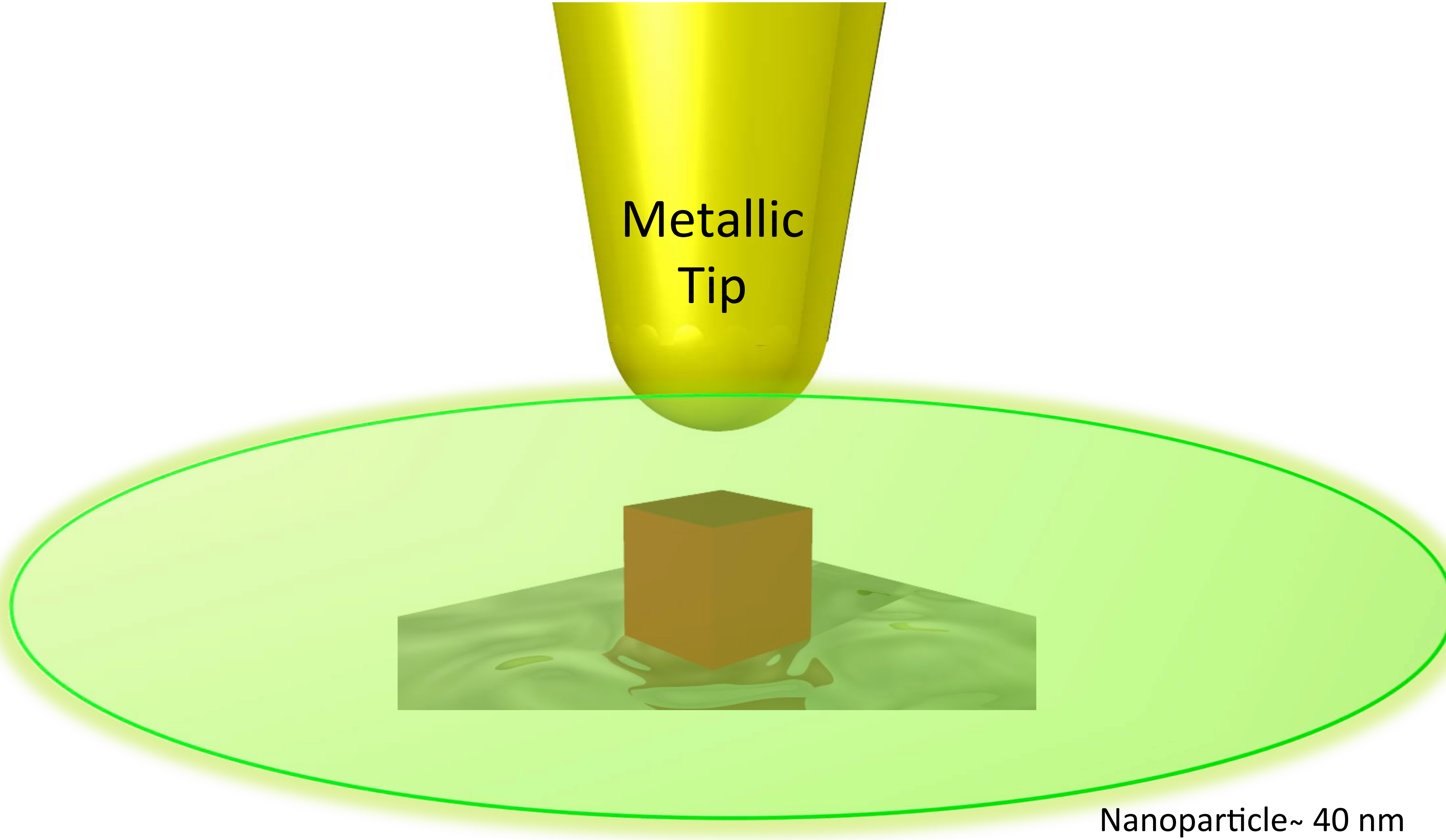


cm^{-1}	Tentative type	Diameter / nm
	829 nm	
1569.1	S	1.5
1553.8	S	1.1
	632.8 nm	
1572.0	S	1.6
1559.8	M	1.6
1540.7	M	1.3
	532 nm	
1569.3	S	1.5
1561.5	S	1.3
	514.7 nm	
1571.1	S	1.6
1565.9	S	1.4
1556.8	S	1.2

Raman Spectroscopy



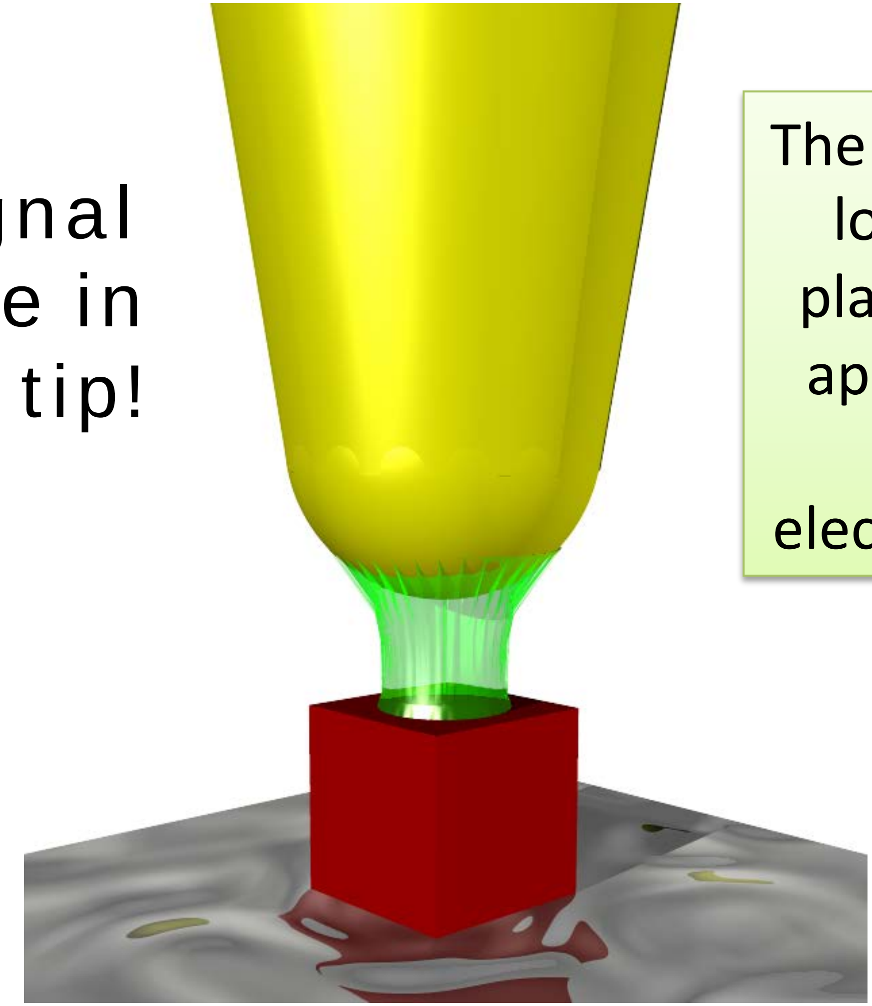
Still we have contributions from a sample region comparable in size to the laser spot but…



Nanoparticle~ 40 nm

Laser spot~ 2000 nm

Sample signal comparable in size to the tip!

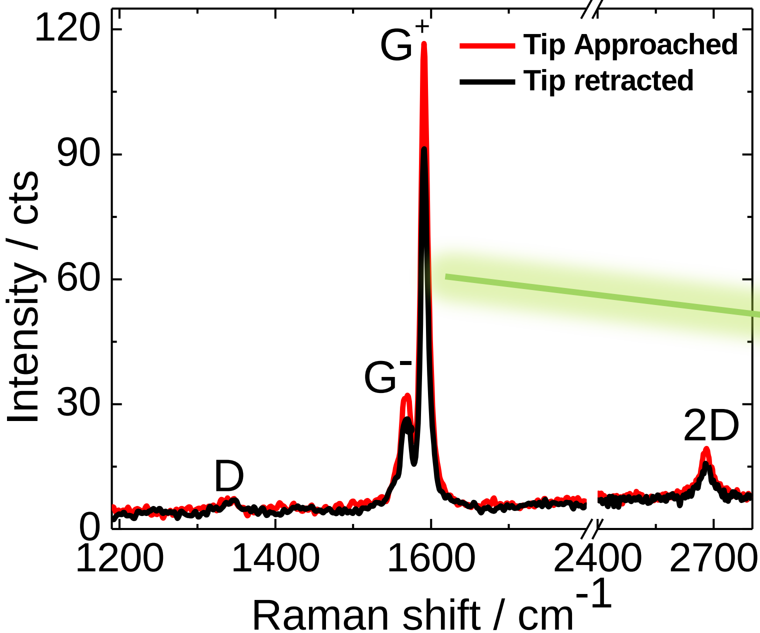


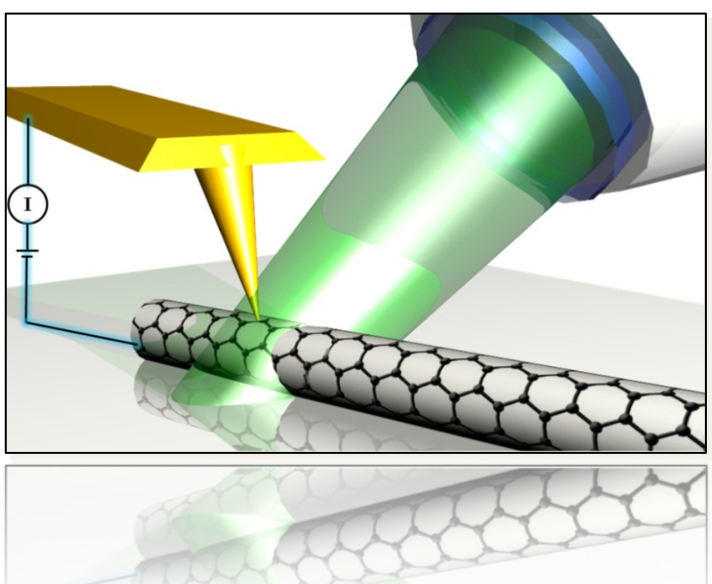
The key: Excitation of localized surface plasmons at the tip apex confines and amplifies the electromagnetic field

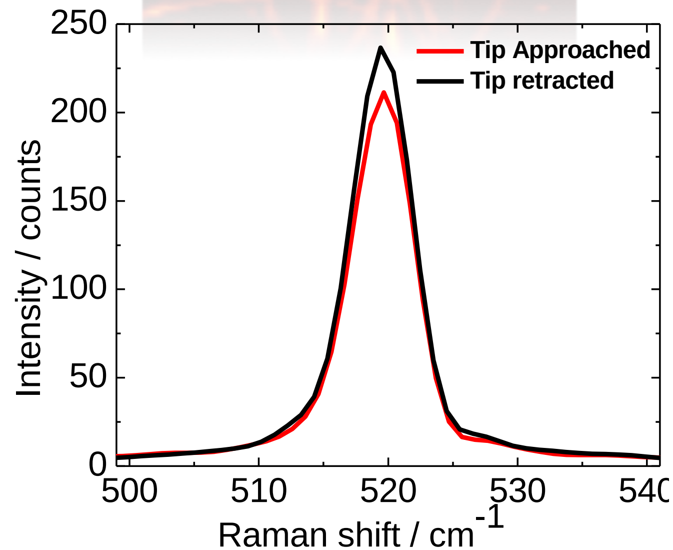
TERS: Tip-enhanced Raman Spectroscopy

Tip-enhanced Raman Spectroscopy

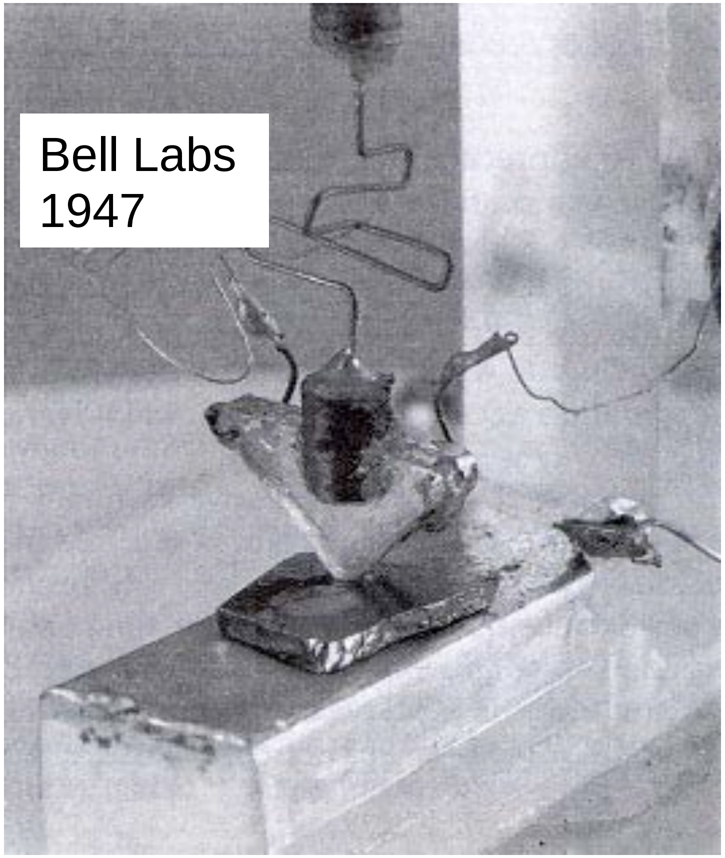
TERS

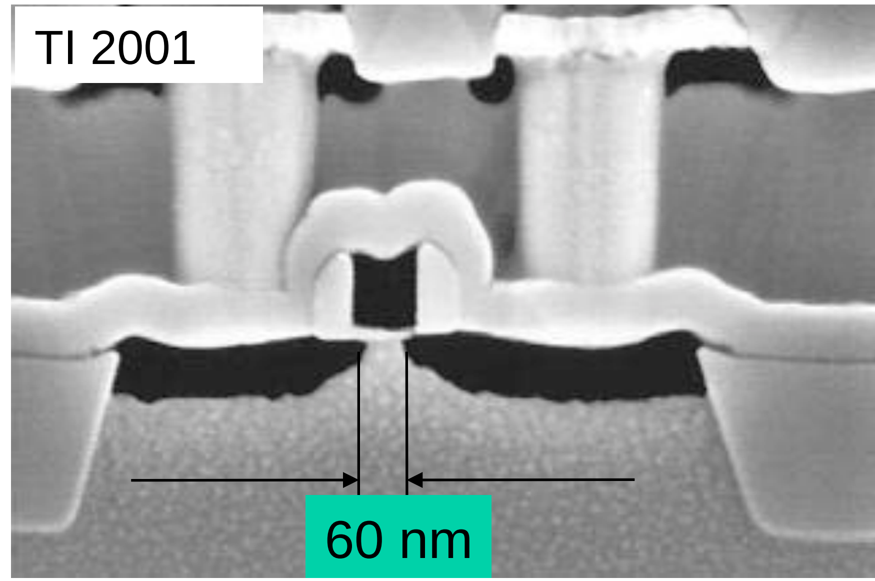






Transistors





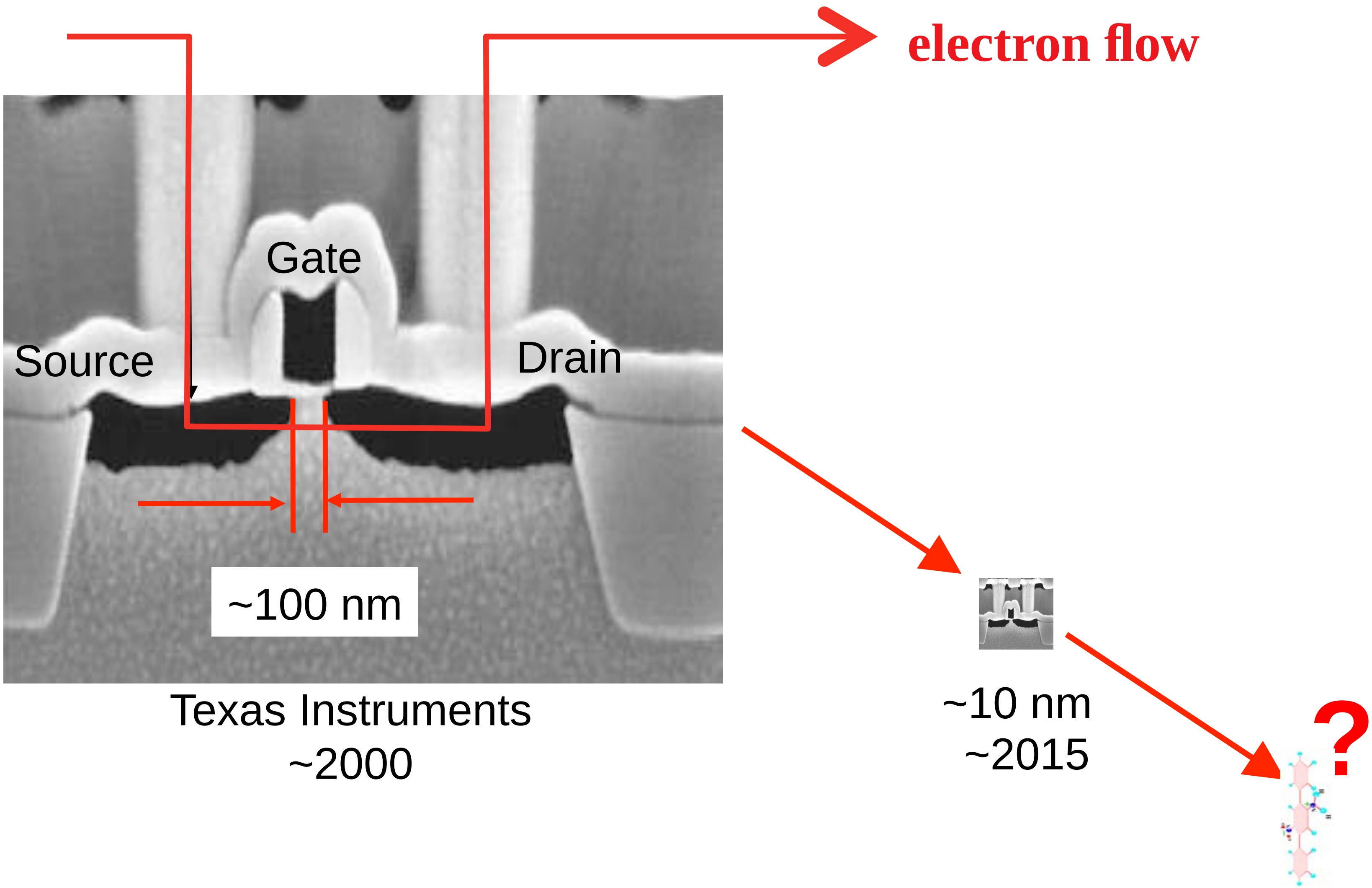
Technology generation: $L \rightarrow L/\sqrt{2}$

"Moore's Law"

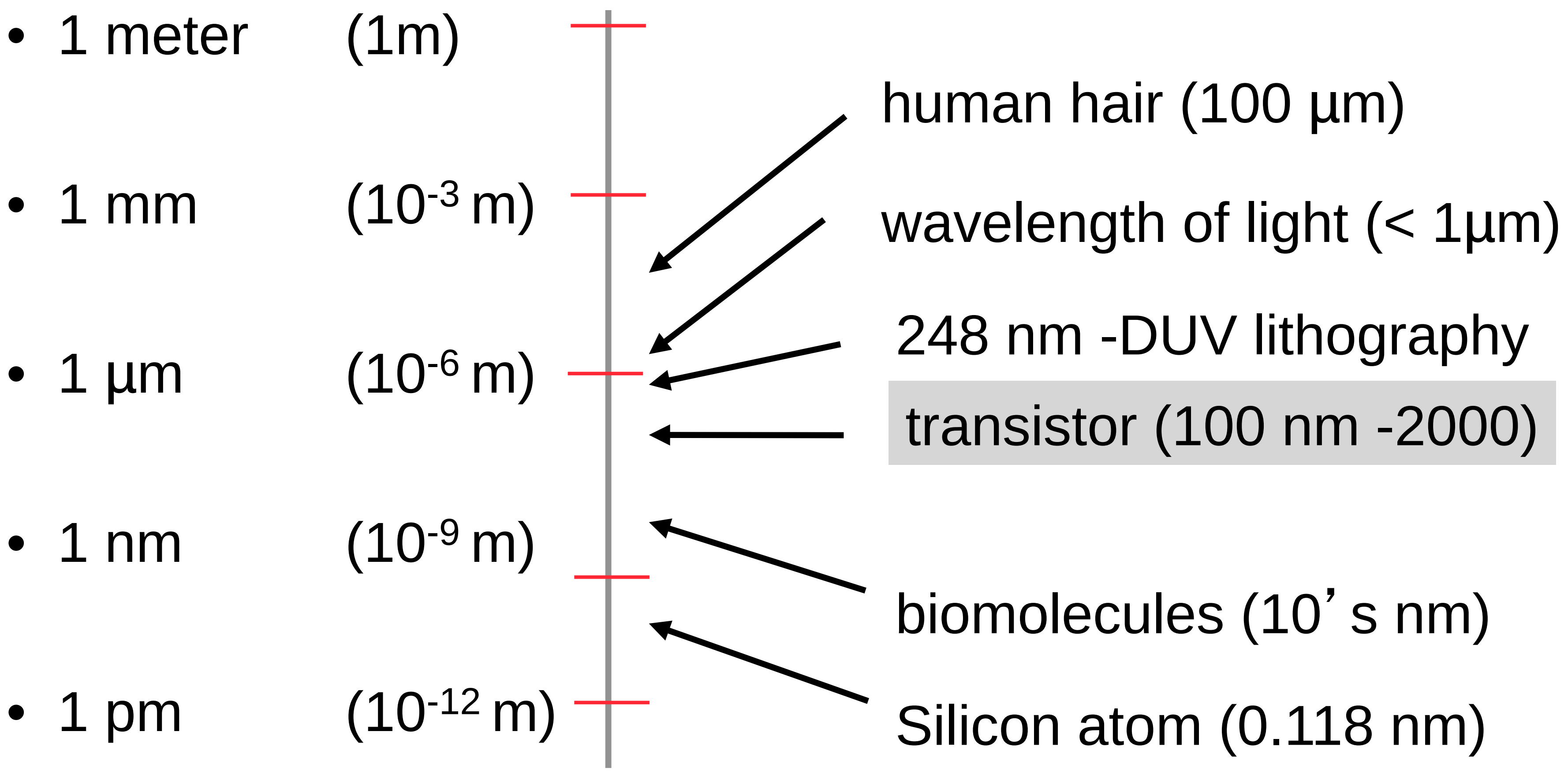
"Transistorized" PBS, Nov. 8, 1999 www.pbs.org/transistor/

21st Century Electronics:

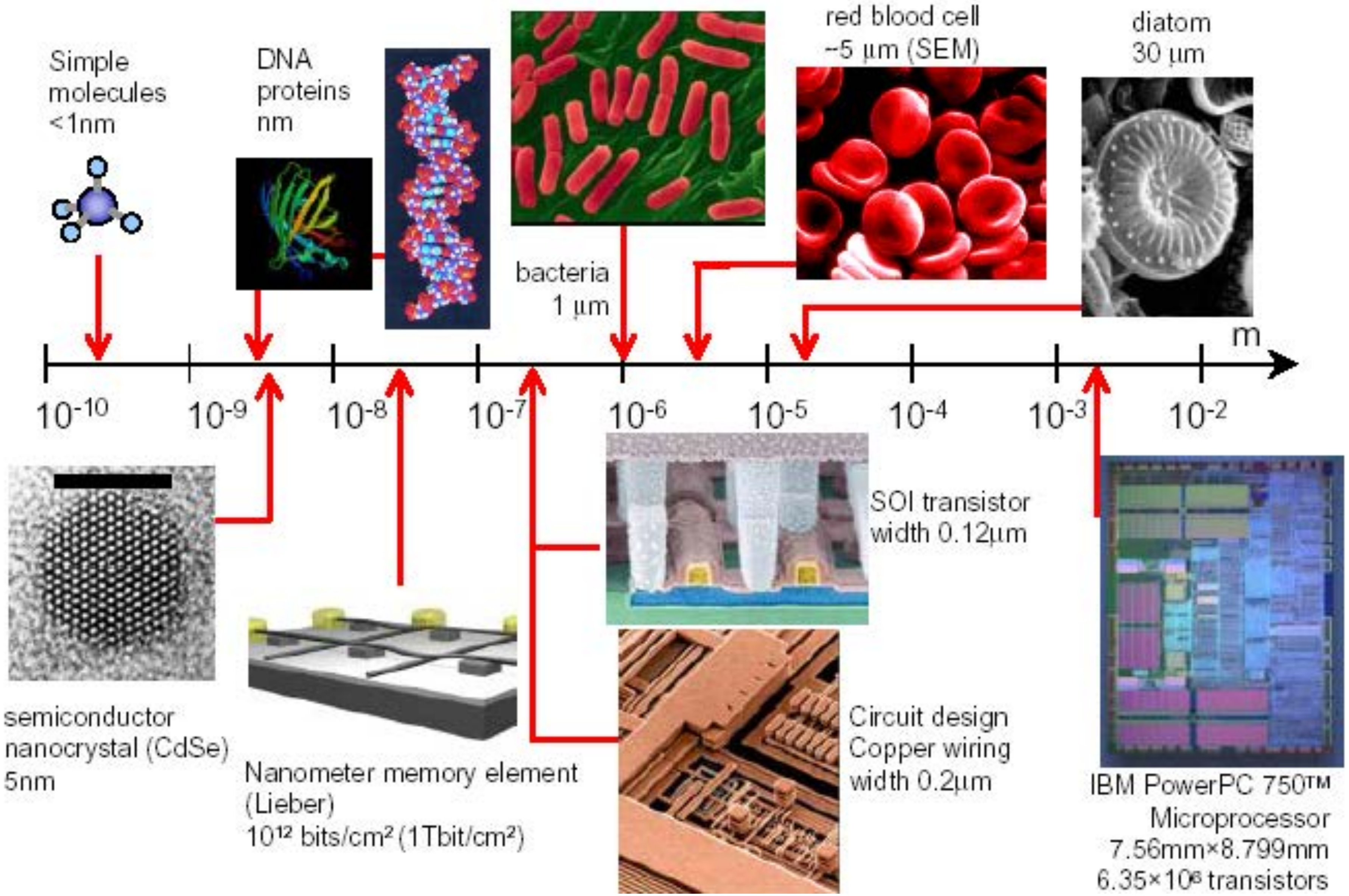
Transistors at the nano/molecular scale



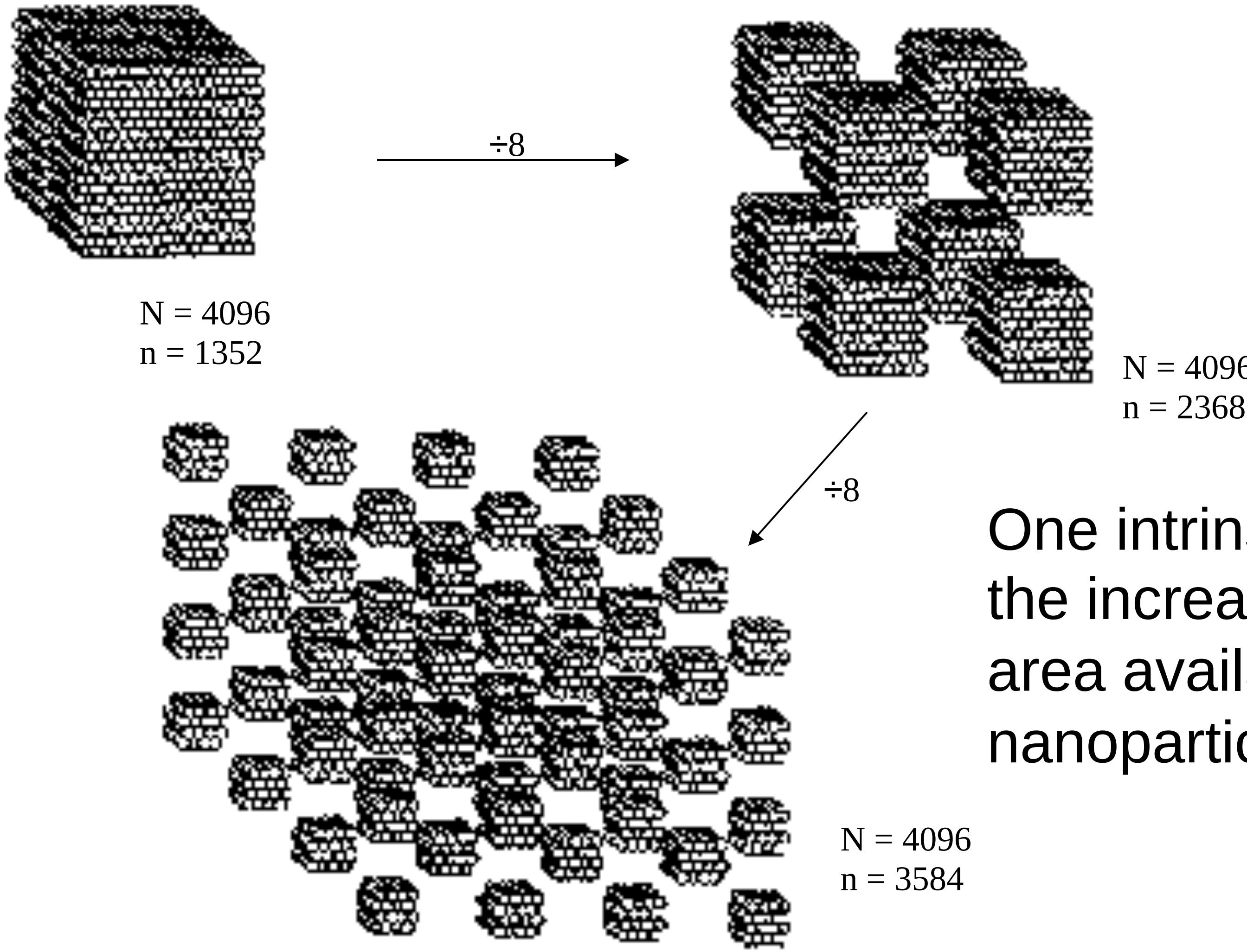
The Scale of Things



Putting it in Scale



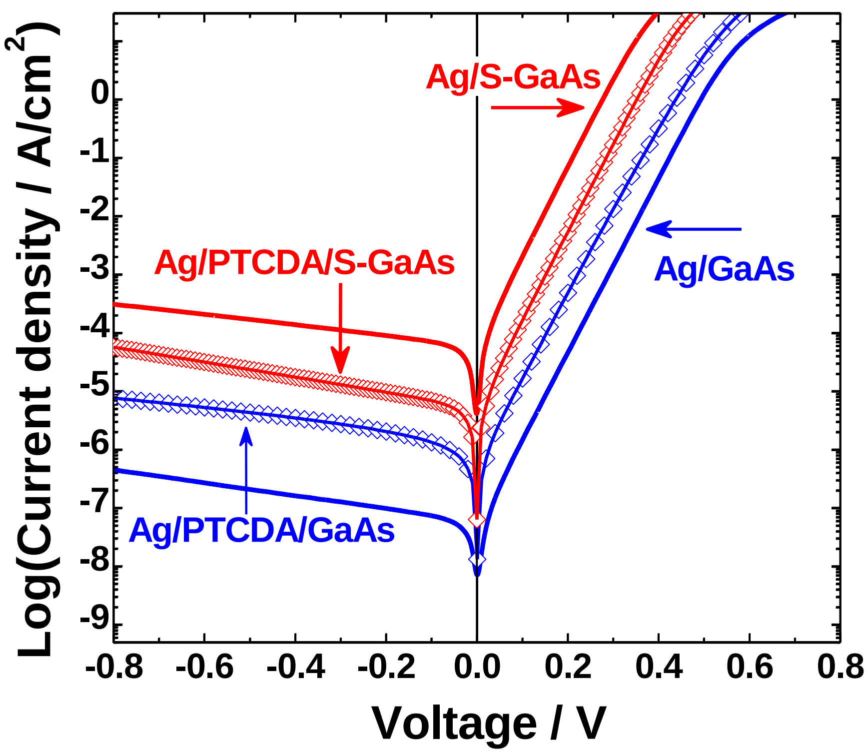
Surface Area

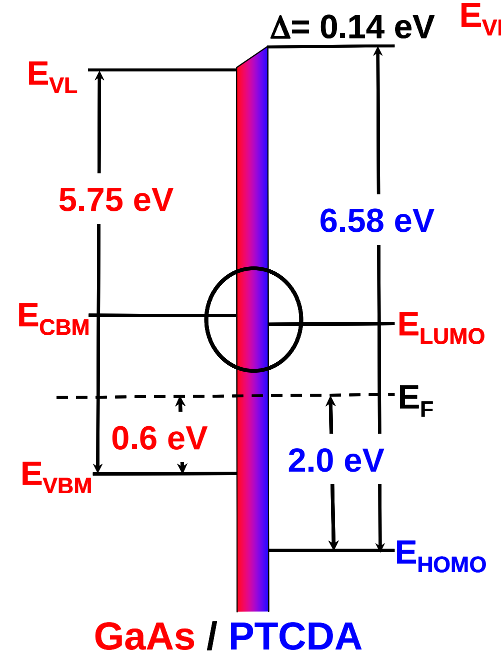


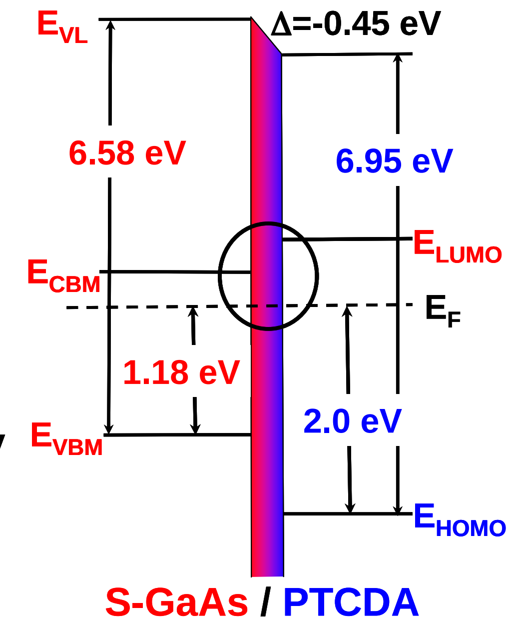
N = total atoms; n = surface atoms

One intrinsic benefit is the increased surface area available in nanoparticles.

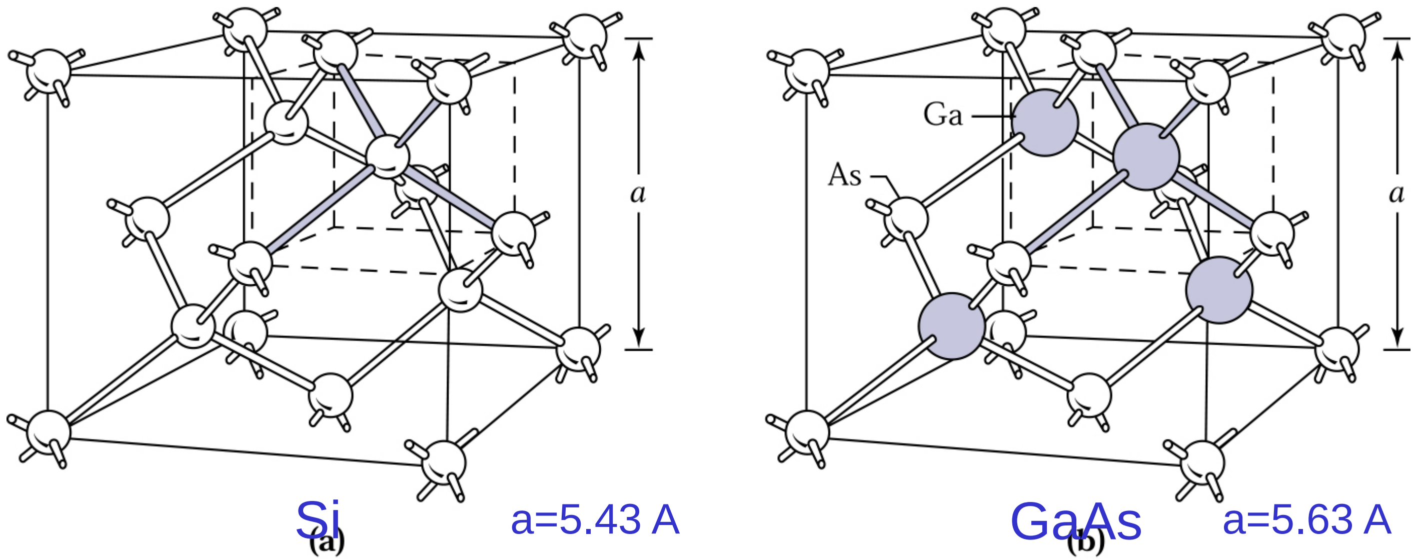
J-V characteristics of organic modified Schottky diodes







Crystal structure



Si a=5.43 A GaAs a=5.63 A

Diamond & Zincblende lattices – two interpenetrating fcc sublattices one displaced from the other by ¼ of the distance along the diagonal of the cell ($a\sqrt{3}/4$)