Introduction to Nanotechnology

- Textbook：

  Nanophysics and Nanotechnology

  by:

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Systematic of Making Things Smaller- Pre-Quantum

1. Mechanical Frequencies increase in Small System

2. Thermal Time Constants and Temperature Differences *Decrease*

3. Viscous Forces Becomes Dominant for Small Particles in Fluid Media

4. Fractional Forces can Disappear in Symmetric Molecular Scale Systems

Thermal Time Constants and Temperature Differences *Decrease*

Consider a body of heat capacity C (per unit volume) at temperature T connected to a large mass of temperature T=0 by a thermal link of cross section A, length L and thermal conductivity k_T.

The heat energy flow dQ/dt is $k_T AT/L$ and equals to the loss rate of thermal energy from the warm mass, dQ/dt = CVdT/dt
The resulting equation $dT/T = -(k_T A/LCV)dt$ leads to a solution

$$T=T(0)\exp(-t/\tau_{th}) \qquad \text{where } \tau_{th} : LCV/k_T A$$

Under isotropic scaling τ_{th} varies as L^2C/k_T

Thermal time constant decrease as the size is reduced.

In steady sate with flow dQ/dt, we see that the temperature difference T is $T=(dQ/dt)(L/k_T A)$
Since the mechanical power dQ/dt scales as L^2, this result implies that the typical temperature difference T scales, in three dimensional, as L.

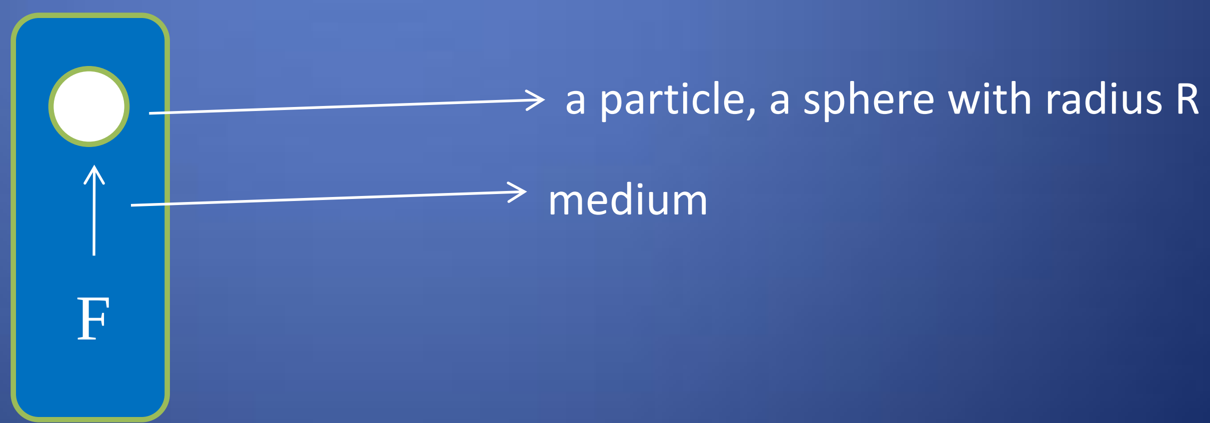
Temperature differences are reduced as the size scale is reduced.

Viscous Forces Becomes Dominant for Small Particles in Fluid Media

The force needed to move a sphere of radius R and velocity V

Stokes's Law $F: 6\pi\eta RV$

Viscosity Index of the medium



$F: 6\pi\eta RV$

$F: mg$

Falling particle of mass of m under gravity

$V: mg/6\pi\eta R$

--- a particle of 10 μm radius and density 2000 kg/m^3 falls in air at V of 23 mm/s

--- a particle of 15 nm and density 500 kg/m^3 fall in air at V of 13 nm/s.

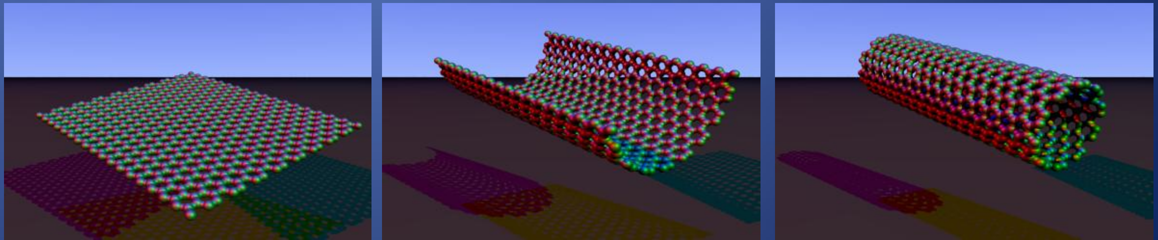
Viscous Forces Becomes Dominant for Small Particles in Fluid Media

Frictional Forces can Disappear in Symmetric Molecular Scale Systems

Friction is the force resisting the relative motion of solid surfaces, fluid layers, and material elements sliding against each other. Friction is not itself a fundamental force but arises from interatomic and intermolecular forces between the two contacting surfaces.

Viscous and Frictional forces are nearly "0" in nano-scale system.

Carbon nano-tubes are essentially rolled sheets of graphite which have no dangling bonds perpendicular to their surfaces. Graphite is well known for its lubricating properties, which arise from the easy translation of one sheet against the net sheet. It is clear that there are no molecules at all between the layers of graphite, and the same in nanotube. The whole structure is made of carbon atoms. The medium between the very close space moving elements is vacuum.

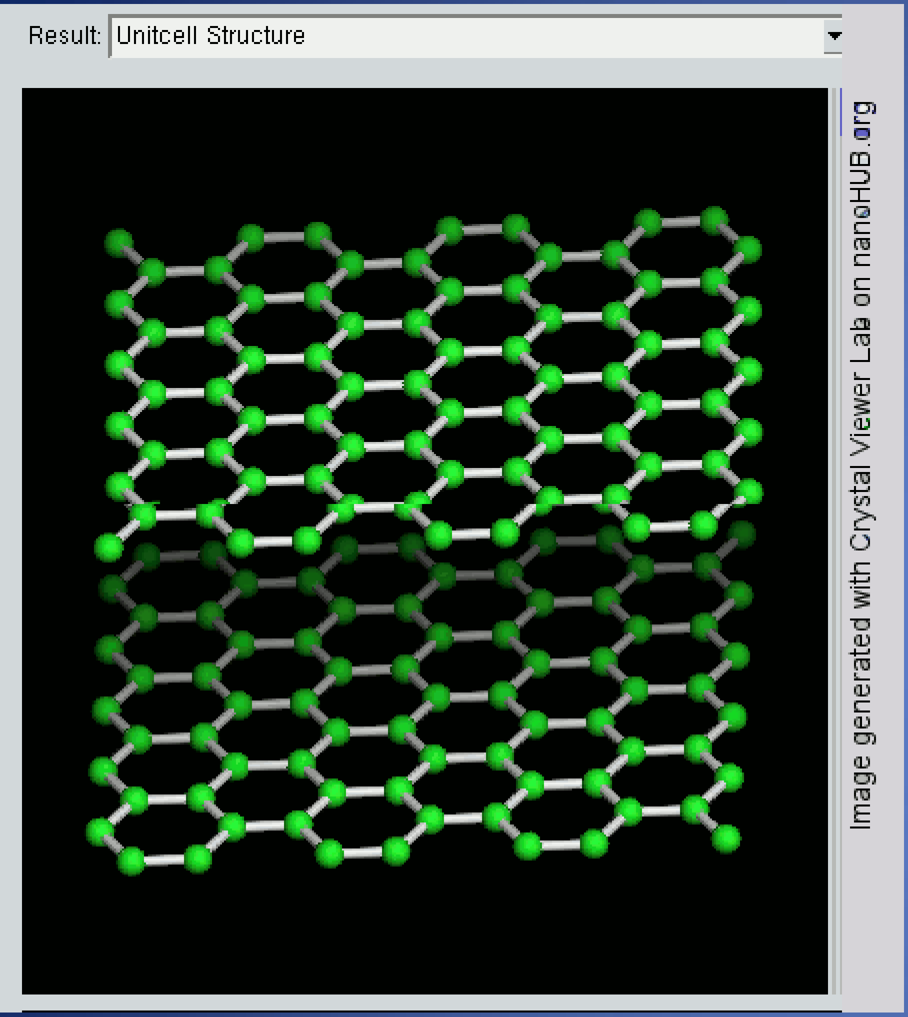


Graphite is made almost entirely of carbon atoms, and as with diamond, is a semimetal native element mineral, and an allotrope of carbon. Graphite, meaning "writing stone", was named by Abraham Gottlob Werner in 1789 from the Ancient Greek γράφω (*graphō*), "to draw/write", for its use in pencils,

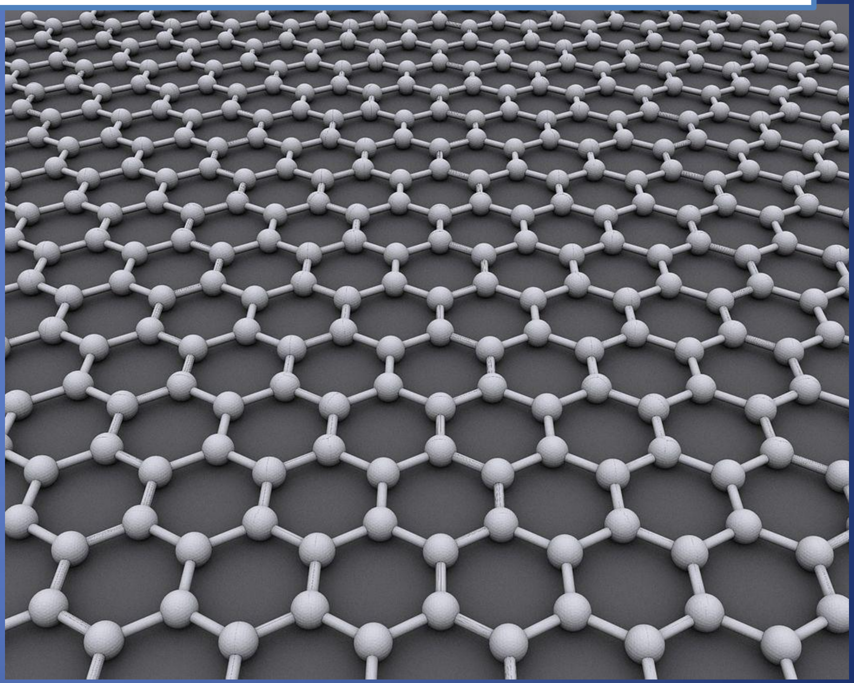
Graphite has a layered, planar structure. In each layer, the carbon atoms are arranged in a honeycomb lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm. The two known forms of graphite,*alpha* (hexagonal) and *beta* (rhombohedral), have very similar physical properties,

Graphite specimen

Graphene is pure carbon in the form of a very thin, nearly transparent sheet, one atom thick. It is remarkably strong for its very low weight (100 times stronger than steel) and it conducts heat and electricity with great efficiency



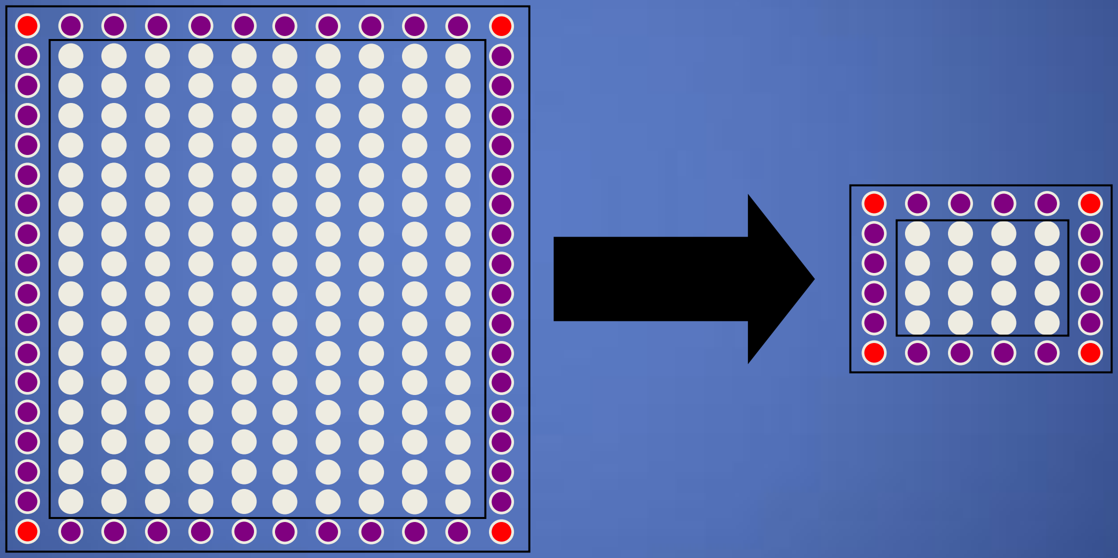
Ball-and-stick model of Graphite
(two graphene layers)



Graphene is an atomic-scale honeycomb lattice made of carbon atoms.

Why Small?

Nanoscale materials can have properties that are unrealizable in bulk materials



Making a material nanoscale can change its

- **Melting temperature**
- **Magnetization**
- **Ability to hold charge**
- **Structure**
- **Chemical reactivity**
- **… among other things**

Units

- Meter (m)
- Millimeter (mm) = 10^{-3} m
- Micrometer (μm) = 10^{-6} m
- Nanometer (nm) = 10^{-9} m
- Picometer (pm) = 10^{-12} m
- Femtometer (fm) = 10^{-15} m

Length scales

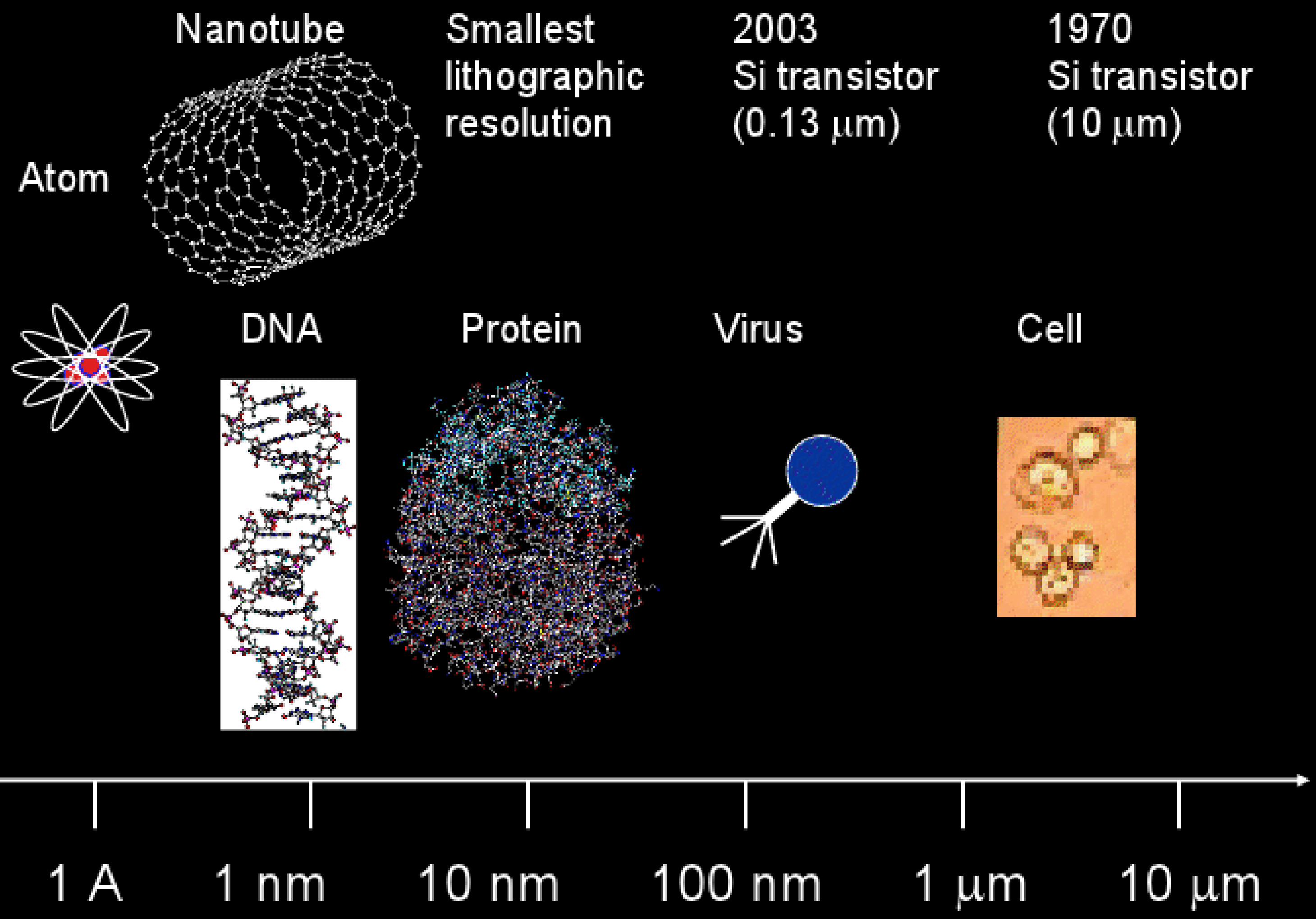
- Atoms
  - ~ angstrom 10^{-10} m
- Light
  - wavelength ~ μm
- Electrons
  - De Broglie wavelength = h/p (quantum mechanics)
  - = sqrt (150/V) in angstroms (V is energy in volts)
  - ~0.1-10 nm
  - If a nanoelectronic circuit element is about the size of an electron wavelength, wave nature will be *crucial*
  - Conductance quantized at these small scales in units of e^2/h
- Mean free path (MFP)
  - 10^{-10} m in metals at room temperature
  - 10^{-4} m in ultra high quality semiconductors at low temperatures

Energies

- Electronic transistion energies
  - ~ 1-10 eV
- Fermi energy
  - 1-10 eV in metals
  - 1-10 meV in semiconductors
- kT
  - 30 meV at room temperature

kT is the product of the Boltzmann constant, *k*, and the temperature, *T*. This product is used in physics as a scaling factor for energy values in molecular-scale systems (sometimes it is used as a unit of energy), as the rates and frequencies of many processes and phenomena depend not on their energy alone, but on the ratio of that energy and *kT*, that is, on *E* / *kT* (see Arrhenius equation, Boltzmann factor). For a system in equilibrium incanonical ensemble, the probability of the system being in state with energy E is proportional to $e^{-\Delta E / kT}$. More fundamentally, *kT* is the amount of heat required to increase the thermodynamic entropy of a system, in natural units, by one nat.

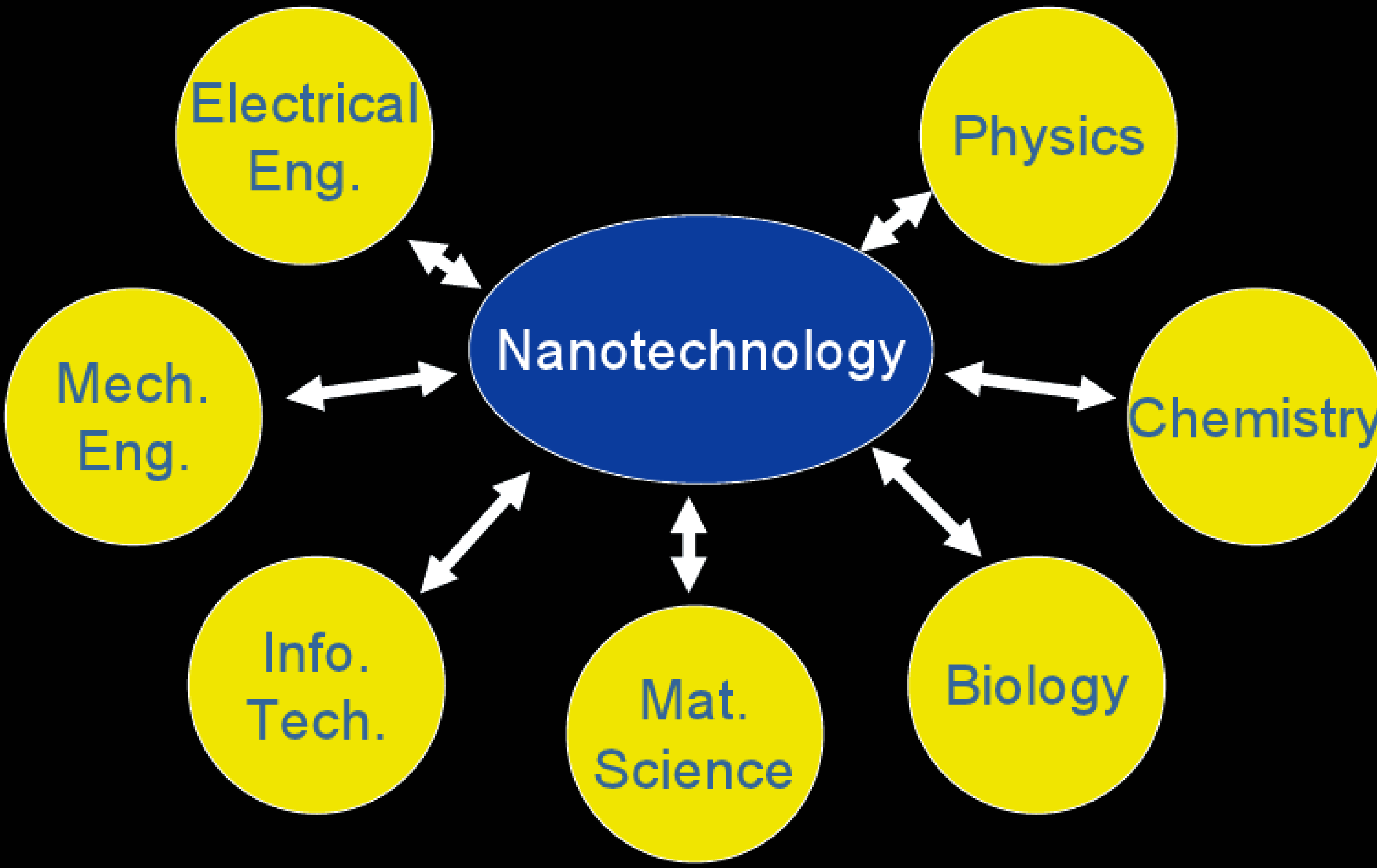
Length scales



What is nanotechnology?

- "Top down" approach
  - Micron scale lithography
    - optical, ultra-violet
    - Focused Ion Beam
  - 10-100 nm
    - Electron-beam lithography
- "Bottom up" approach
  - Chemical self-assembly
    - Man-made synthesis (e.g. carbon nanotubes)
    - Biological synthesis (DNA, proteins)
  - Manipulation of individual atoms
    - Atomic Force Microscopy
    - Scanning Tunneling microscopy

Nanotechnology is multidisciplinary:



Nano-manufacturing

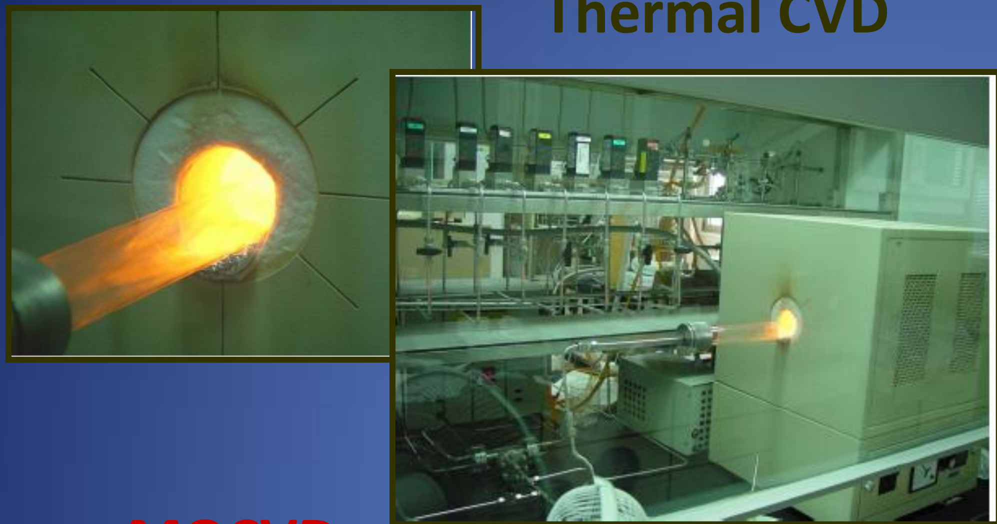
- Lithography can do 10 nm
- Tricks to 2 nm
- Biosystems can add 2 carbon atoms at a time
  - typical in lipid biosynthesis
  - enzymes are nano machines
- We do not know how to design enzymes, only copy them
- As such, nanotechnology does not yet exist according to Drexler's definition

Some nanotechnology uses

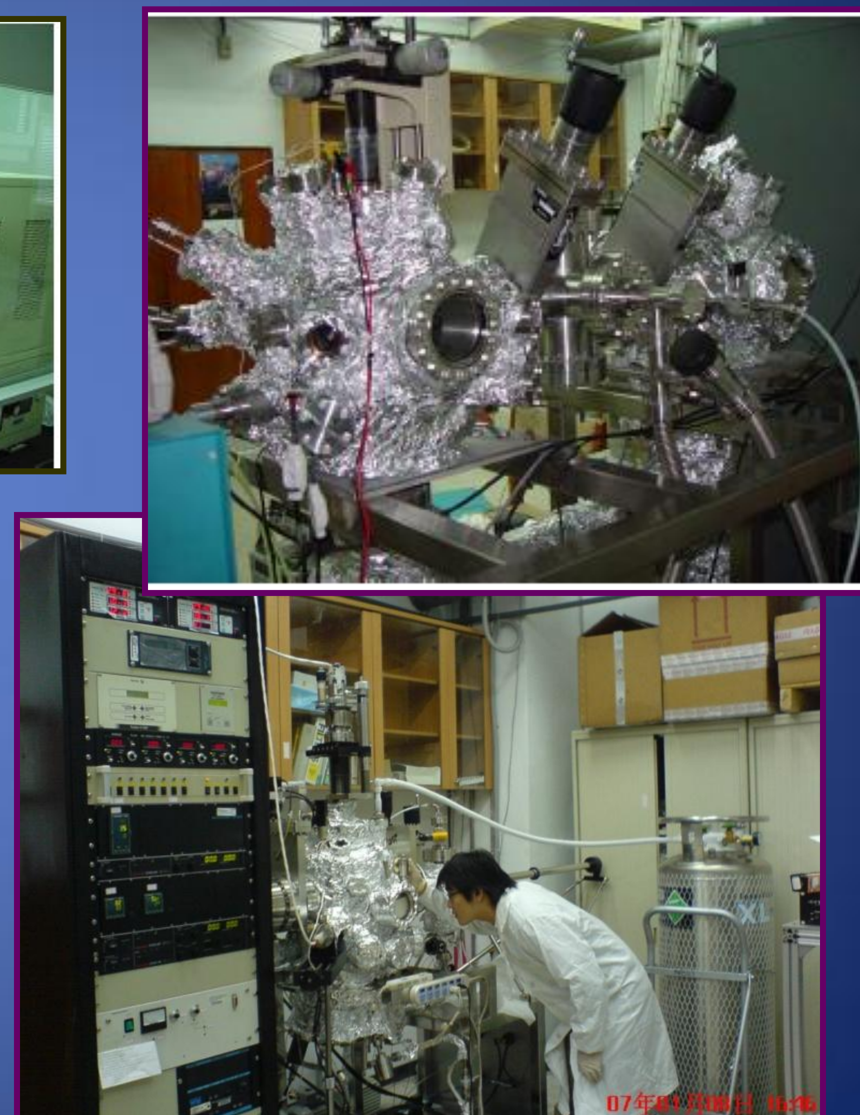
- Nanoparticles:
  - Catalysts for industrial chemical processing
- Nanocapsules
  - Possible organ specific drug delivery
- Nanomaterials
  - Improved strength and weight
  - E.g. carbon nanotube based materials could be stronger and lighter than steel
- Nanomechanical devices
  - RF signal processing
- Nanofluidic devices
  - Lab on a chip
- Nanoelectronic devices (focus of this course)
  - Computation
  - Communication
  - Nano-bio-electronic interfaces
    - Chemical and biological weapons detection
    - DNA sequencing
    - Point-of-care clinical diagnoses
    - Fundamental studies of molecular biology

Modern Alchemy (I)

Thermal CVD



Plasma-assisted MBE



MOCVD

Core Process Techniques at NTU CCMS-AML

CVD

- Microwave plasma
- Electron-cyclotron-resonance plasma
- Thermal- and MO-CVD
- Inductively Coupled Plasma

Gas phase reaction, Gas-solid interaction
Formation kinetics

PVD

- Magnetron sputtering
- Ion beam sputtering
- Atom- and Ion-beam assisted PVD
- Molecular beam epitaxy

Hydrogen vs. H-free growth environments
Film formation via physical route (varying K.E.) vs. chemical route (reactive sputtering)

Highly energized vapor deposition/etching processes under situations far away from equilibrium

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films.

Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline,polycrystalline, amorphous, and epitaxial. These materials include: silicon, carbon fiber, carbon nanofibers,filaments, carbon nanotubes, SiO_2, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride, titanium nitride, and various high-k dielectrics. The CVD process is also used to produce synthetic diamonds

Physical vapor deposition (**PVD**) describes a variety of vacuum deposition methods used to deposit thin films by the condensation of a vaporized form of the desired film material onto various workpiece surfaces (e.g., onto semiconductor wafers).

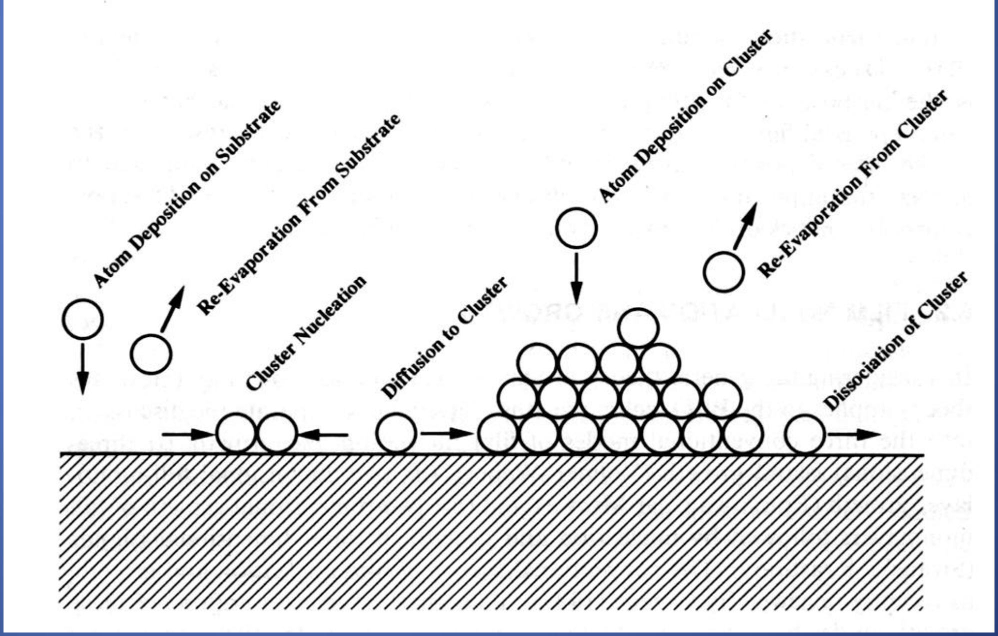
The coating method involves purely physical processes such as high-temperature vacuum evaporation with subsequent condensation, or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapor deposition

PVD is used in the manufacture of items, including semiconductor devices, aluminized PET film for balloons and snack bags, and coated cutting tools for metalworking. Besides PVD tools for fabrication, special smaller tools (mainly for scientific purposes) have been developed. They mainly serve the purpose of extreme thin films like atomic layers and are used mostly for small substrates. A good example are mini e-beam evaporators which can deposit monolayers of virtually all materials with melting points up to 3500 °C. Common coatings applied by PVD are Titanium nitride, Zirconium nitride, Chromium nitride, Titanium aluminum nitride.

Gas Phase Syntheses

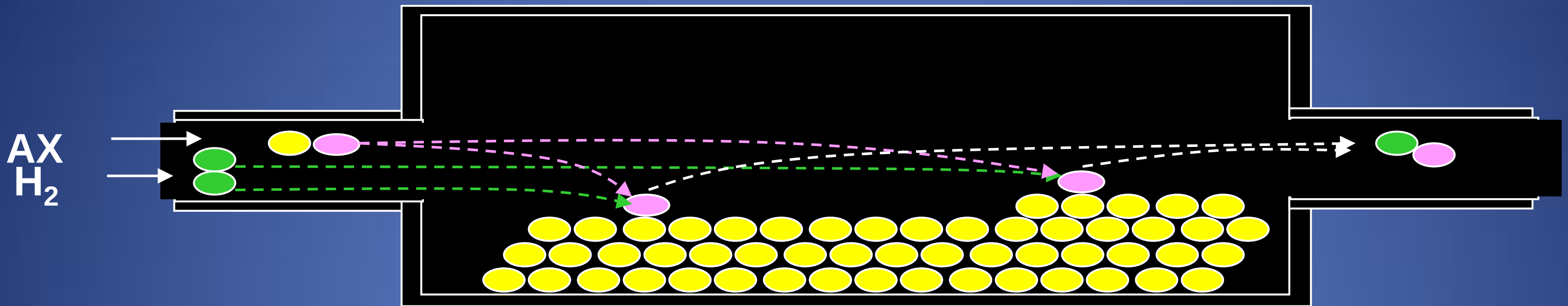
- Evaporation-Condensation (Earliest methods)
- Sputtering
- Laser Ablation
- Arc Discharge
- Aerosol Process
- Spray Pyrolysis
- Plasma Spray

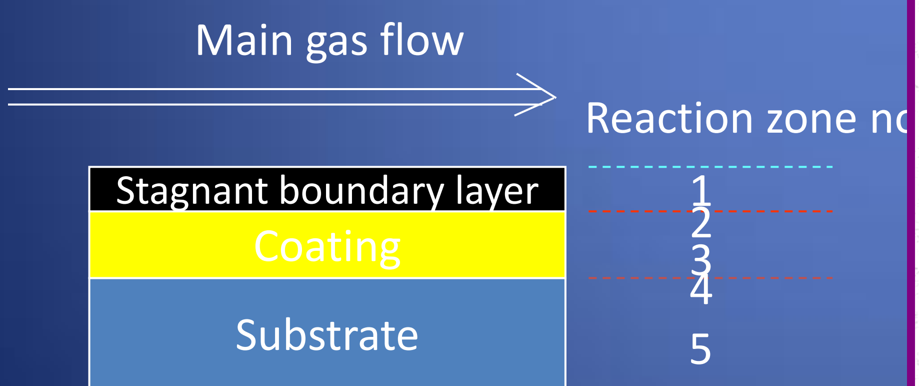
atomic process in the nucleation of three-dimensional clusters of deposited film atoms on a substrate



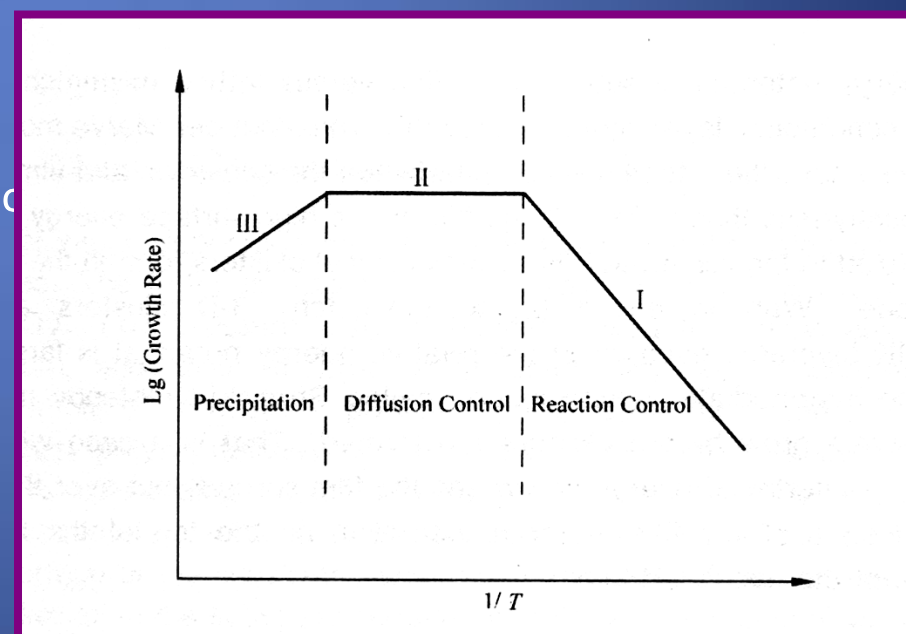
(J. S. Horowitz and J. A. Sprague, Chap. 8, Pulsed Laser Deposition of Thin Film, Eds., D. B. Chrisey and G. K. Hubler, Wiley Interscience)

Schematic of Chemical Vapor Deposition





Important reaction zones in CVD

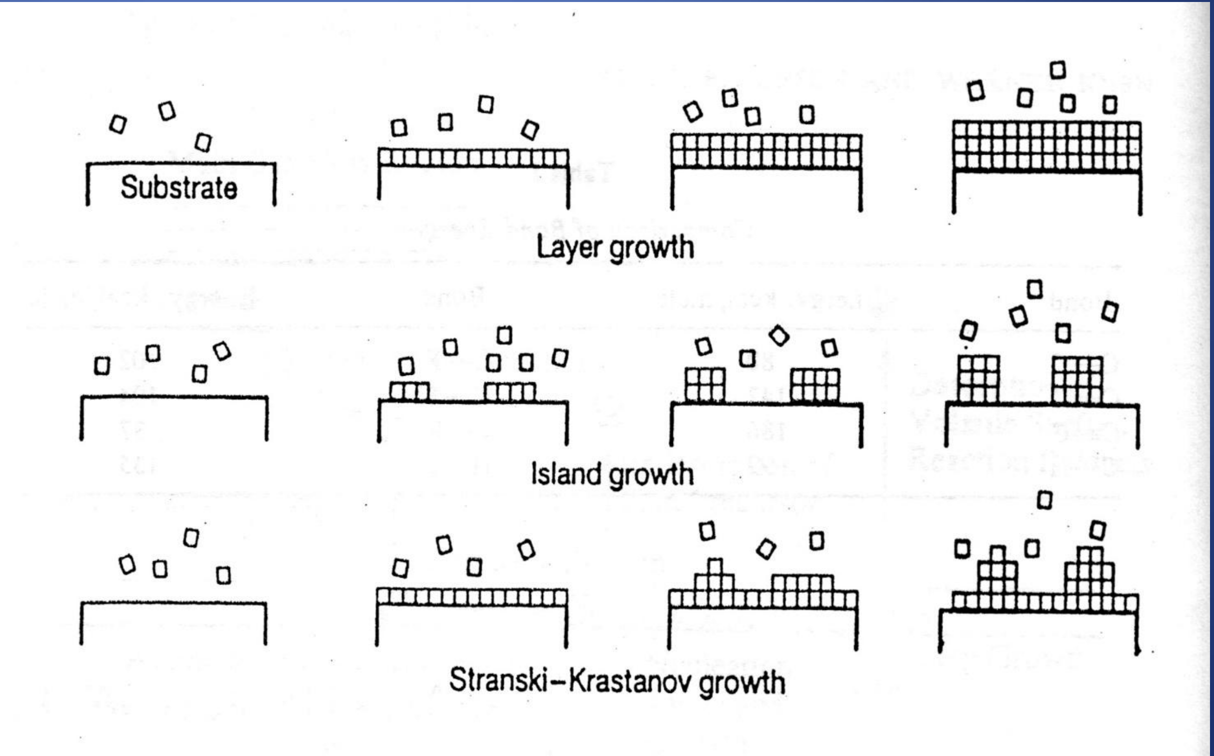


Nucleation and Growth of Films: The Three Conventional Modes

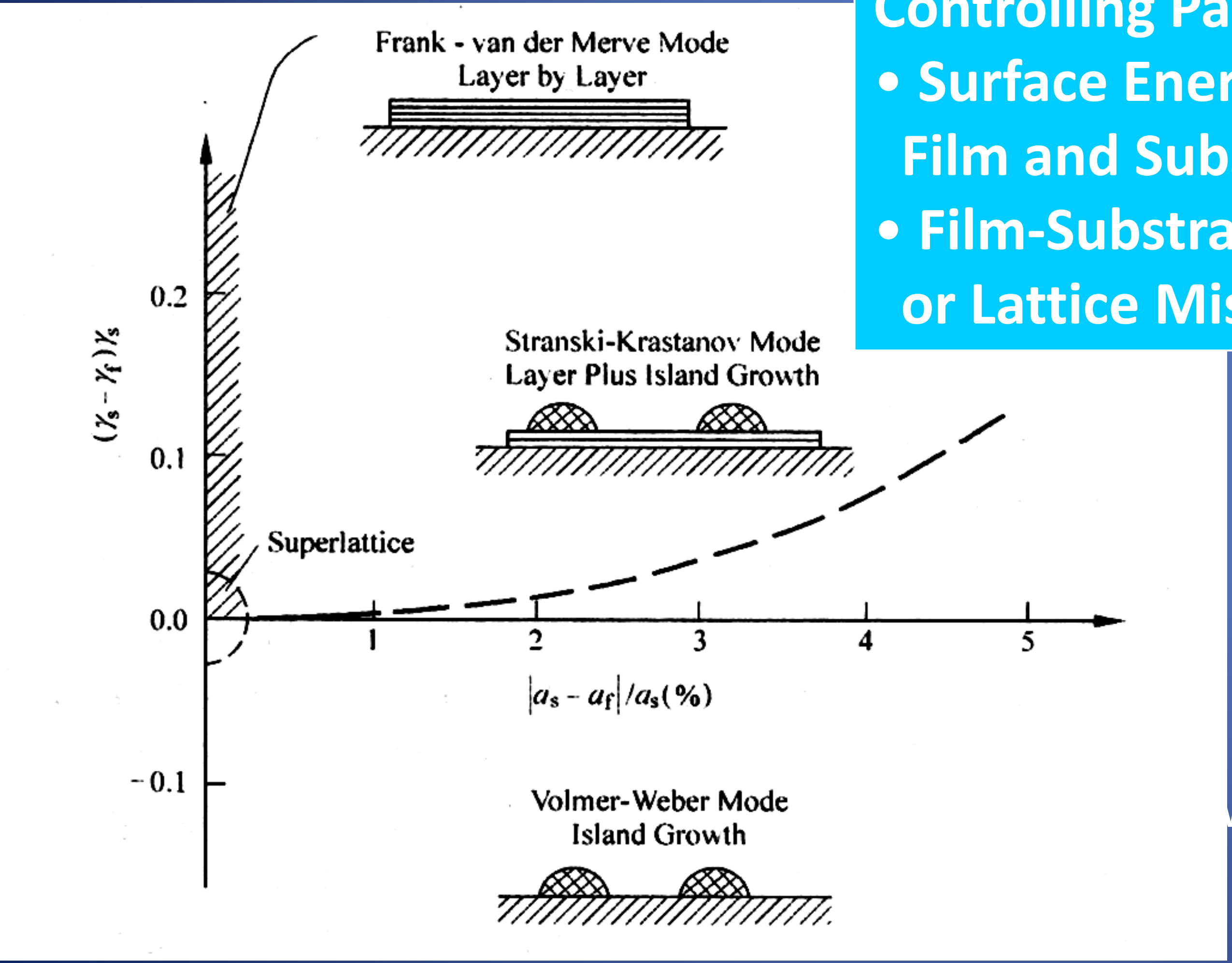
2-d full-monolayer
Frank-van der Merwe

3-d (or “0-d”) island
Volmer-Weber

2-d and 3-d
Stranski-Krastinov



Selection of Growth Modes



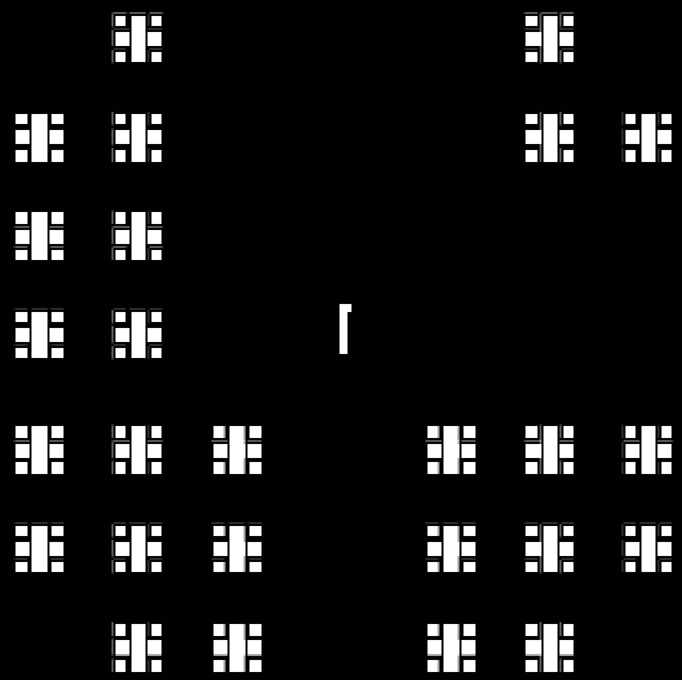
Controlling Parameters:

- Surface Energies of both Film and Substrate
- Film-Substrate Interface Energy or Lattice Mismatch

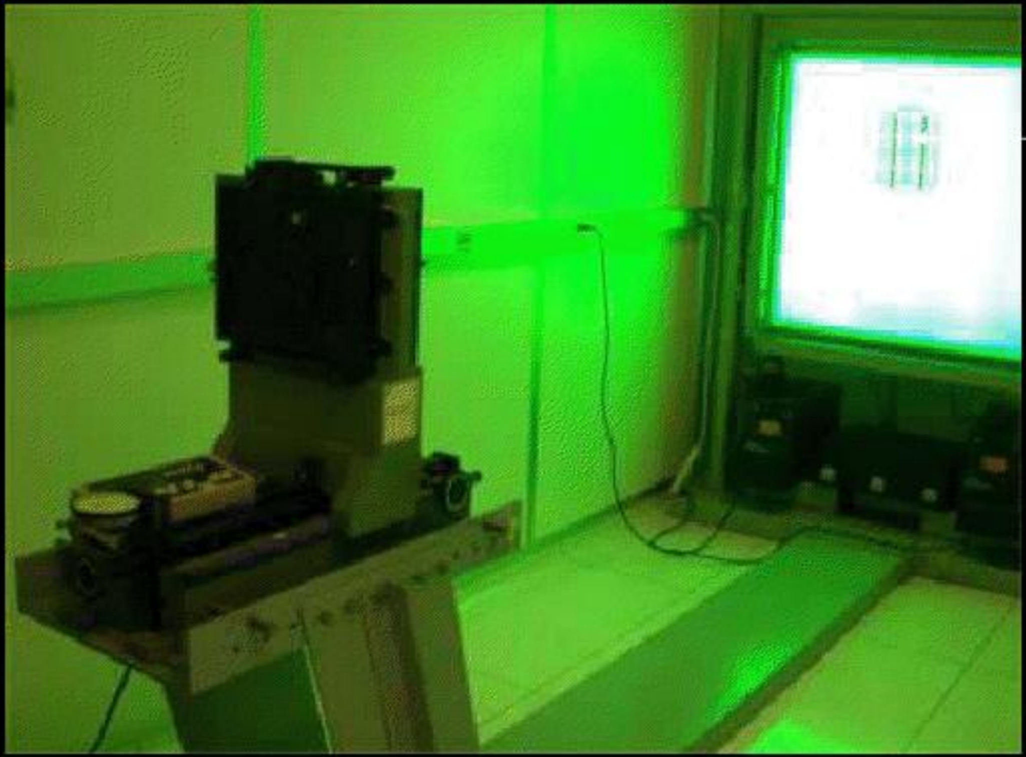
v, et al, TMS, 1986.

Photomasks

Design geometry on computer.



Mask fabrication

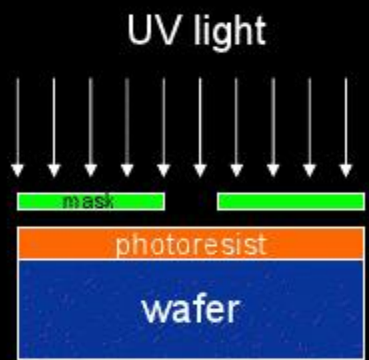


transparency

After Exposure
Developer
Stop bath
Fixer

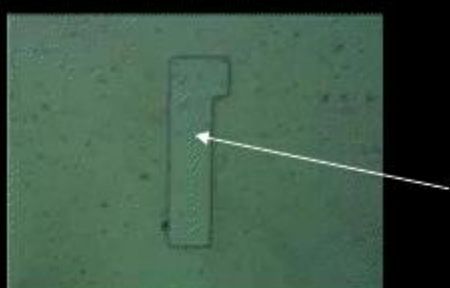
Dark room (1/20 reduction)

Expose to UV light



Development
For Shipley 1827
Water : MF351 = 5.5 : 1

Mask Aligner



Exposed regions dissolved in developer leaving bare wafer

This is the step which limits the spatial resolution.

Spin on photoresist

wafer

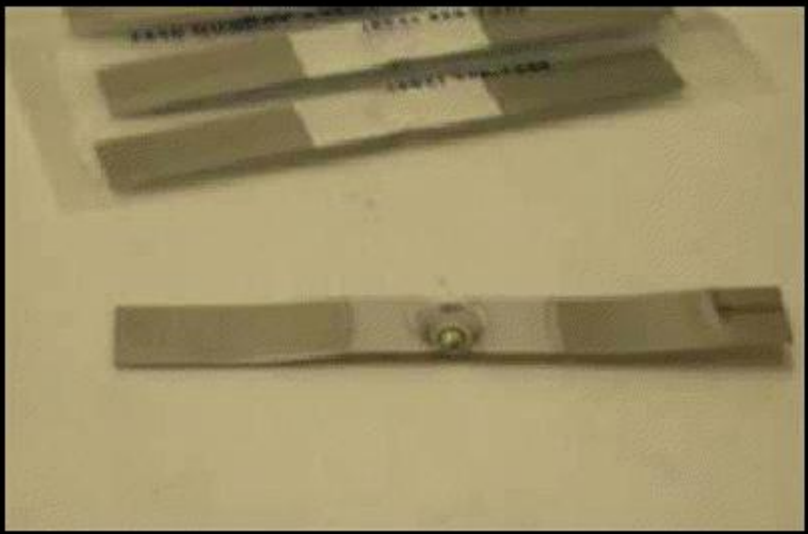
Photo resist spinner

Soft bake

Oven for soft baking of photo resist (at 90C for 30 min)

Thermal evaporation

Thermo evaporator



Alumina coated W boat

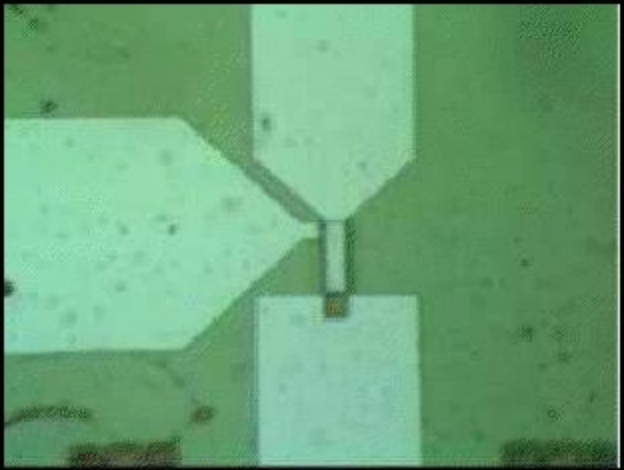
Useful for e.g.
Al, Ni, Au, Cr, Ti, NiCr, Pb, Sn

E-beam evaporation

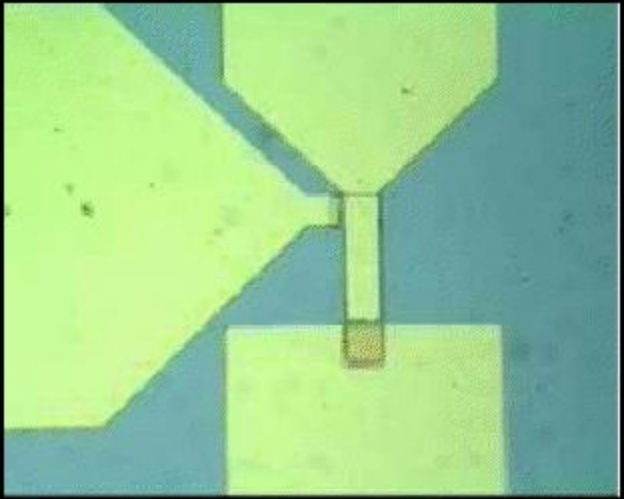
Electron beam evaporator

Au

Liftoff



Opening of photo resist for Ti/Au gate



After deposition of Ti/Au, then soaking in acetone

Resolution of optical lithography

$$R = \frac{3}{2}\sqrt{\frac{\lambda z}{2}}$$

Contact printing

z is resist thickness
(typically 0.1-1 μm)

$$R = 0.61\frac{\lambda}{NA}$$

Projection printing

NA is numerical aperture
(typically 0.5)

Light sources

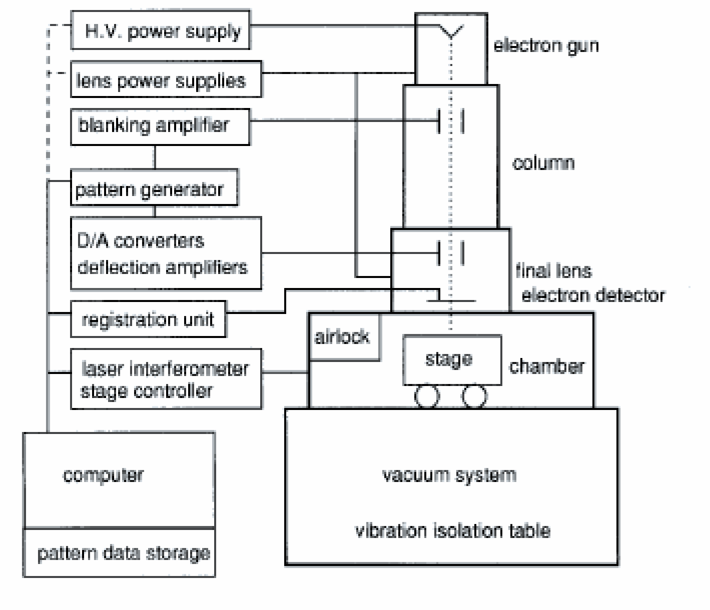
Source	λ	Resolution
• Hg lamp (g-line)	436 nm	400 nm
• Hg lamp (i-line)	365 nm	350 nm
• KrF	248 nm	150 nm
• ArF	193 nm	80 nm
• F_2	157 nm	research

increasing cost

Extreme UV, x-ray lithography research topics.
Difficulties lie in sources, and materials for optics and masks.

Electron Beam Lithography

- Advantages
  - Resolution
    - electron wavelength small
    - beamsize 1 nm
    - resolution from scattering typically 10 nm
  - Flexibility
    - All patterns under computer control
- Disadvantages
  - Cost
    - Need high vacuum
    - Need precision electron focusing magnets
  - Throughput
    - Only one pixel exposed at a time
    - Not commercially viable except for a few applications

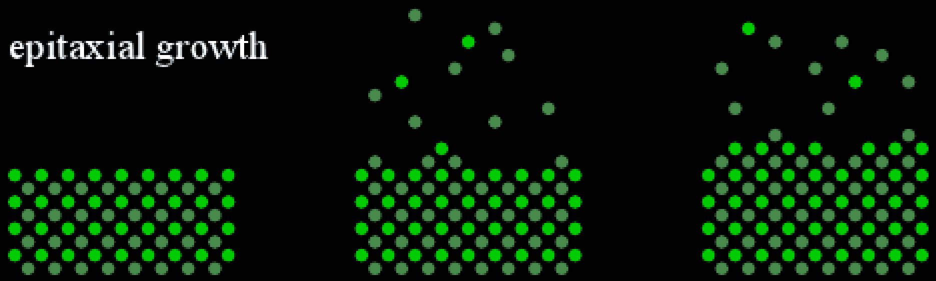


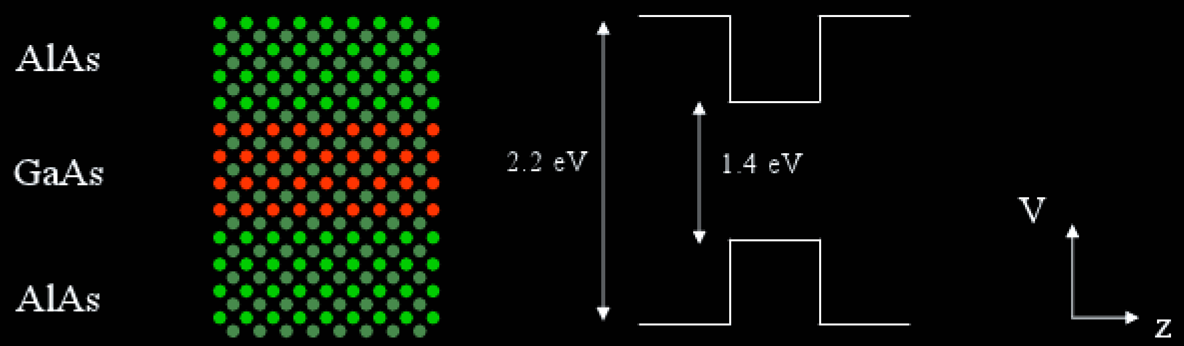
Reference: SPIE Handbook of Microlithography, Micromachining, and Microfabrication available at http://www.cnf.cornell.edu/spiebook/toc.htm

In spite of its disadvantages,
e-beam lithography is the main tool for nanotechnology research.

MBE

epitaxial growth



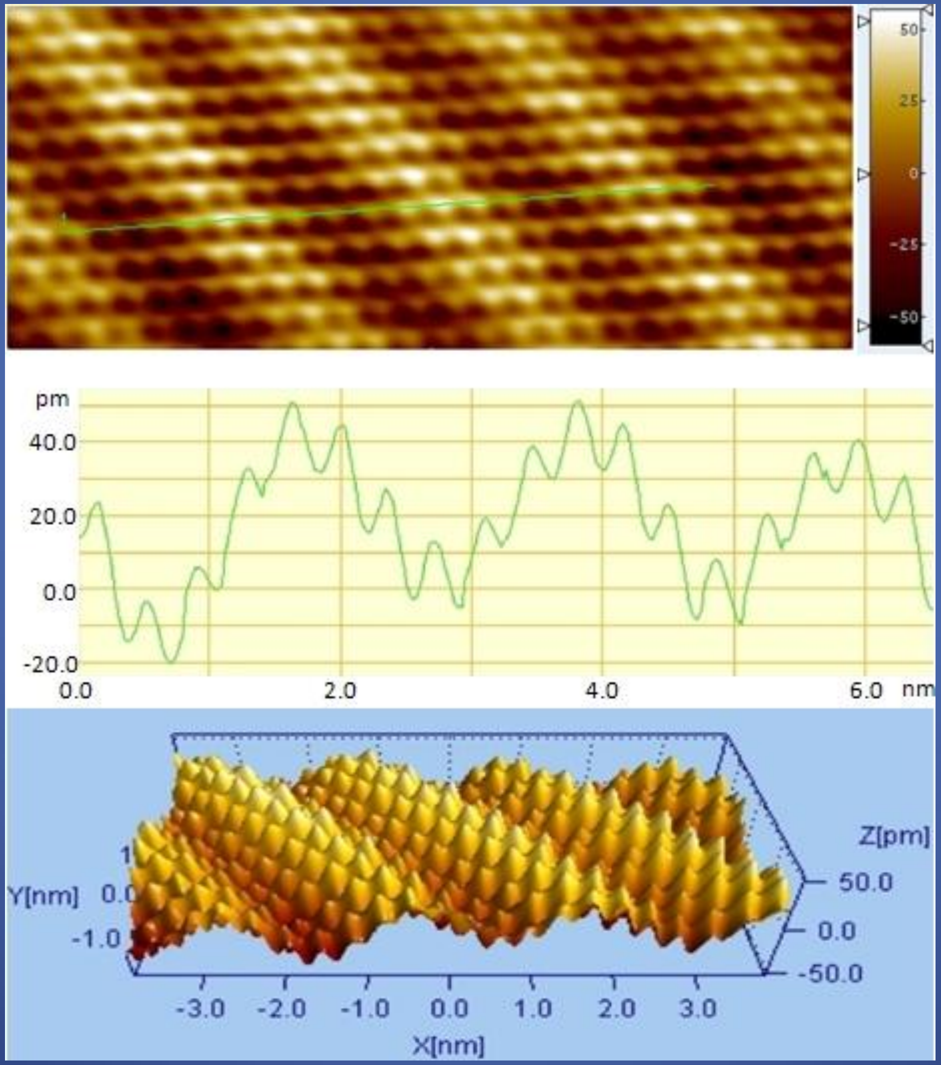


Also InP, InGaAs, InAlAs, InGaAsP …

Characterization

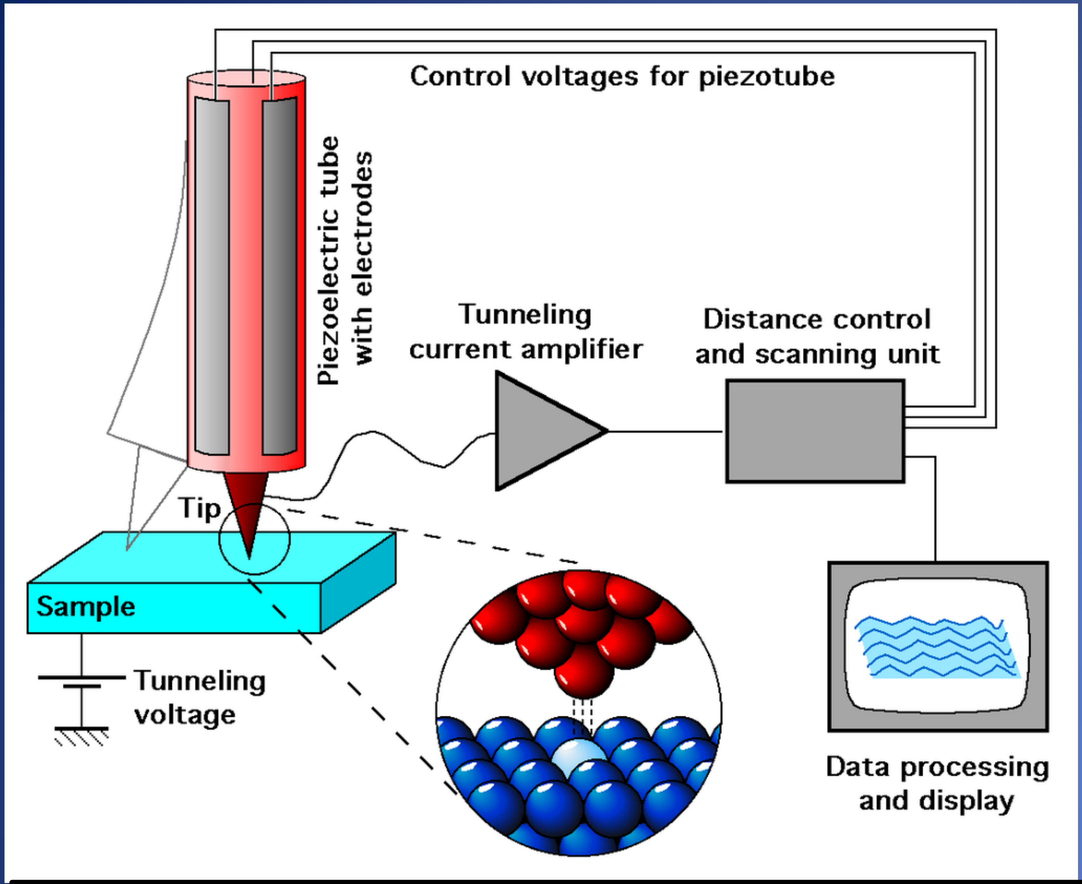
- Optical microscopy cannot see better than wavelength of light, ~ 1 μm
- Scanning electron microscope (SEM)
- Transmission electron microscope (TEM)
- Scanning probe microscopy (SPM)
- Atomic force microscope (AFM)

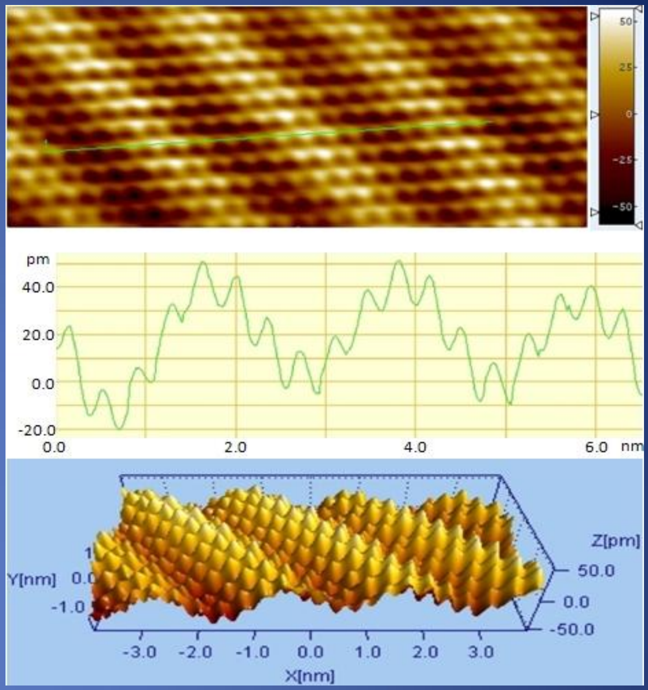
STM


50
25
0
-25
-50
pm
40.0
20.0
0.0
-20.0
0.0
2.0
4.0
6.0
nm
Z[pm]
50.0
0.0
-50.0
Y[nm]
-1.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
X[nm]

A **scanning tunneling microscope** (**STM**) is an instrument for imaging surfaces at the atomic level. Its development in 1981 earned its inventors, Gerd Binnig and Heinrich Rohrer (at IBM Zürich), the Nobel Prize in Physics in 1986.

For an STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra-high vacuum but also in air, water, and various other liquid or gas ambients, and at temperatures ranging from near zero kelvin to a few hundred degrees Celsius

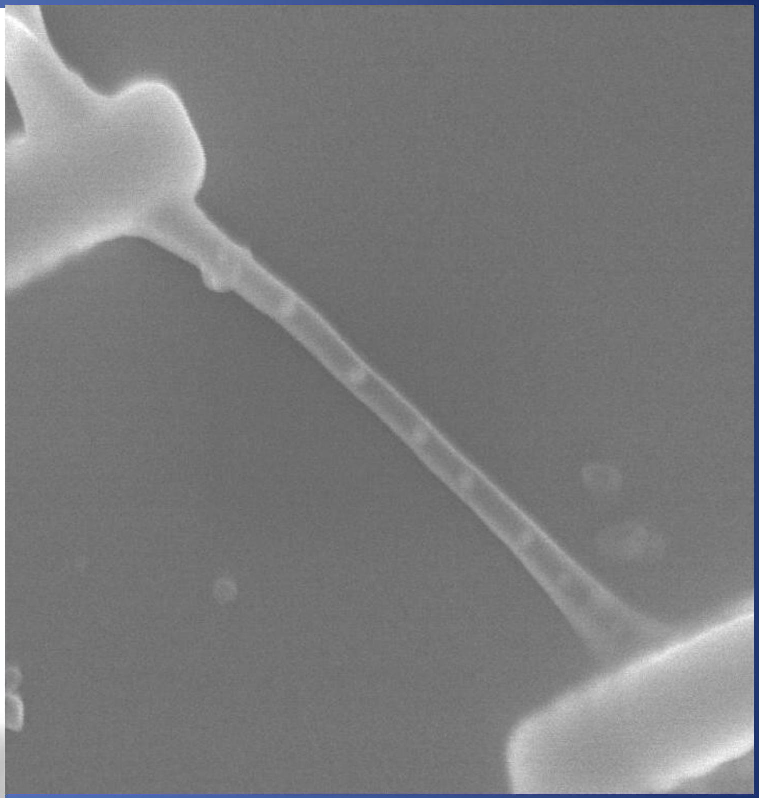




The STM is based on the concept of quantum tunneling. When a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them. The resulting *tunneling current* is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample. Information is acquired by monitoring the current as the tip's position scans across the surface, and is usually displayed in image form. STM can be a challenging technique, as it requires extremely clean and stable surfaces, sharp tips, excellent vibration control, and sophisticated electronics, but nonetheless many hobbyists have built their own.

http://en.wikipedia.org/wiki/Scanning_tunneling_microscope

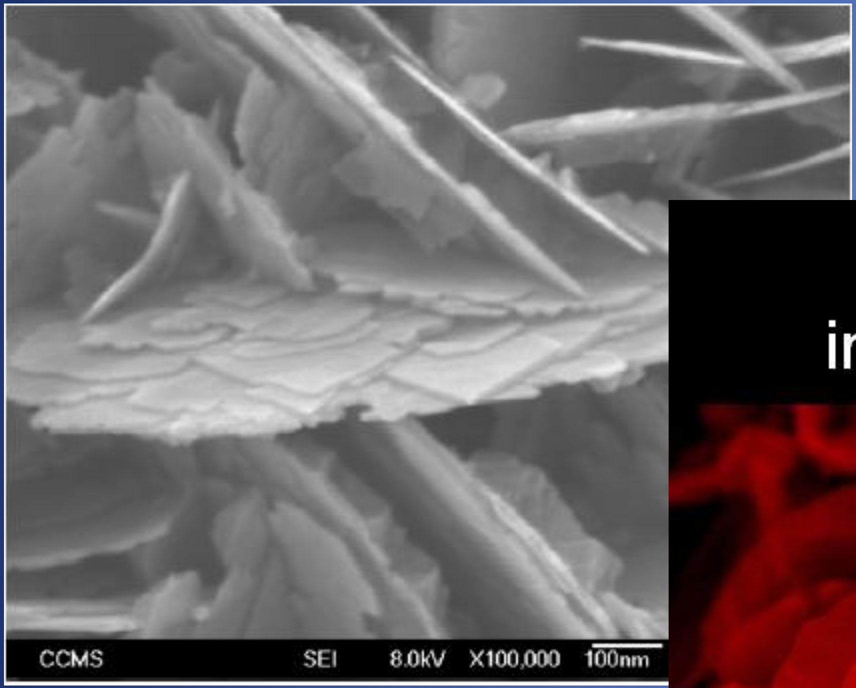
SEM



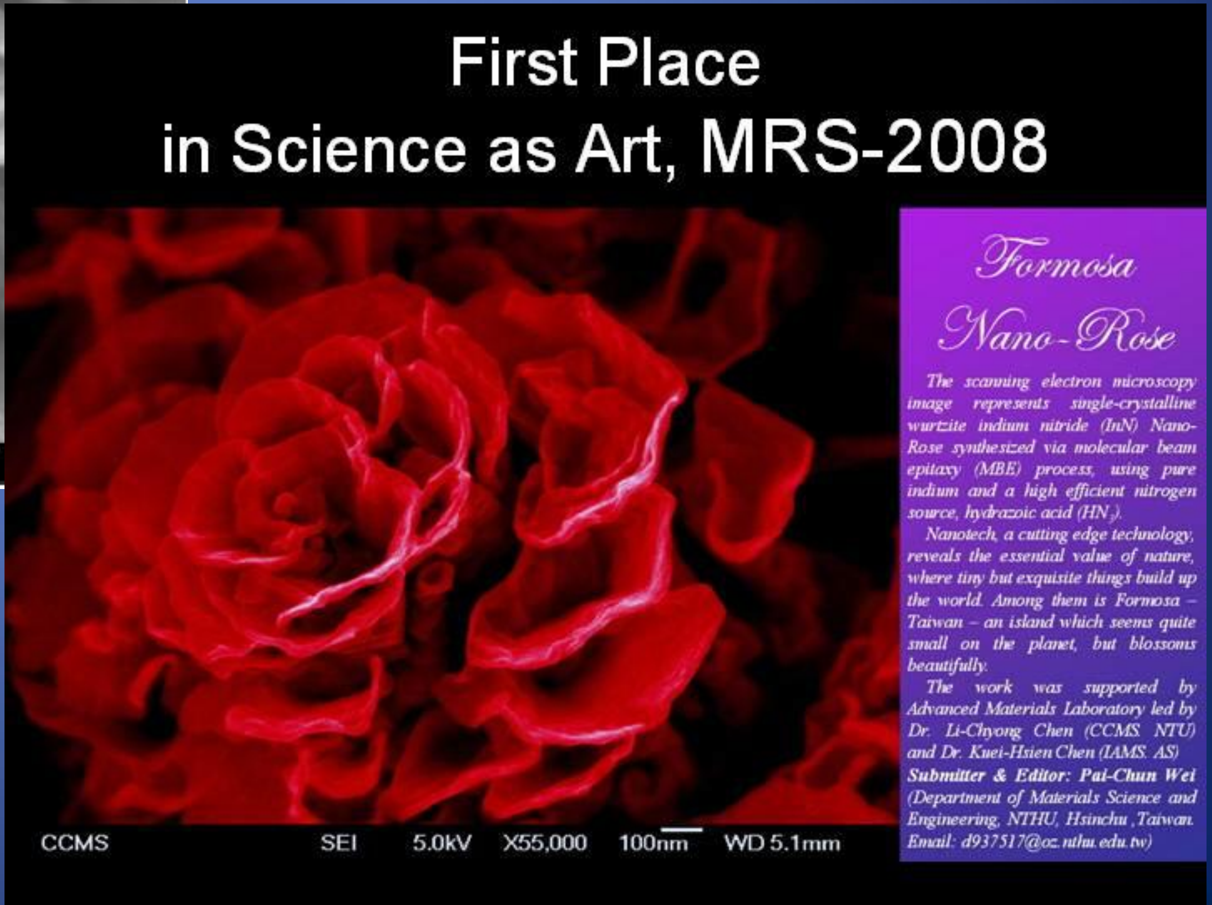
A **scanning electron microscope** (**SEM**) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures.

The most common mode of detection is by secondary electrons emitted by atoms excited by the electron beam. On a flat surface, the plume of secondary electrons is mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the topography of the surface is created.

SEM

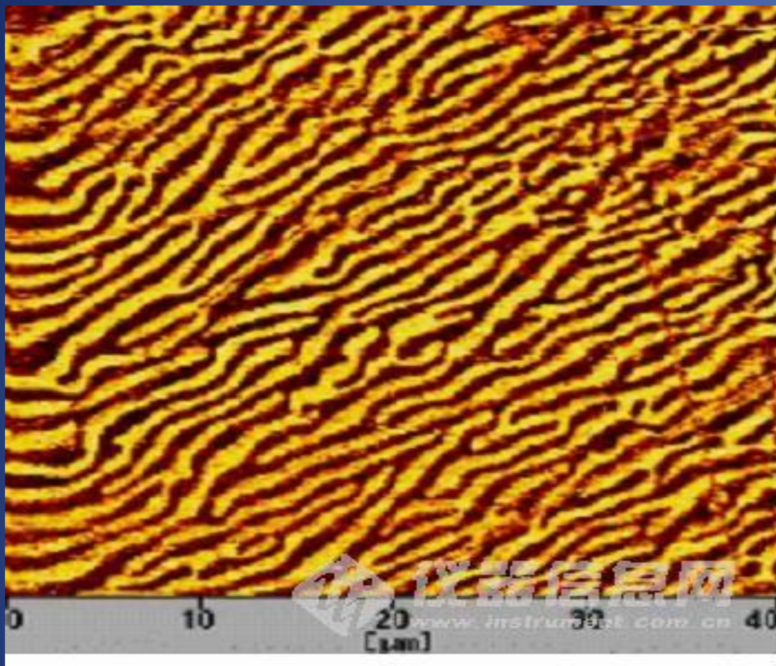


CCMS
SEI
8.0kV
X100,000
100nm



First Place
in Science as Art, MRS-2008
CCMS
SEI
5.0kV
X55,000
100nm
WD 5.1mm
Formosa
Nano-Rose
The scanning electron microscopy image represents single-crystalline wurtzite indium nitride (InN) Nano-Rose synthesized via molecular beam epitaxy (MBE) process, using pure indium and a high efficient nitrogen source, hydrazoic acid (HN_3).
Nanotech, a cutting edge technology, reveals the essential value of nature, where tiny but exquisite things build up the world. Among them is Formosa – Taiwan – an island which seems quite small on the planet, but blossoms beautifully.
The work was supported by Advanced Materials Laboratory led by Dr. Li-Chyong Chen (CCMS. NTU) and Dr. Kuei-Hsien Chen (IAMS. AS)
Submitter & Editor: Pai-Chun Wei
(Department of Materials Science and Engineering, NTHU, Hsinchu ,Taiwan. Email: d937517@oz.nthu.edu.tw)

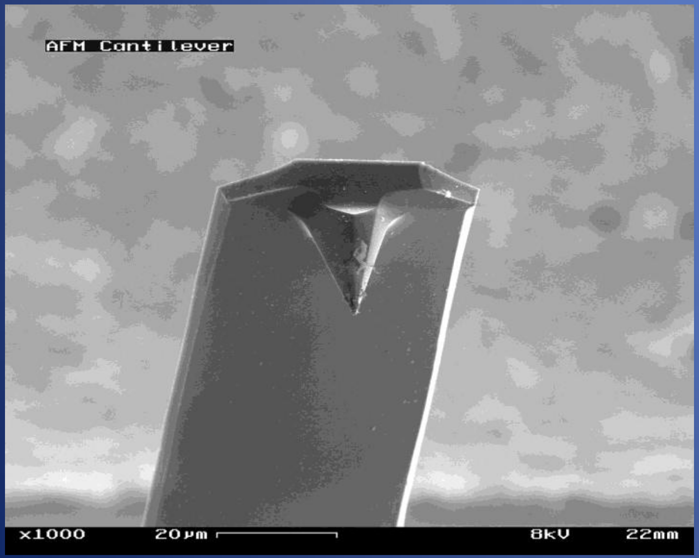
AFM



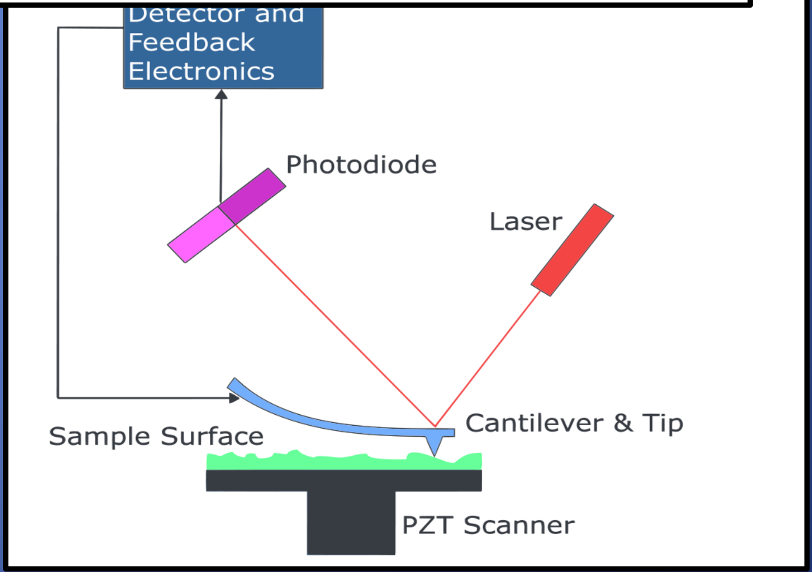
Atomic force microscopy (**AFM**) or **scanning force microscopy** (**SFM**) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s at IBM Research - Zurich, a development that earned them the Nobel Prize for Physics in 1986.

The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe.

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvatureon the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces Casimir forces, solvation forces, etc. Along with force, additional quantities may simultaneously be measured through the use of specialized types of probes.



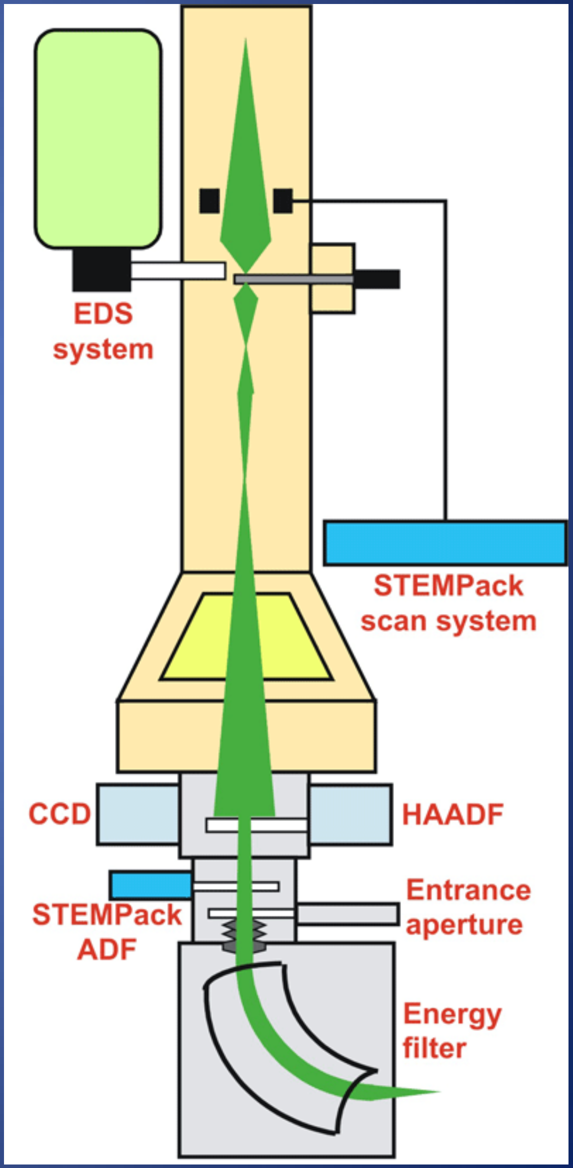
Electron micrograph of a used AFM cantilever image width ~100 micrometers...



Block diagram of atomic force microscope using beam deflection detection. As the cantilever is displaced via its interaction with the surface, so too will the reflection of the laser beam be displaced on the surface of the photodiode.

TEM

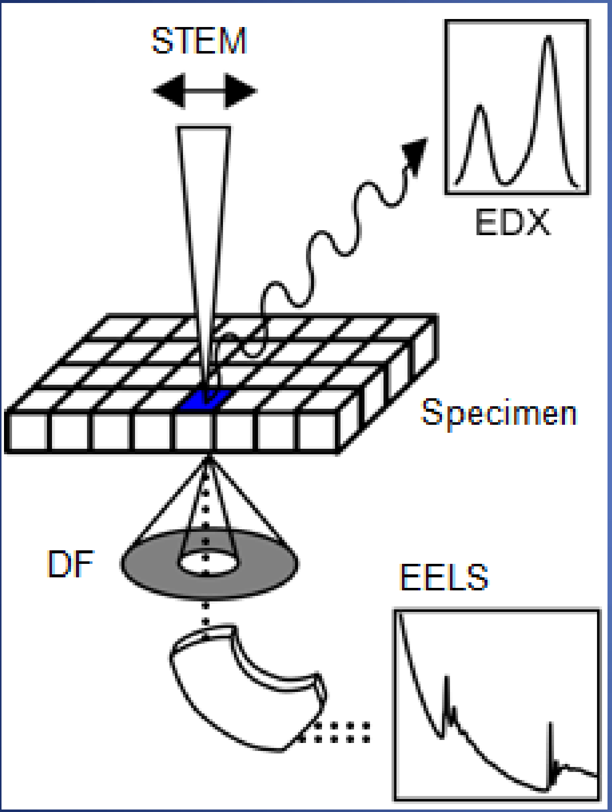
TECNAI
EDAX
www.cam.zjut.edu.cn

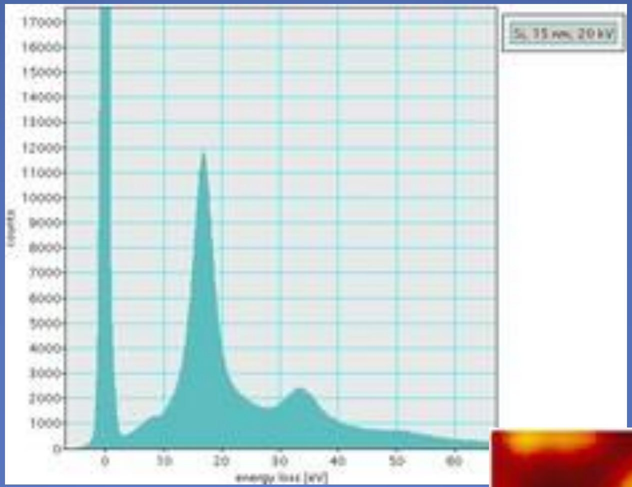


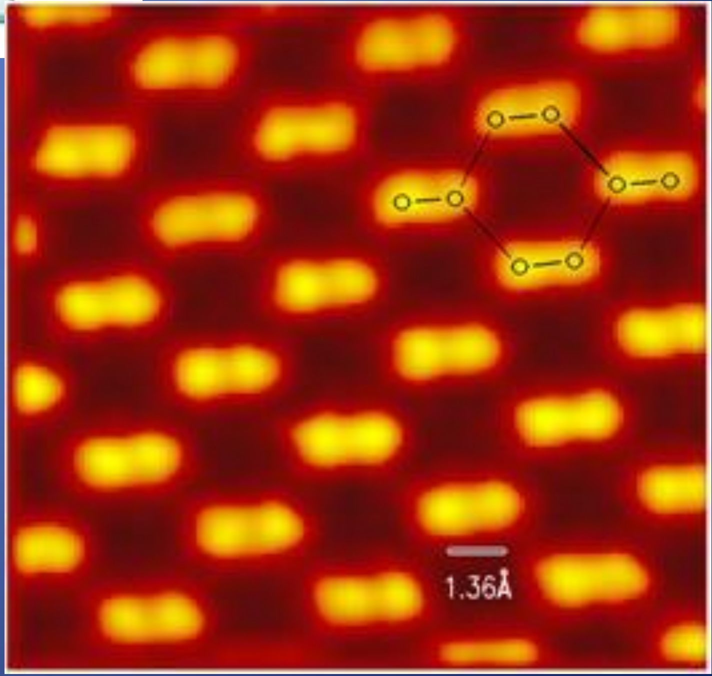
EDS system
STEMPack scan system
CCD
HAADF
Entrance aperture
STEMPack ADF
Energy filter

Transmission electron microscopy (**TEM**) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as afluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEM (EELS)


STEM
EDX
Specimen
DF
EELS

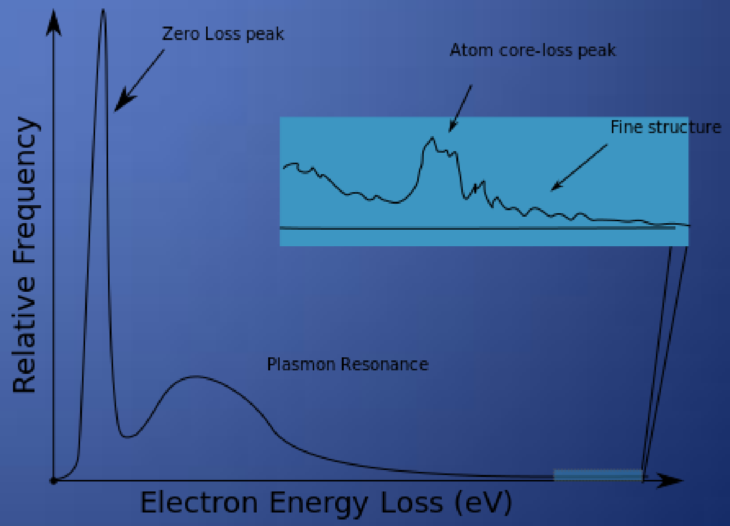

17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
10
20
30
40
50
60


1.36Å

In **electron energy loss spectroscopy** (**EELS**) a material is exposed to a beam of electrons with a known, narrow range of kinetic energies.

Some of the electrons will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected.

The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. Inelastic interactions include phonon excitations, inter and intra band transitions, plasmon excitations, inner shell ionizations, and Cherenkov radiation.



Idealised schematic of an EELS spectrum, indicating zero-loss peak, plasmon resonance, and core-loss electron peak

Composition Analysis

1. EL
2. EDS **(Energy-dispersive X-ray spectroscopy)**
3. AES **(Auger electron spectroscopy)**
4. NMR
5. ICP MASS
6. MALDI （Matrix-assisted laser desorption/ionization）

Energy-dispersive X-ray spectroscopy (**EDS**, **EDX**, or **XEDS**), sometimes called **energy dispersive X-ray analysis** (**EDXA**) or **energy dispersive X-ray microanalysis** (**EDXMA**), is an analytical technique used for the elemental analysis or chemical characterization of a sample.

Auger electron spectroscopy (AES; pronounced [oʒe] in French) is a common analytical technique used specifically in the study of surfaces and, more generally, in the area of materials science. Underlying the spectroscopic technique is the Auger effect, as it has come to be called, which is based on the analysis of energetic electrons emitted from an excited atom after a series of internal relaxation events.

NMR, MRI

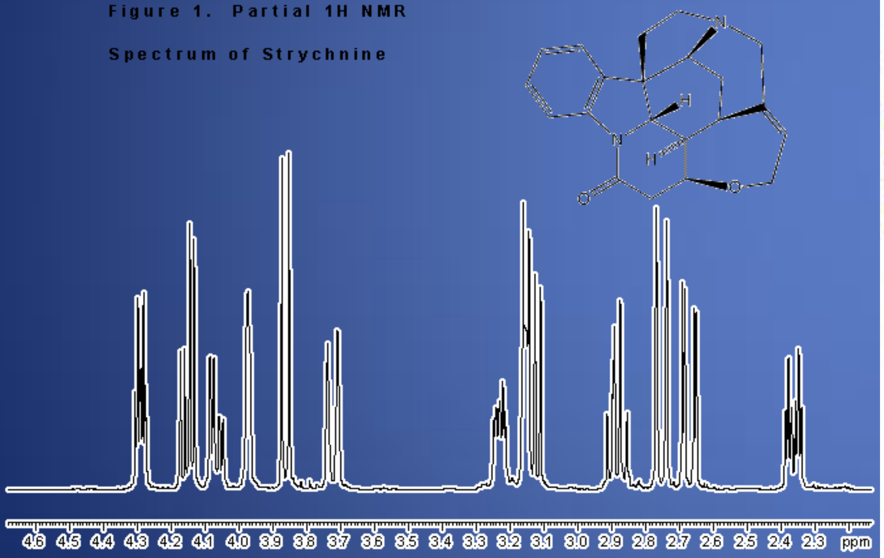
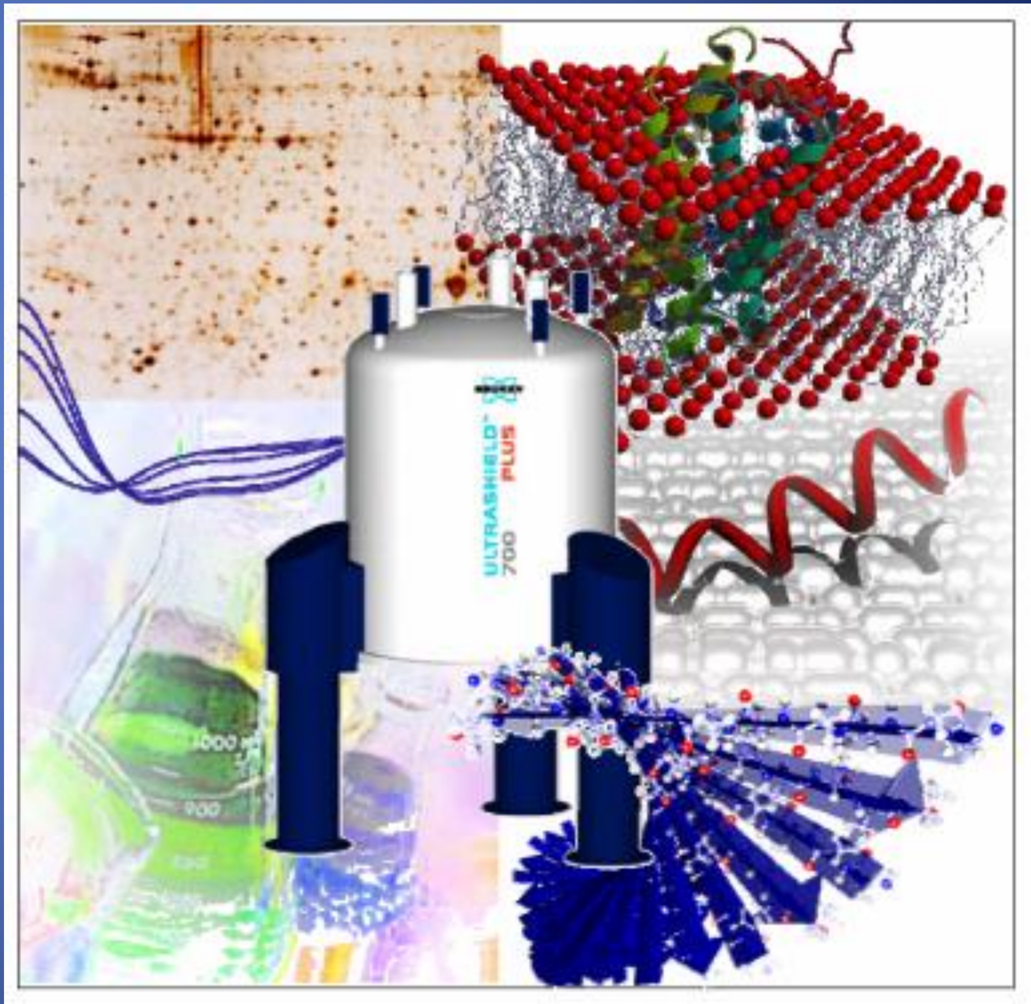
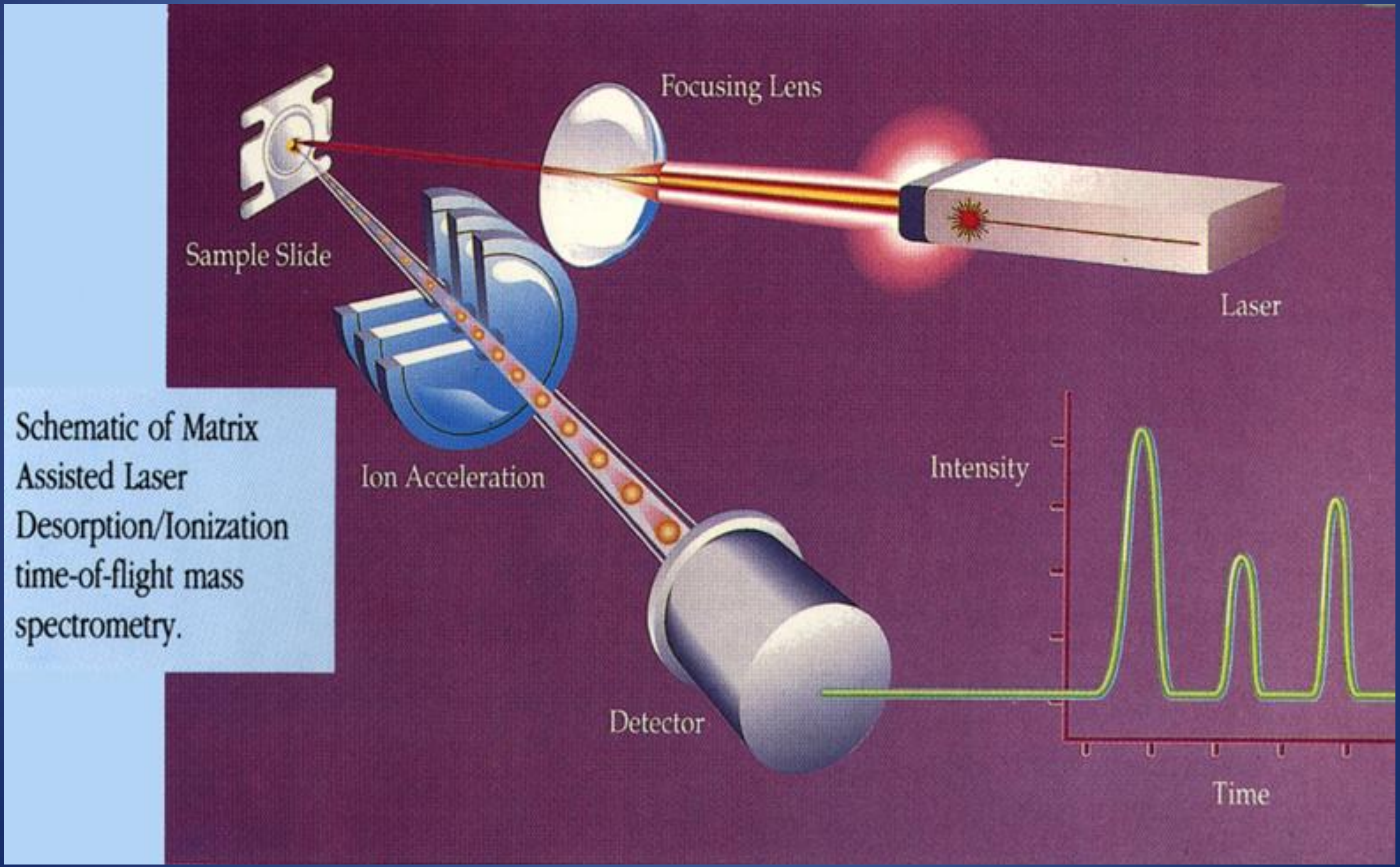


Figure 1. Partial 1H NMR Spectrum of Strychnine



MALDI （Matrix-assisted laser desorption/ionization)



Structure Analysis

1. XRD
2. TEM
3. FTIR
4. Raman

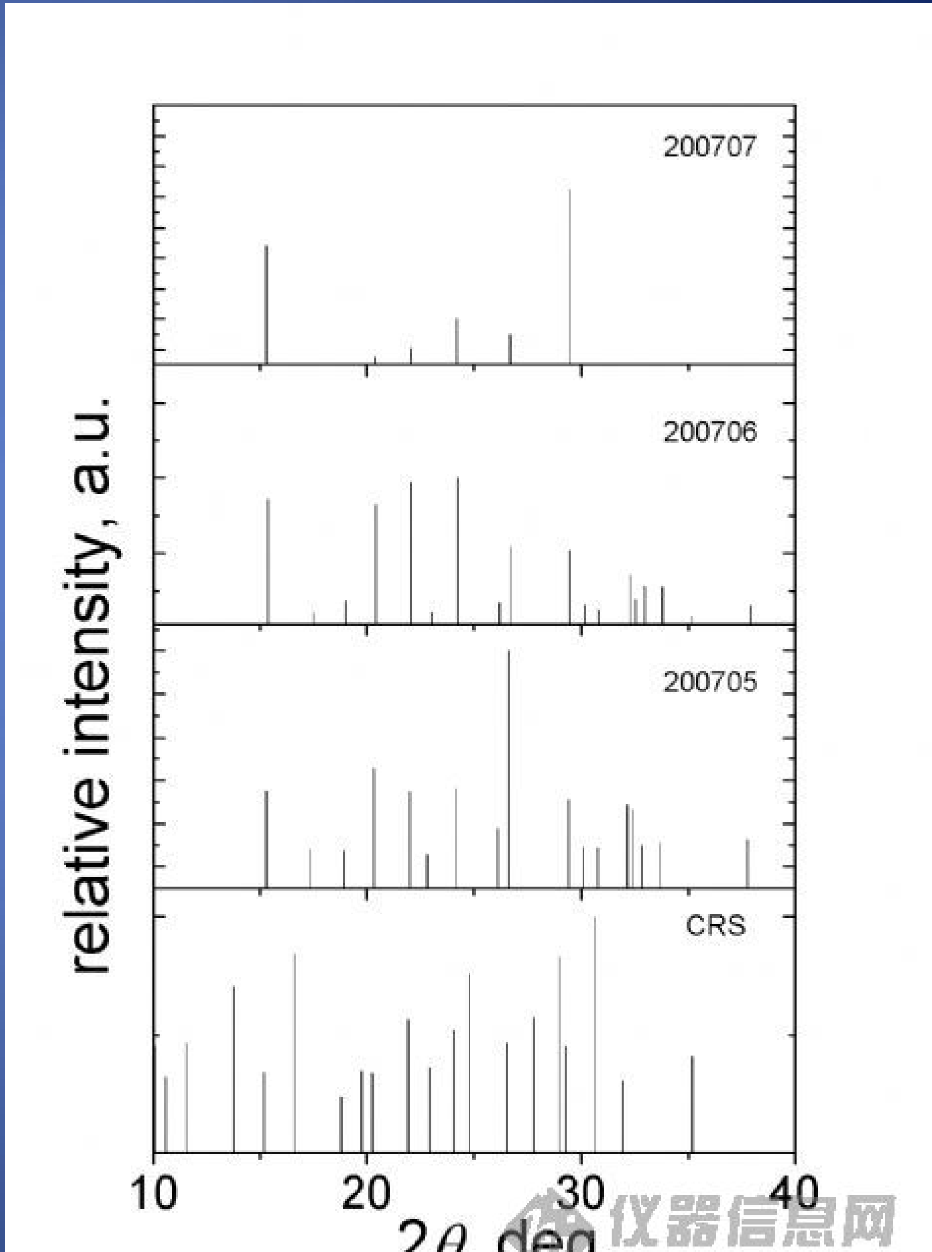
Electronic properties

1. Optical Absorption
2. Photoluminescence
3. STS
4. XPS
5. SRRC

Other Thermal and Magnetic Measurements

1. Thermal conductivity)
2. TGA
3. DSC
4. SQUID (Superconducting Quantum Interference Device)

XRD

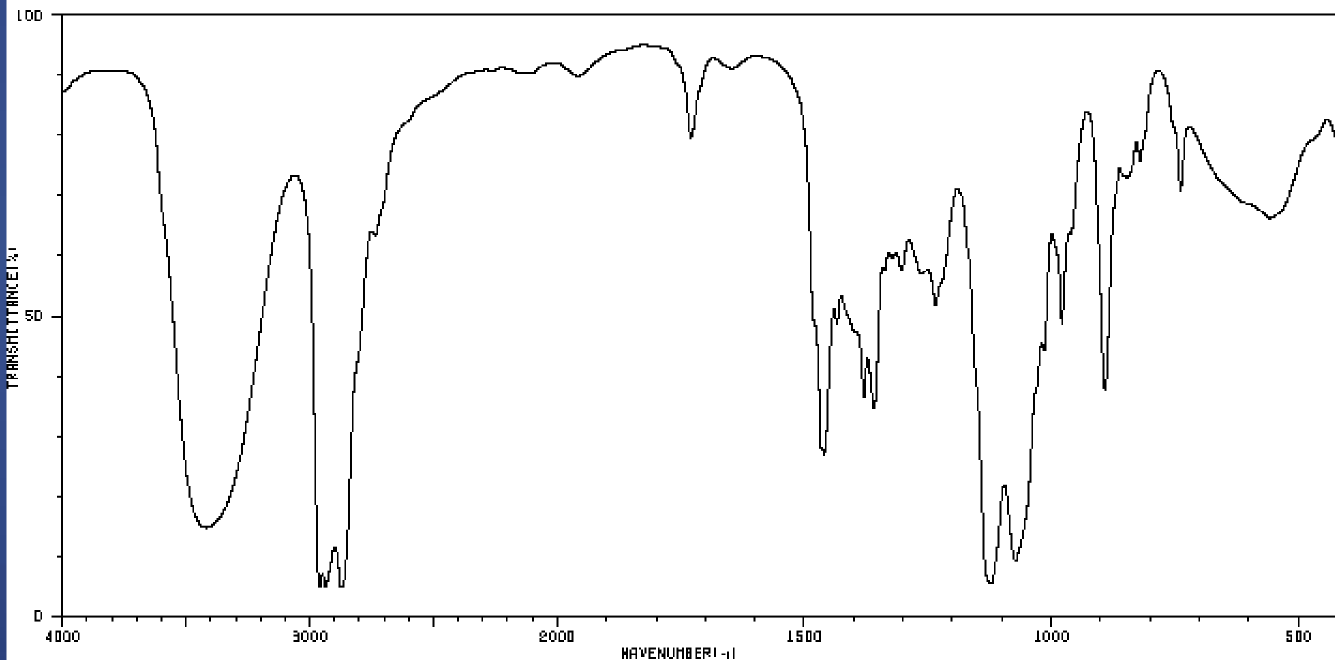


FTIR

HIT-NO=1110	SCORE= ( )	SDBS-NO=662	IR-NIDA-05124 : LIQUID FILM

ETHYLENE GLYCOL MONOBUTYL ETHER

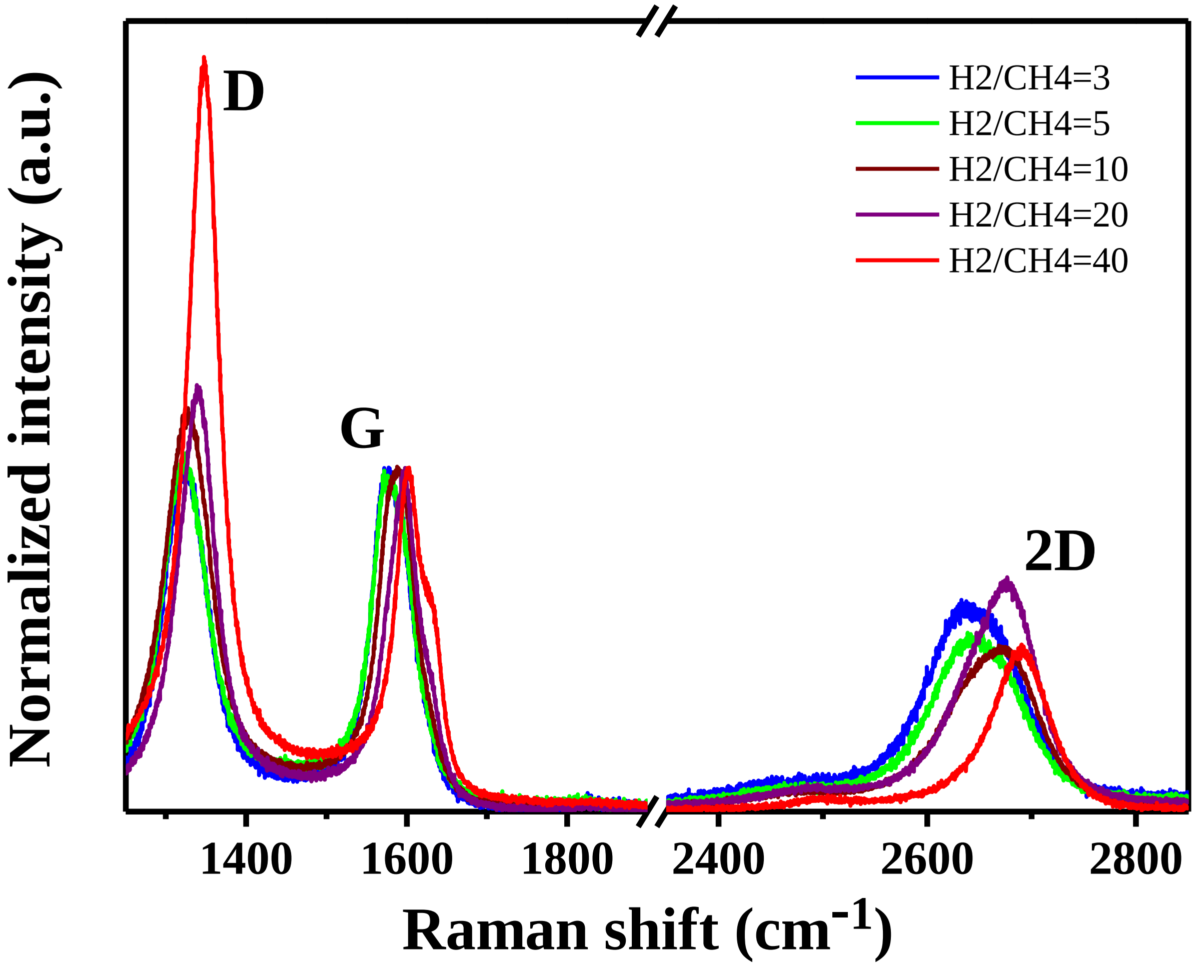
$C_6H_{14}O_2$



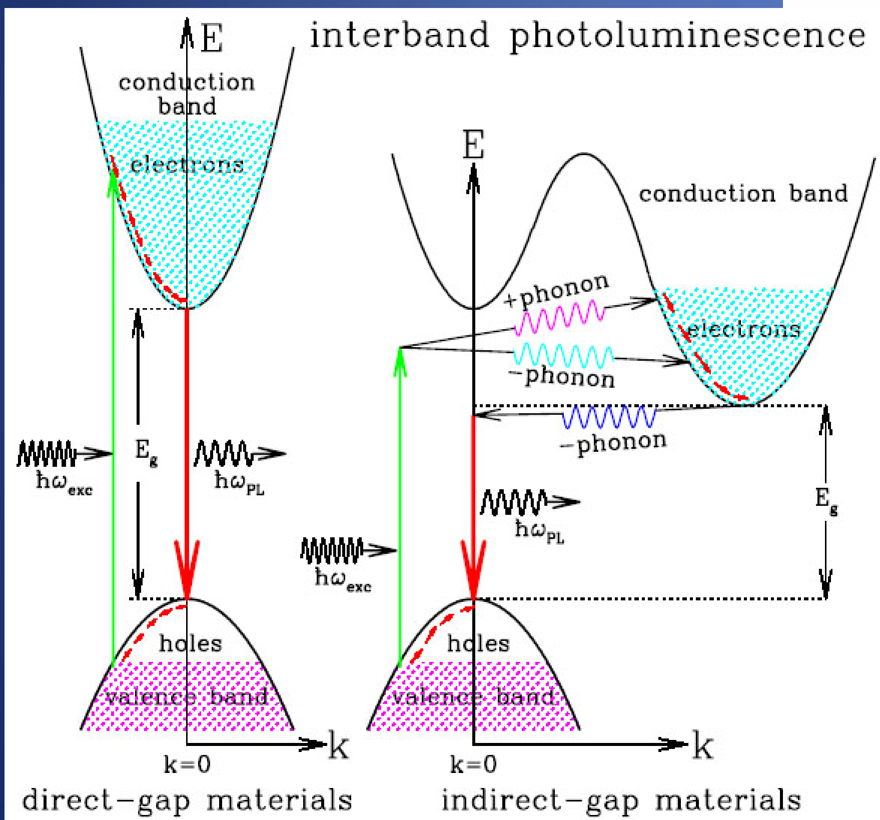
3416	14	1466	26	1236	60	820	72
2959	4	1460	26	1123	5	738	68
2935	4	1434	47	1073	9	556	64
2871	4	1379	36	1014	43		
1961	86	1360	33	979	47		
1956	86	1322	57	891	36		
1729	77	1303	56	848	70		

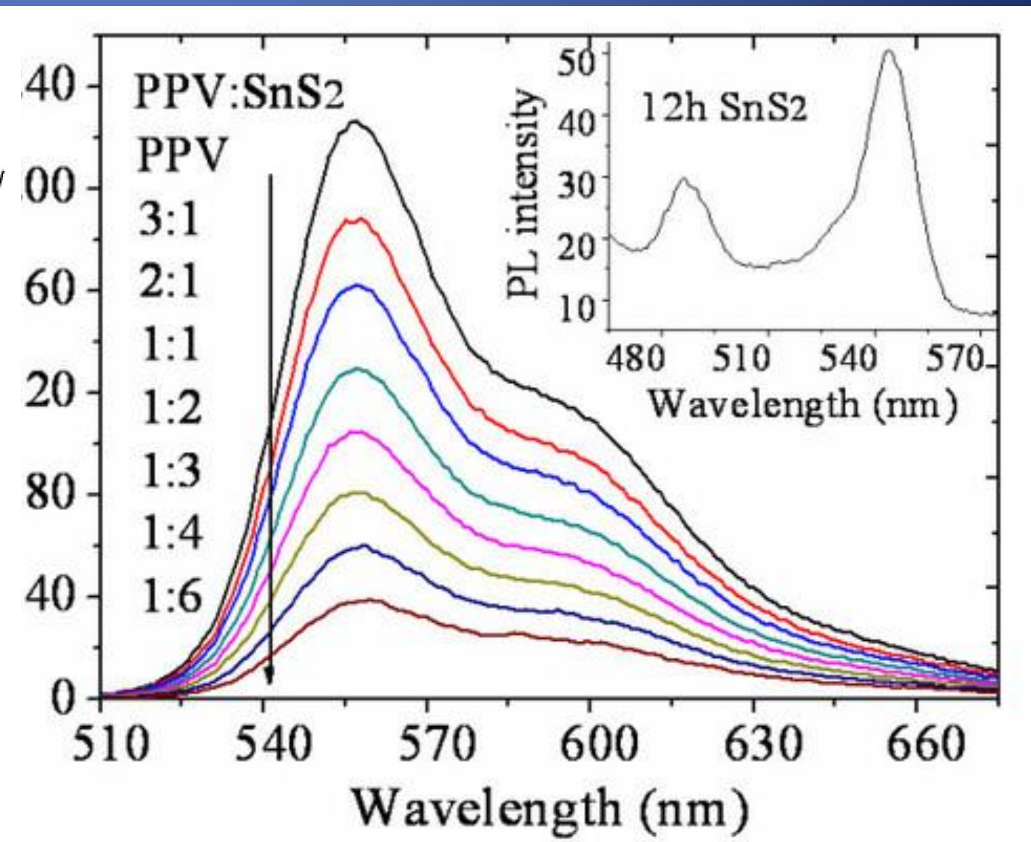
$CH_3—(CH_2)_3—O—(CH_2)_2—OH$

Raman

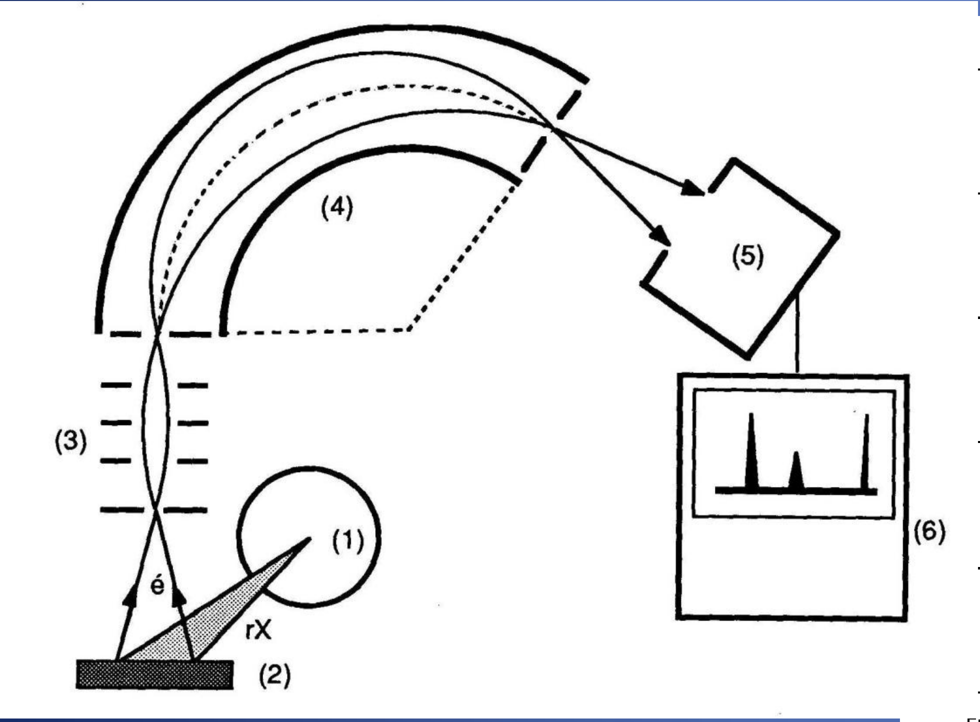

D
G
2D
H2/CH4=3
H2/CH4=5
H2/CH4=10
H2/CH4=20
H2/CH4=40
Normalized intensity (a.u.)
1400
1600
1800
2400
2600
2800
Raman shift (cm-1)

Photoluminescence (PL & CL)

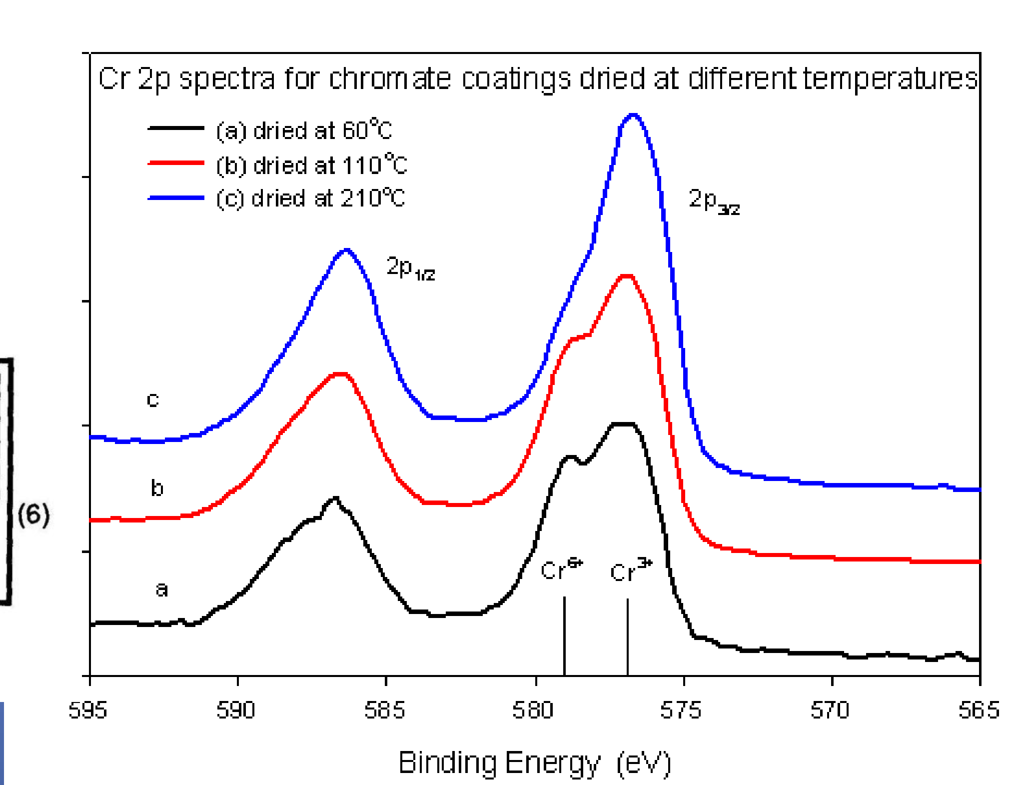




XPS

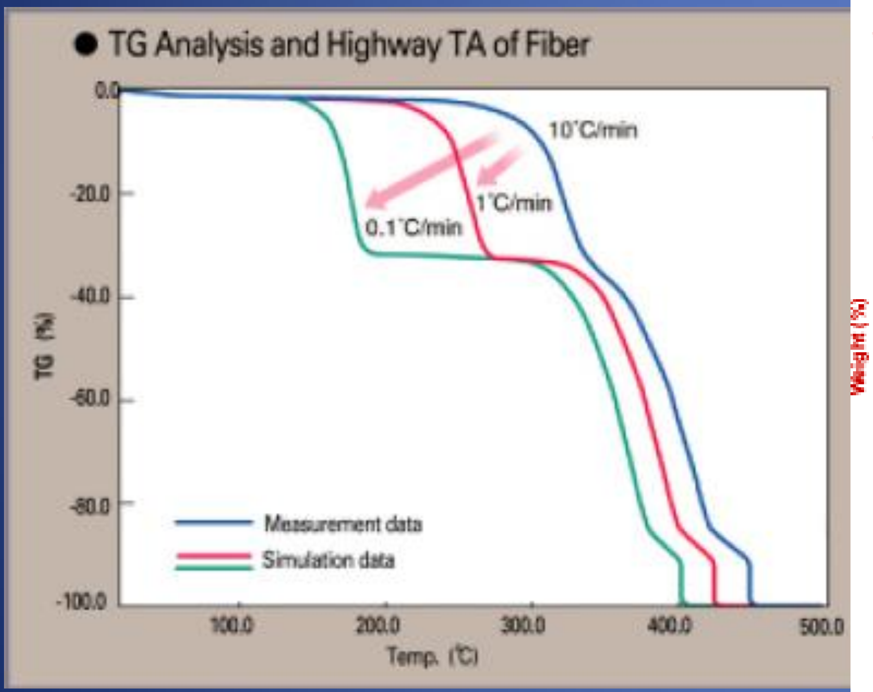


(1)
(2)
(3)
(4)
(5)
(6)
é
rX

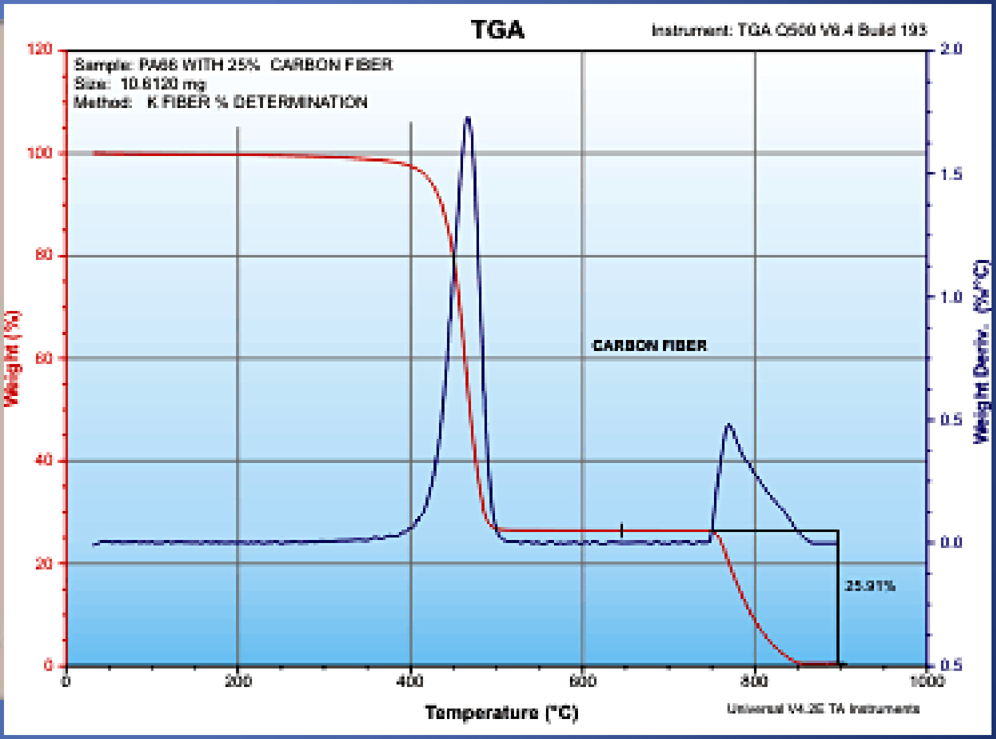


Cr 2p spectra for chromate coatings dried at different temperatures
(a) dried at 60°C
(b) dried at 110°C
(c) dried at 210°C
2p3/2
2p1/2
c
b
a
Cr6+
Cr3+
595
590
585
580
575
570
565
Binding Energy (eV)

TGA & DSC



TG Analysis and Highway TA of Fiber
10°C/min
1°C/min
0.1°C/min
TG (%)
0.0
-20.0
-40.0
-60.0
-80.0
-100.0
100.0
200.0
300.0
400.0
500.0
Temp. (°C)
Measurement data
Simulation data



TGA
Instrument: TGA Q500 V6.4 Build 193
Sample: PA66 WITH 25% CARBON FIBER
Size: 10.6120 mg
Method: K FIBER % DETERMINATION
CARBON FIBER
25.91%
Weight (%)
Weight Deriv. (%/°C)
Temperature (°C)
Universal V4.2E TA Instruments

SQUID (Superconducting Quantum Interference Device)