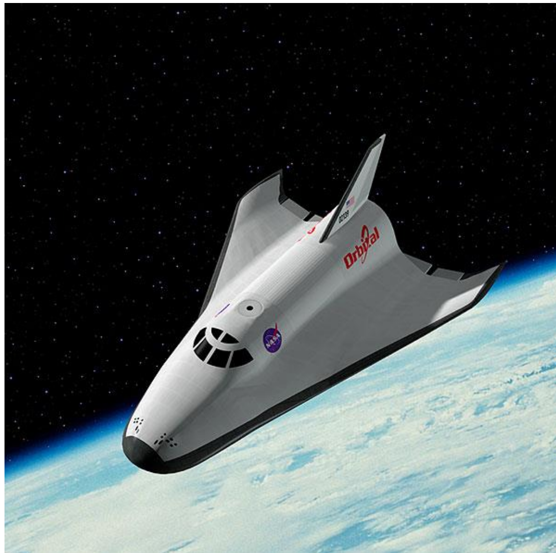
Nanofabrication

ECE 594

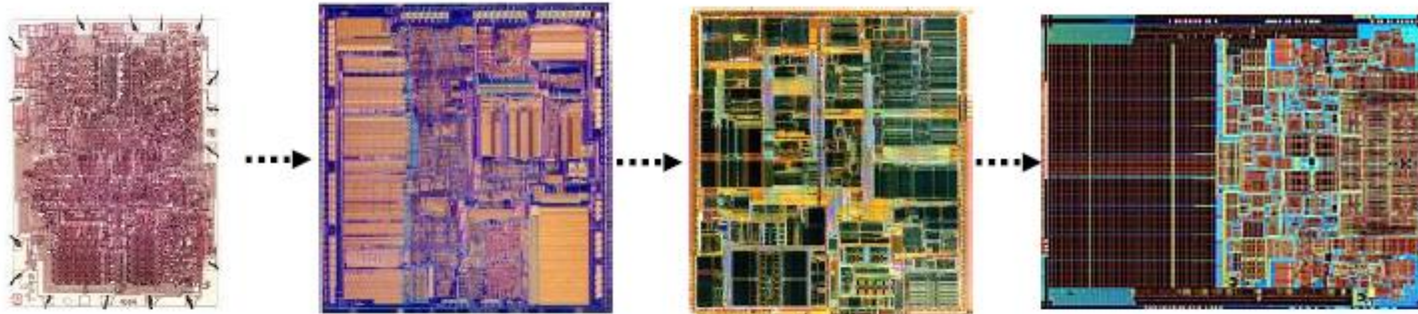
Outline

- Introduction, Course Overview
- Nanofabrication technology
- Photolithography
- Charged beams
- Scanning probes
- Replication, pattern transfer
- Indirect nanofabrication
- Bottom-up techniques: growth, self-assembly
- Nano characterization
- SEM
- TEM
- Raman
- CNT,Graphene Fabrication and applications of Nano Characterization

Microelectronics and Our Life



Intel Microprocessors – Brief History



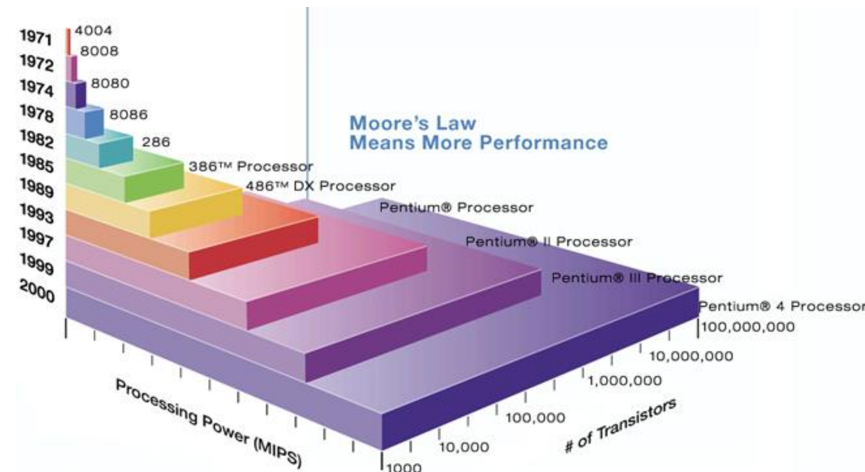
1971	1985	1997	2006
Intel 4004 µP	Intel 386 µP	Intel PII µP	Intel Core 2 Duo
2,300 transistors	275K transistors	7.5 M-transistor	291 M-transistor
108 KHz	33 MHz	300 MHz	2.4 GHz
10 µm linewidth	1.5 µm	0.25 µm	0.065 µm

Goals of Nanofabrication:

Lithography is key technology pacing Moore's Law

Make the feature size as small as possible.

Decrease the cost of nanofabrication.



Nanofabrication Techniques

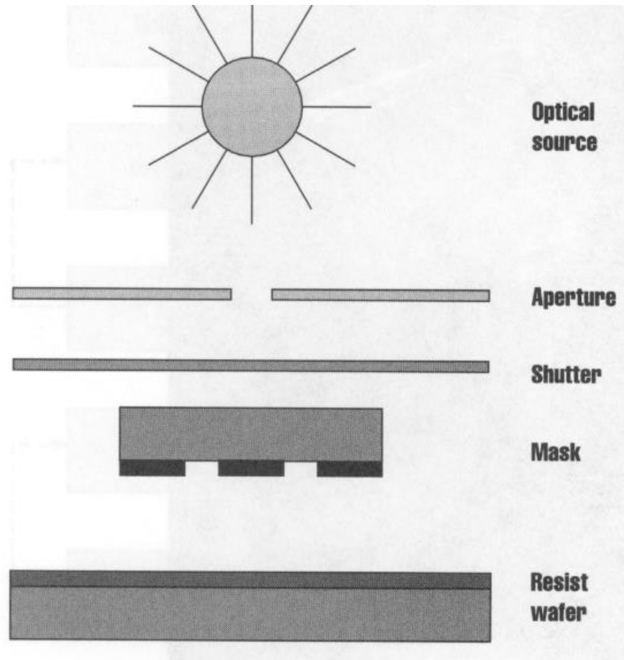
- Top-down” nanofabrication
- –Lithography (patterning)
- • Electron beam
- –2-10nm resolution
- •Optical (deep ultraviolet)
- –80nm resolution (at 193nm)
- • Soft: Stamping, molding, embossing
- –<10nm resolution
- • Scanning probe
- –<2nm resolution
- –Deposition
- • Spin-on, spray-on
- • Evaporation or sputtering
- • Chemical vapor deposition
- –Etching
- • Wet chemical
- • Reactive ion etching (dry)
- • Focused ion beam milling
- –Material modification
- •Diffusion, ion implantation

- •“Bottom-up” nanofabrication
- –Chemical synthesis
- •Nanotubes and nanowires
- •Quantum dots and nanoparticles
- • Polymers
- • Proteins
- •Nanofibers produced by proteins
- –Functional arrangement
- • Self assembly
- –Monolayers
- –Block copolymers
- –Functionalized nanoscale structures
- • Fluidic or field assisted assembly
- • Surface tension directed assembly
- • Templated growth
- –Step edges and defect or strain fields
- –Porous materials
- –Scanning probe manipulation
- •AFM, STM with atomic
- resolution

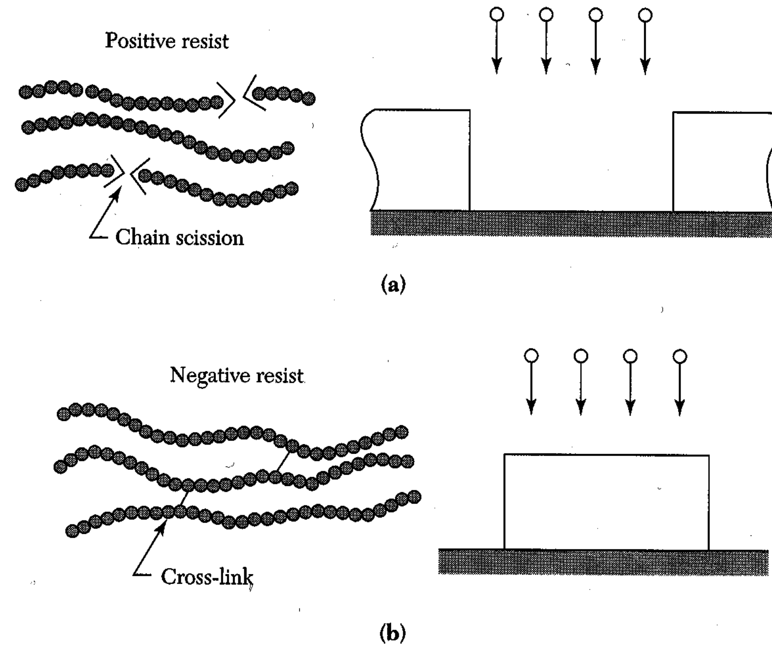
Lithography

- **Photolithography**
  - Contact
  - Proximity
  - Projection
- X-Ray Lithography
- **Charged Beam Lithography**
- Electron Beam Lithography
- Ion Beam Lithography
- **Scanning probe lithography**
- **Nanoprint**
- **Soft lithography**

Photolithography



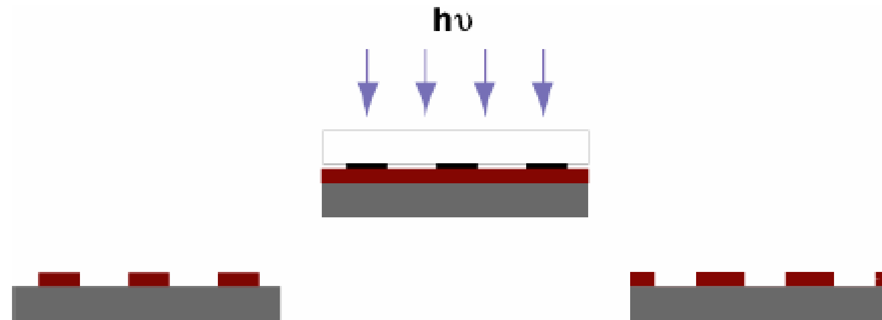
Scheme of photolithography



Photoresist (PR)

Definition: Use light to transfer a geometric pattern from a photo mask to a light-sensitive chemical photo resist on the substrate.

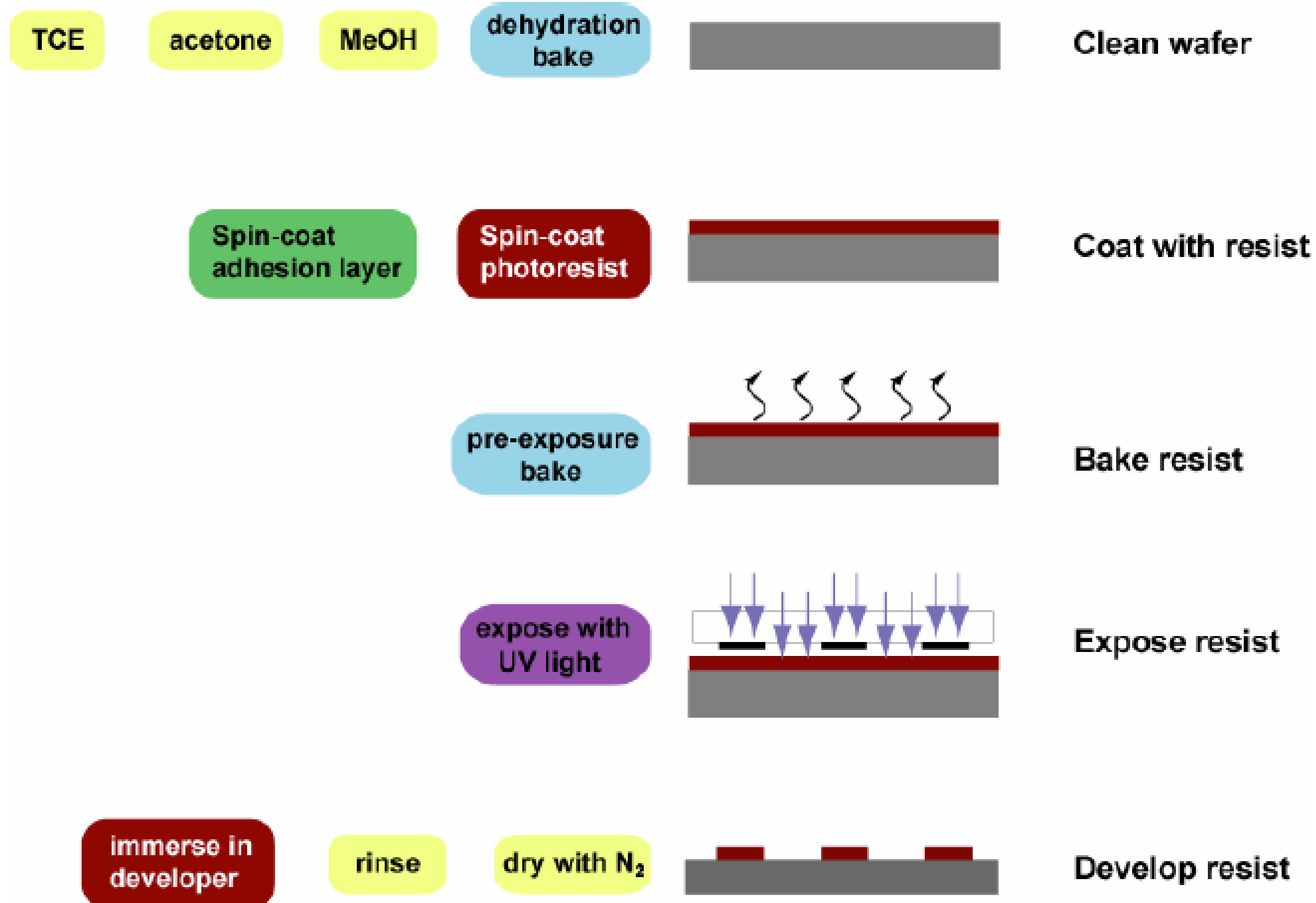
Postive resists and Negative resists



- **Positive resists**
  - Novolac/diazide photoresists
  - PMMA
- **Advantages**
  - High resolution (300 nm)
  - Aqueous based solvents
  - Ease of processing
  - No swelling upon development
- **Disadvantages**
  - Less sensitive

- **Negative resists**
  - Poly chloromethylstyrene
  - AZ 5206 (Clariant)
  - SU-8 (Microchem)
- **Advantages**
  - More sensitive
  - Better chemical resistance
  - Less expensive
- **Disadvantages**
  - Less resolution (1 μm)
  - Organic based solvents

Lithography Process Flow



Basic procedure of Lithography

Cleaning – substrate

Wet chemical treatment to eliminate the If organic or inorganic contaminations

Preparation –substrate

Heat substrate to drive off any moisture

HMDS: promote adhesion of the photoresist to the wafer

Photoresist application

The wafer is covered with photo resist by spin coating.

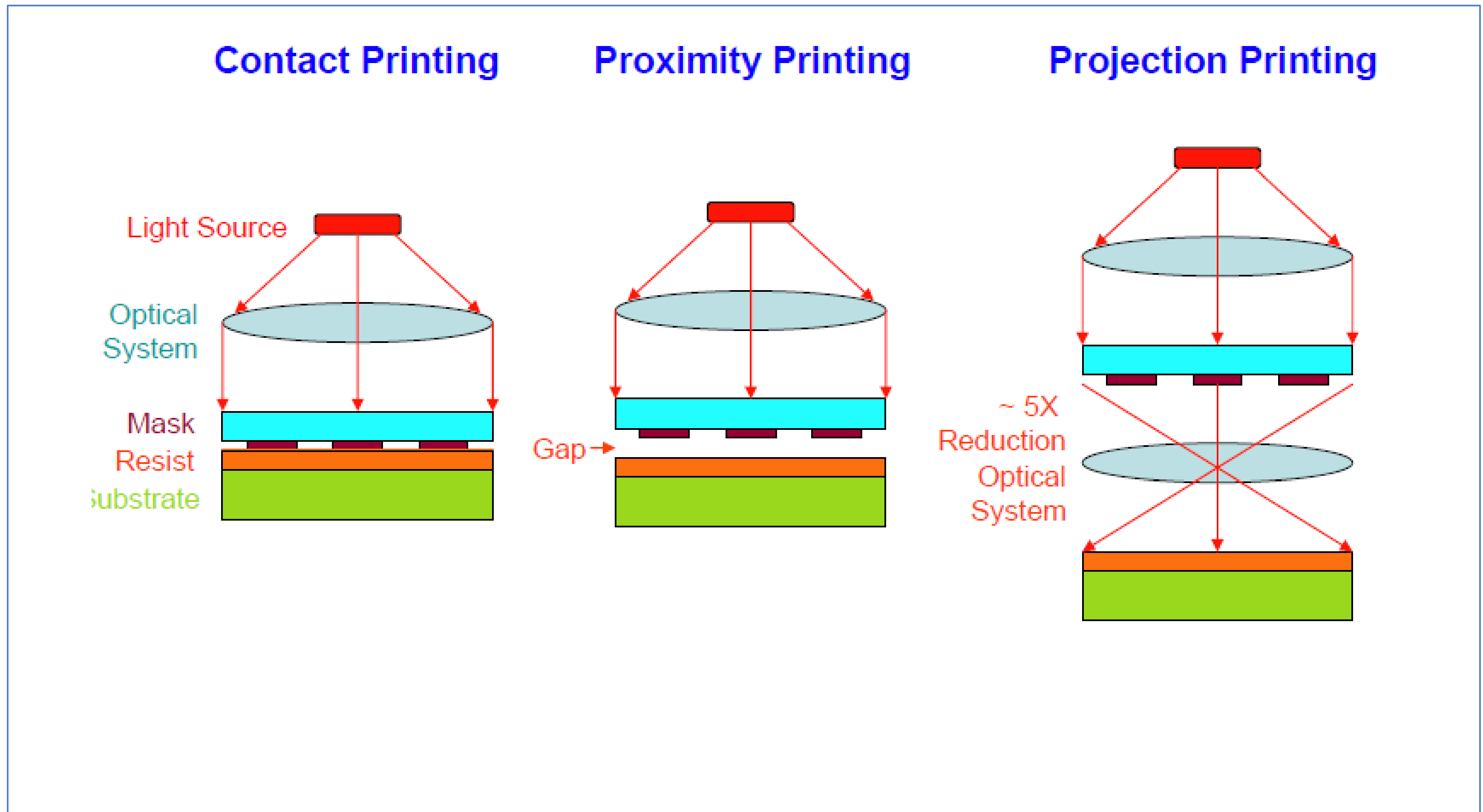
Resist Removal

- **Positive photoresist stripper**
- acetone
- tricholoroethylene (TCE)
- phenol-based strippers (indus-Ri-Chem J-100)
- Shipley SVC150 & SVC175
- **Negative photoresist stripper**
- methyl ethyl ketone (MEK), CH3COC2H5
- methyl isobutyl ketone (MIBK), CH3COC4H9
- Shipley NRX422

Substrate Cleaning

- **Particularly troublesome grease, oil or wax stains**
- 2-5 min ultrasonic bath in trichloroethylene (TCE)
- or trichloroethane (TCA), 65-75ºC (carcinogenic)
- **Standard grease removal**
- 2-5 min ultrasonic bath in acetone
- 2-5 min ultrasonic bath in methanol
- 2-5 min ultrasonic bath in D.I. H_2O
- Repeat the first three steps 3 times
- 30 sec rinse under free flowing D.I. H_2O
- **Oxide and other material removal**
- 5 min $H_2O:H_2O_2:NH_3OH$ 4:1:1 70-80ºC (cleaning Ge)
- 30 sec 50% HF (Glass or SiO2)
- D.I. H_2O 3 rinses
- 5 min $H_2O:H_2O_2:HCl$ 5:1:1 70-80ºC
- D.I. H_2O_3 rinses

Types of Photolithography



Photolithography Systems

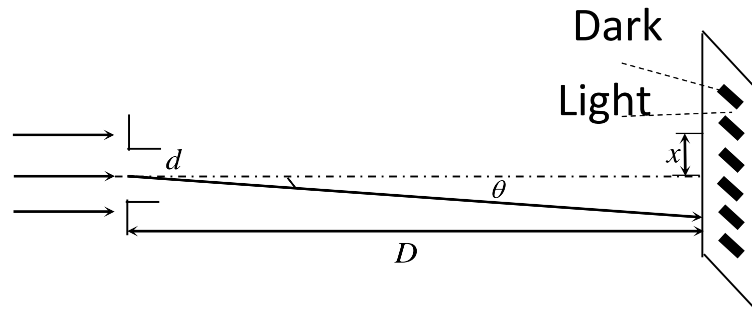
Contact: Resist is in contact with the mask: 1:1 magnification
Advantages: Inexpensive equipment ($~50,000-150,000), moderately high resolution (~0.5 um or better)
Disadvantages: Contact with the mask degrades the mask (pinholes and scratches are created on the metal-oxide layers of the mask, particles or dirt are directly imaged in the wafer, Wafer bowing or local loss of planarization results in non-uniform resolution due to mask-wafer gap variations., and no magnification.

Proximity: Resist is almost, but not in contact with the mask: 1:1 magnification
Advantages: Inexpensive equipment, low resolution (~1-2 um or slightly better)
Disadvantages: Diffraction effects limit accuracy of pattern transfer. Less repeatable than contact methods, no magnification.

Projection: Mask image is projected a distance from the mask and de-magnified to a smaller image: 1:4 -1:10 magnification.

Advantages: Can be very high resolution (~0.065 um or slightly better), No mask contact results in almost no mask wear (high production compatible), mask defects or particles on mask are reduced in size on the wafer.
Disadvantages: Extremely expensive and complicated equipment, diffraction effects limit accuracy of pattern transfer.

Optics - Basics and Diffraction **Slit Diffraction**



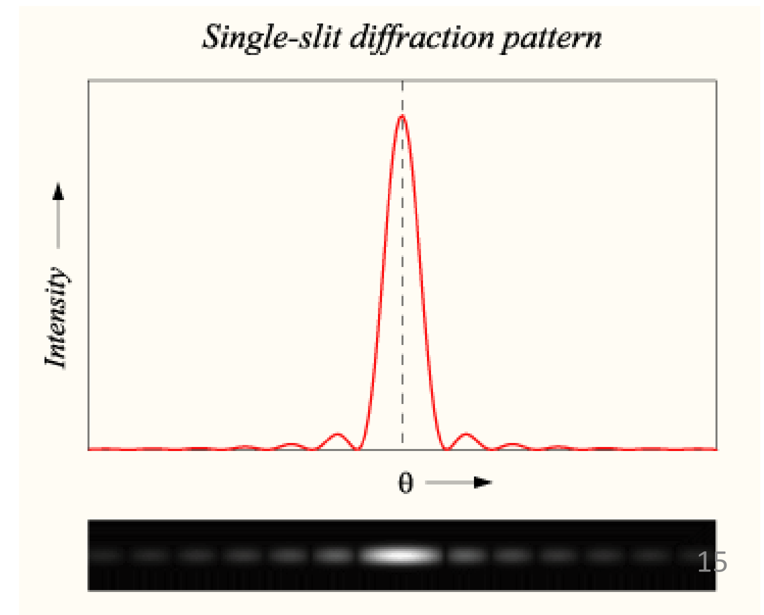
$$D >> d \qquad \sin\theta \approx \theta \approx \frac{x}{D}$$

Center dark fringes condition：

$$d\sin\theta = k\lambda \quad (k=\pm 1, \pm 2, \pm 3, \cdots)$$

Center of Dark Fringes

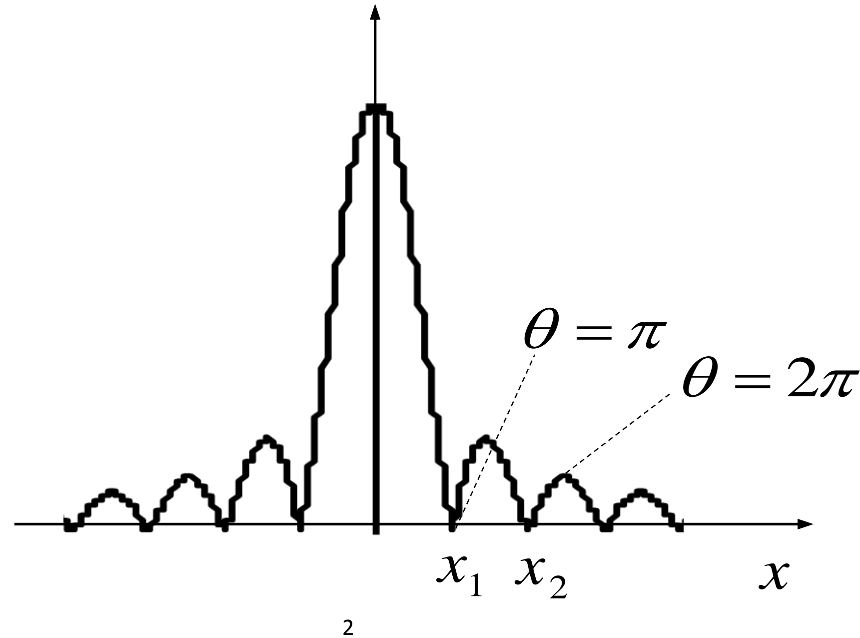
$$x = K\frac{D\lambda}{d}$$



Optics - Basics and Diffraction

Intensity Distribution of Light

I: intensity



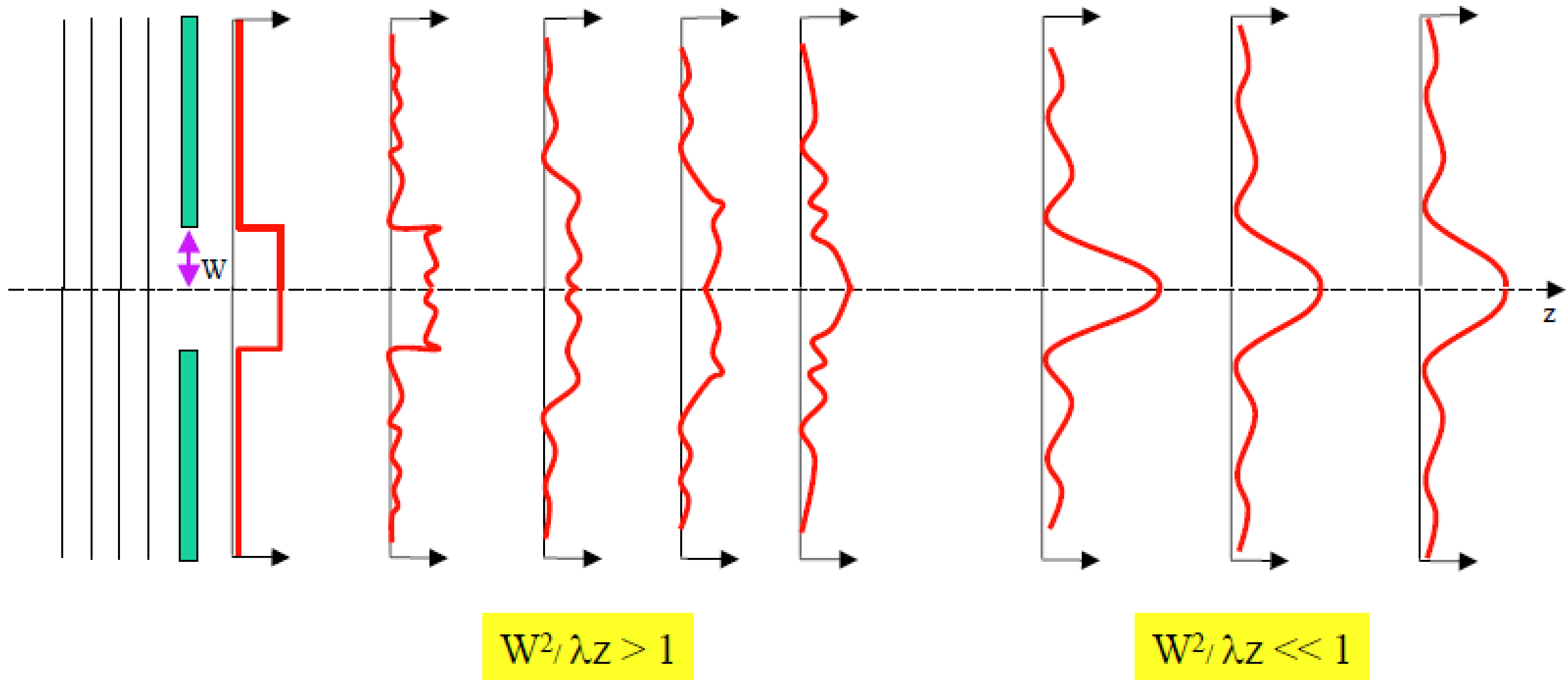
$$I = I_0 \frac{\sin^2 \beta}{\beta^2} \quad \left(\beta = \frac{\pi d \sin \theta}{\lambda} \right)$$

Optics - Basics and Diffraction

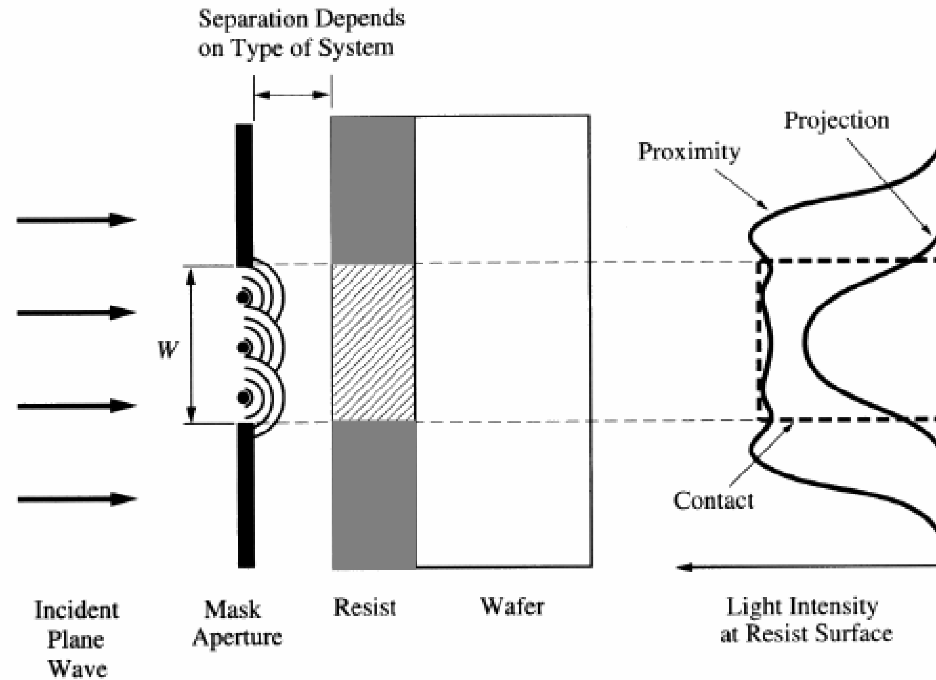
Fresnel & Fraunhofer Diffraction

Near Field (Frensel) Diffraction
Λ close to aperture size W

Far Field (Fraunhofer) Diffraction
Source and Image at infinity



Comparison of Areal Images of the Three types of Photolithography Systems



Type of spreading depends on separation mask - wafer:

• Hard contact	(Almost) no diffraction
• Proximity	Near field or Fresnel diffraction
• Projection	Far field or Fraunhofer diffraction

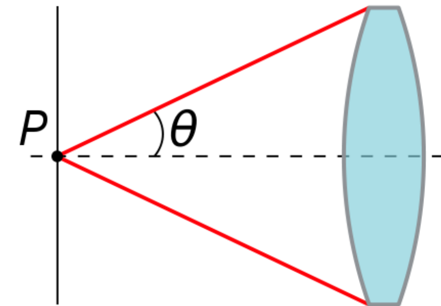
Resolution in Projection Systems

Feature size: $$CD = \kappa_1 \frac{\lambda}{NA}$$

CD is the minimum feature size (**critical dimension**, *target design rule*)
λ is the wavelength of light
NA is the numerical aperture

NA=nsinθ n: index of refraction

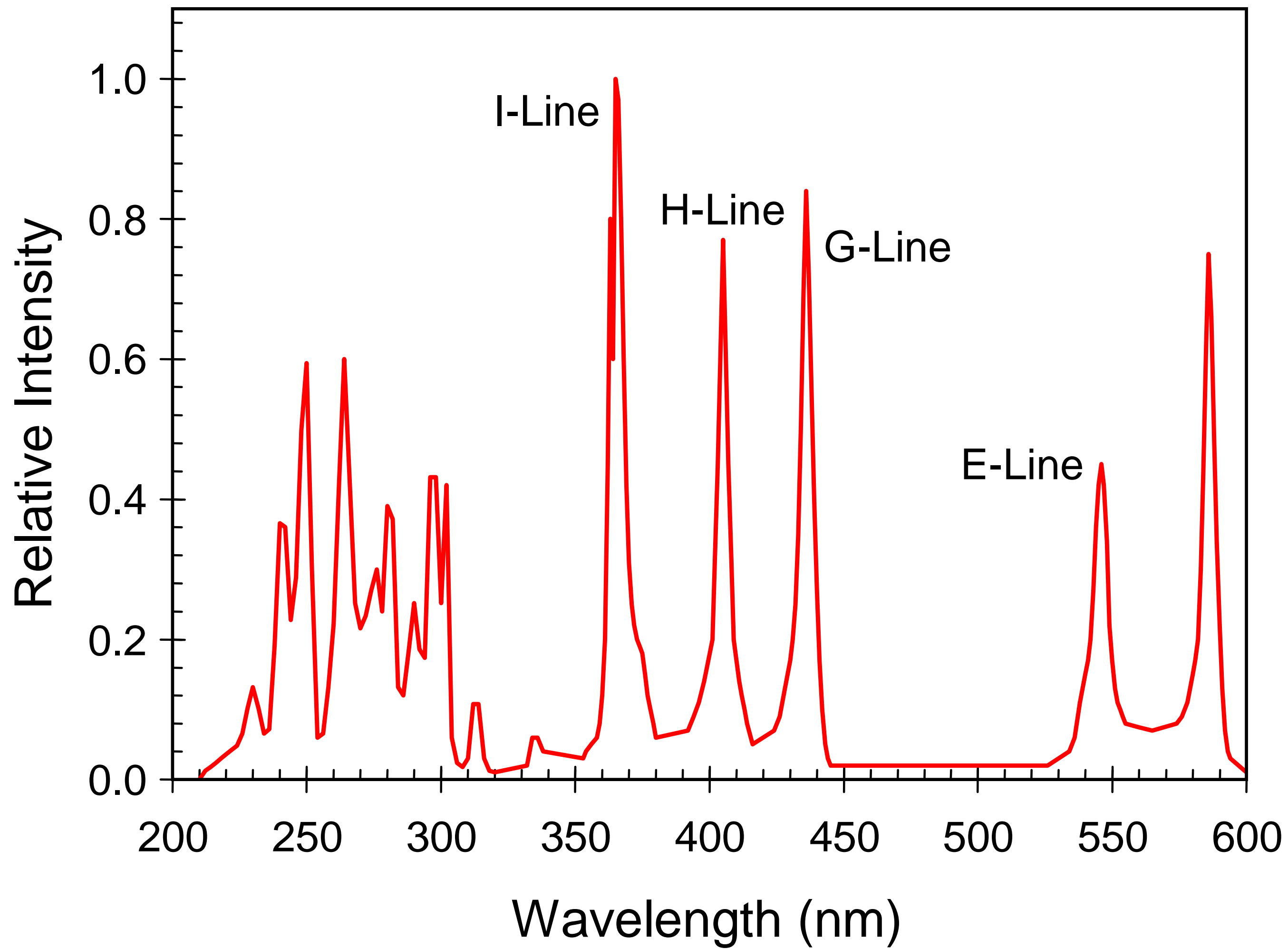
κ1 constant, depend on the system



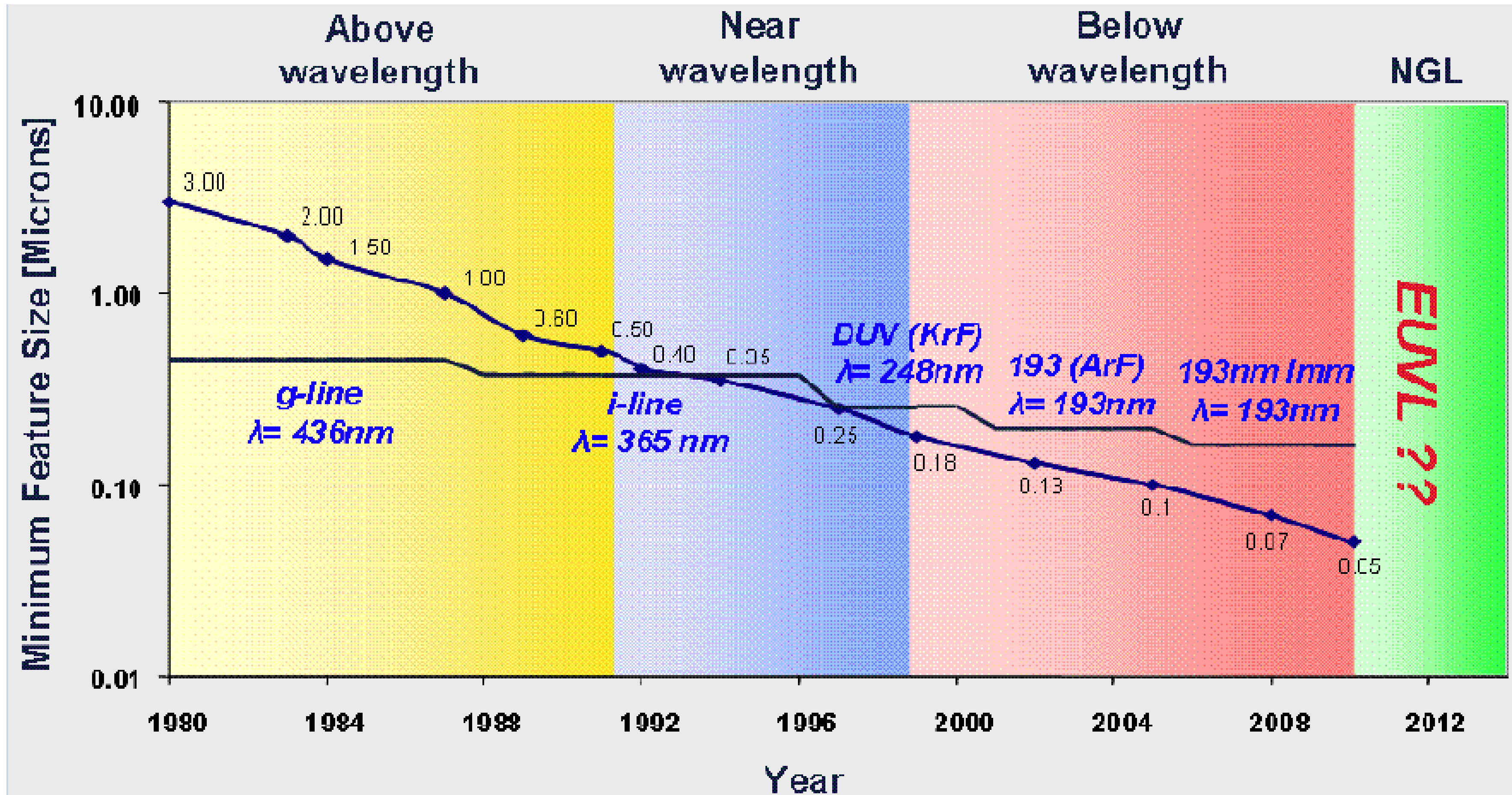
How to Improve Resolution in projection systems ?

Decreasing the wavelength
Lower κ1
Increasing the NA

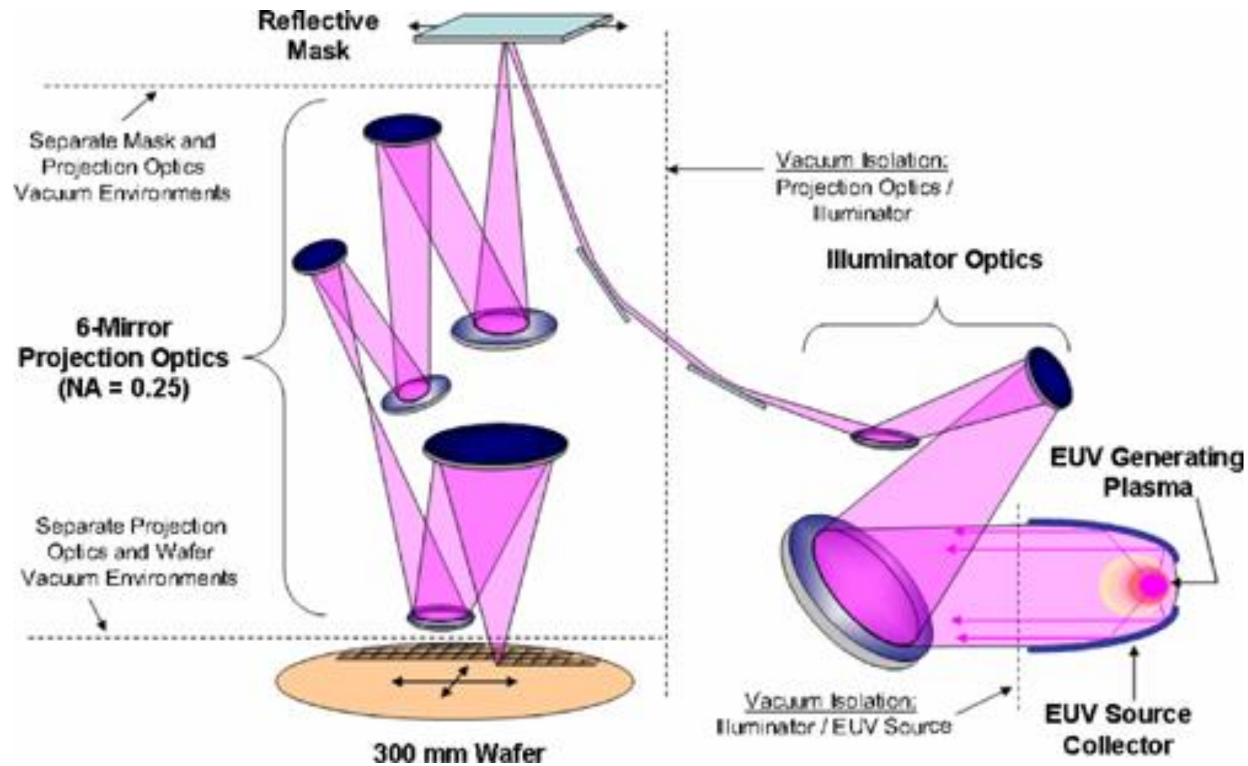
Spectral output of a typical high-pressure mercury arc lamp



Nominal Feature Size Trend & Lithography



Extreme Ultraviolet Lithography



Next-generation lithography technology using the 13.5 nm EUV wavelength

EUVL Source: 1) Laser-Produced Plasma (LPP) method. 2) Discharge-Produced Plasma (DPP)

Advantage:
Short wavelength permits high resolution even with small NA

Disadvantage:
Throughput
Extreme system complexity
High cost of the system, 50M and 20M for DUV

X-Ray Lithography

X-ray lithography originated as a candidate for next-generation lithography

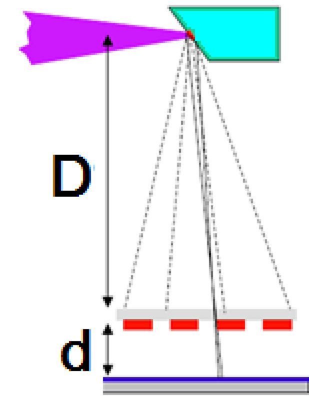
Using X-rays to transfer a geometric pattern from a mask to a light-sensitive chemical photo resist on the substrate, 1:1 pattern transfer .

λ= 1 nm , $R = \kappa\sqrt{\lambda d}$

d= size of gap between mask and substrate(tends to be 5 –40 µm in production)

Resolution = 0.07 –0.2 µm for λ= 1 nm

30 nm resolution is achievable using contact printin



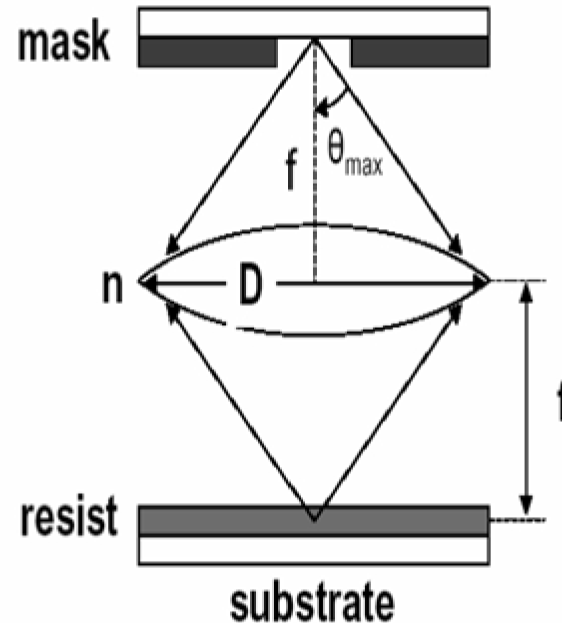
Advantage :

Having short wavelengths (below 1 nm),
X-rays overcome the diffraction limits of optical lithography

Disadvantages:

High cost, $100M .
Hard to get resolution below 50nm. X-ray irradiation will generate photoelectrons and Auger electrons inside the resist, react with polymer causing exposure of the resist.

Photolithography-NA



$$NA = n \cdot \sin(\theta_{max})$$

$$\frac{NA}{n} = \frac{\frac{D}{2}}{\sqrt{\left(\frac{D}{2}\right)^2 + f^2}}$$

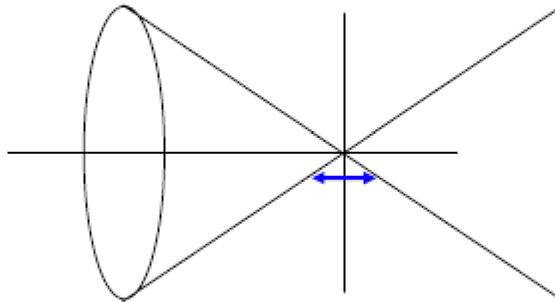
n = index of refraction
M = magnification
f = focal distance
D = lens diameter

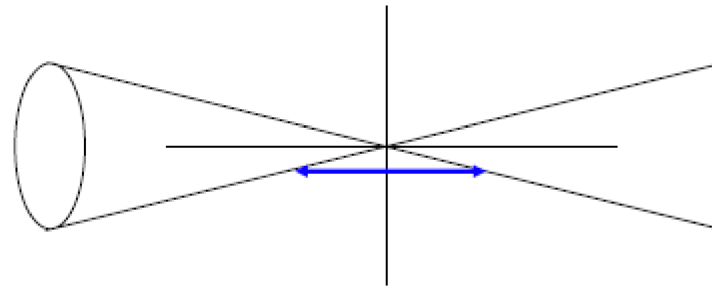
Numerical aperture: NA=nsinθ n: index of refraction
NA is equivalent to diameter of lens
lens with large diameter can collect more light to print on the substrate
(to achieve a tighter focused beam and a smaller spot size)

Photolithography-NA

A lens with a larger NA will be able to visualize finer details
Lenses with larger NA also collect more light and will generally provide a brighter image.

$$D_F = k_2 \cdot \frac{\lambda}{NA^2}$$





High NA – low Df degradation the image quality

I line lens with 0.35NA, 14kg . 0.65NA ,500kg.

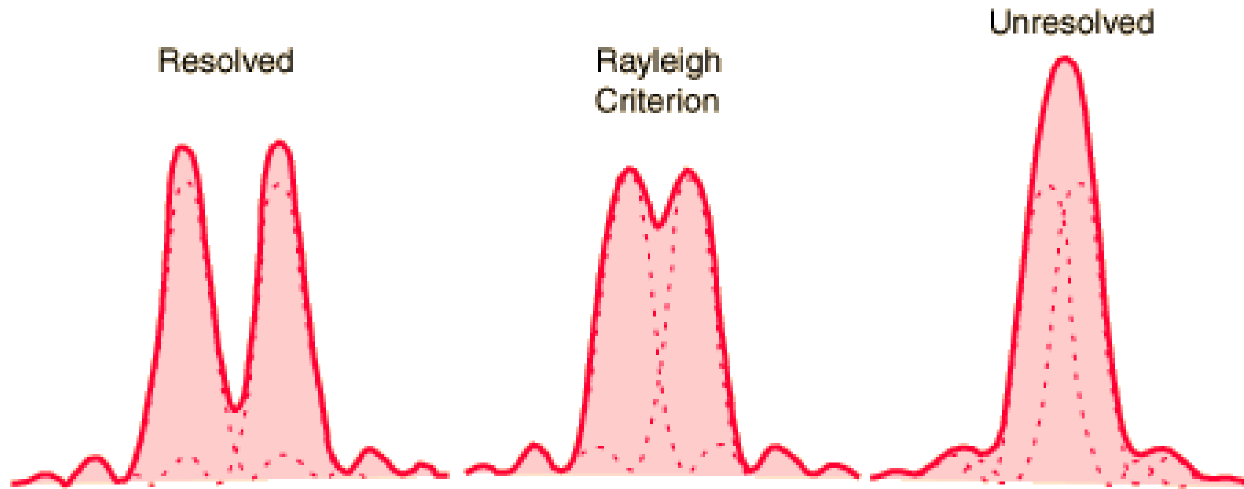
Depth of Focus

How to eliminate the DOF?

Using a telephoto lens at its widest aperture.

κ1 factor

Rayleigh criterion: The minimum resolvable detail of two images through an optical system is diffraction-limited.



Circular aperture: $$\sin(\theta) = 1.22\frac{\lambda f}{d}$$

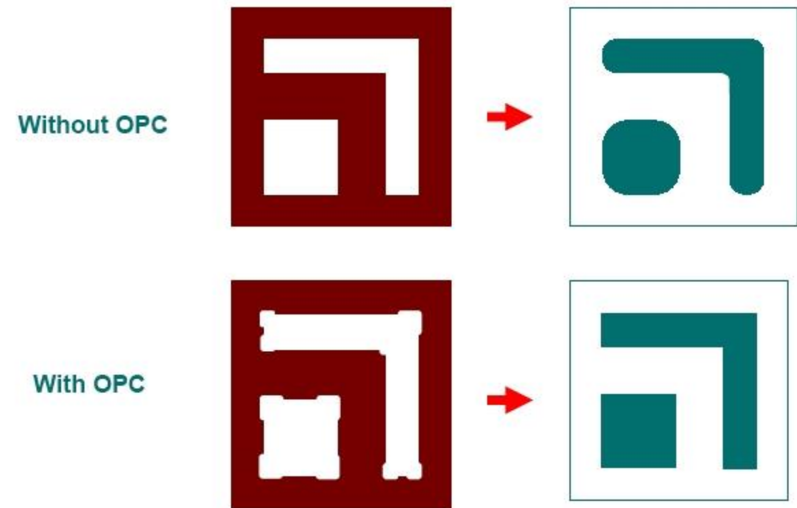
Minimum separation of the two image intensity :

$$R = 0.61\frac{\lambda}{\sin(\theta)}$$

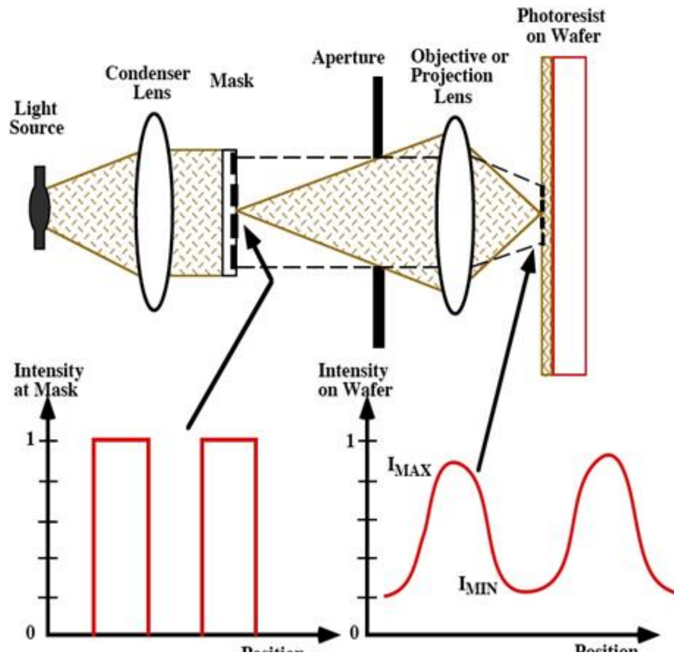
In the latter expression k_1 is an experimental parameter and depends on resist properties and the lithography system (0.6-0.8)

Optical Proximity Correction(OPC)

- Optical Proximity Correction (OPC) can be used to compensate somewhat for diffraction effects.
- Sharp features are lost because higher spatial frequencies are lost due to diffraction. These effects can be calculated and can be compensated for. This improves the resolution by decreasing k_1.



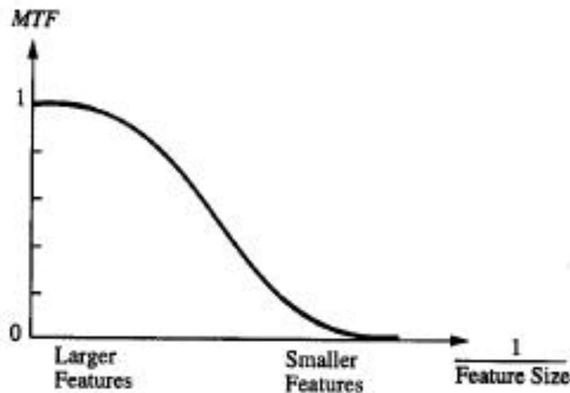
Photolithography- MTF



MTF is the ratio between image intensity modulation over the object intensity modulation

This parameter qualifies the capability of an optical system

$$MTF = \frac{M_{image}}{M_{mask}} \qquad MTF = \left(\frac{I_{max} - I_{min}}{I_{max} + I_{min}} \right)$$



Generally, MTF needs to be > 0.5 for the resist to resolve features

Function describes contrast as a function of size of features on the mask

Nanofabrication by E-beam Lithography

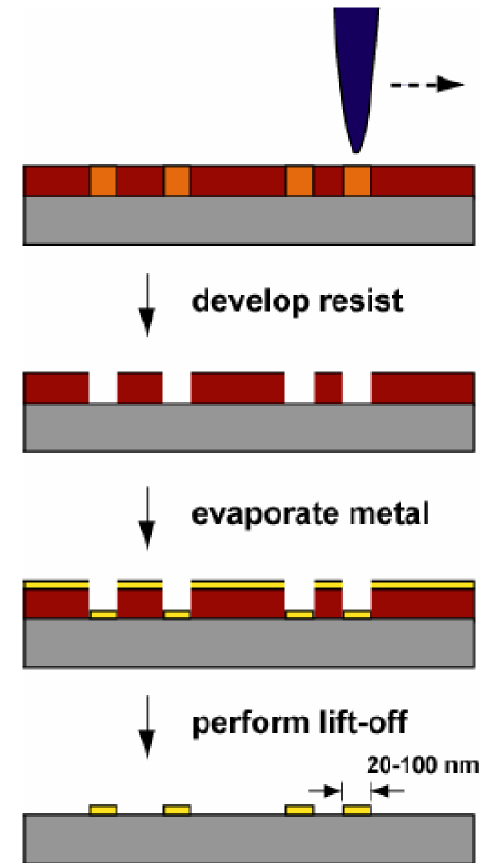
Scanning a e-beam on the photoresit to produce patterned shape.
Diffraction is not a limitation on resolution (λ < 1 Å for 10-50 keV electrons.)
Resolution depends on electron scattering and beam optics the size of the beam, can reach ~ 5 nm.

Advantage :

(1)Generation of micron and submicron resist geometries
(2) Highly automated and precisely controlled operation
(3) Greater depth of focus
(4) Direct patterning without a mask

Disadvantge:

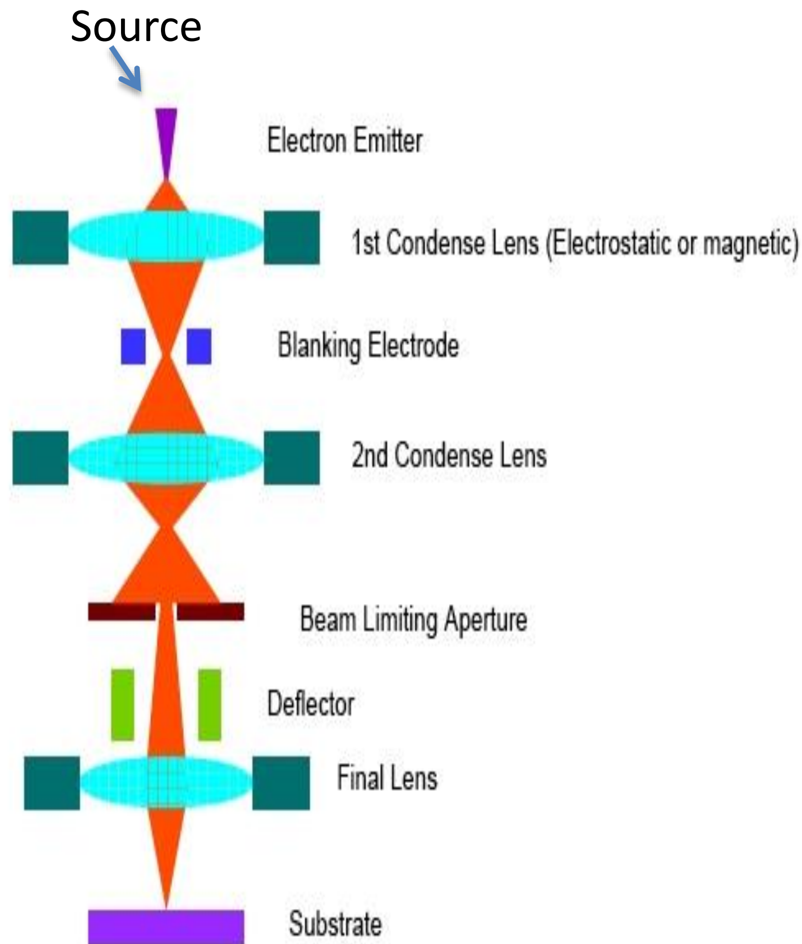
A long exposure time
low-volume production of semiconductor components,
low throughput (approximately 5 wafers / hour at less than 0.1 μ resolution).



Standard Lithography Using

- Maskmaking – Chrome on quartz for high resolution optical lithography
- Direct Writing for fine structure IC design
- Research –
  - Fine structure linewidths
  - Contacts for Nanowires/rods
  - Small feature array patterns

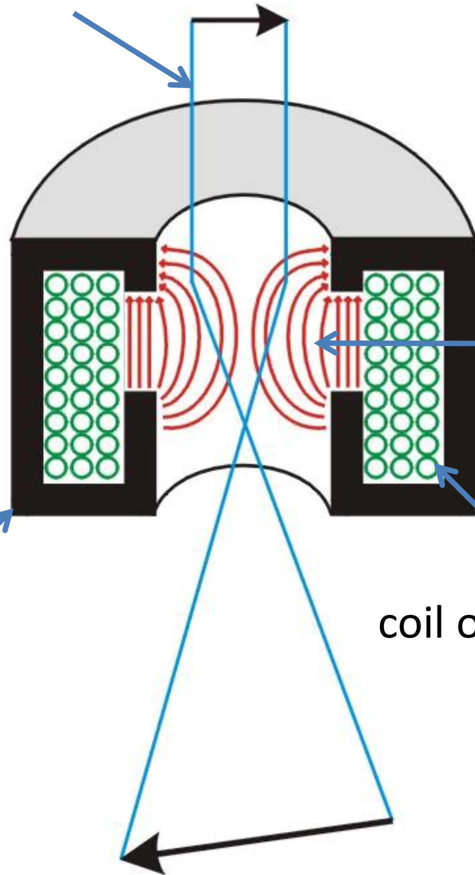
System Architecture



Source
Electrostatic lens
Magnetic lens
Blanker
Deflector
Vacuum system
Pattern Generator

Principle of an Electromagnetic Lens

Electron beam

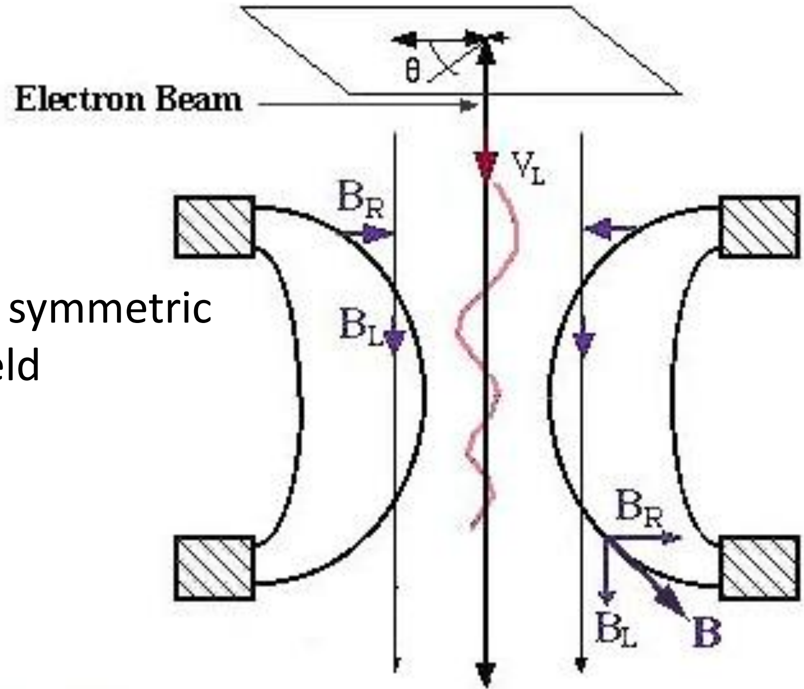


Rotationally symmetric magnetic field

iron pole

coil of copper wires

Schematic of Magnetic lens



Lorentz force F $\mathbf{F} = -e\,(E + \mathbf{v} \times \mathbf{B})$

E: strength of electric field
B: strength of magnetic field
e/v: charge/velocity of electrons

Movement of the electron in the magnetic lens

Exposure source: Electron Beam

$$\lambda = \frac{h}{\left\{2mV_c e(1 + eV_c / 2mc^2)\right\}^{1/2}}$$

λ : wavelength of the electron beam
e : electric charge of the electron
m : mass of the electron
Vc : acceleration voltage
h : Planck's constant
C: speed of light

Acceleration voltage Vc=120KV, λ=0.00336 nm

Electron Sources

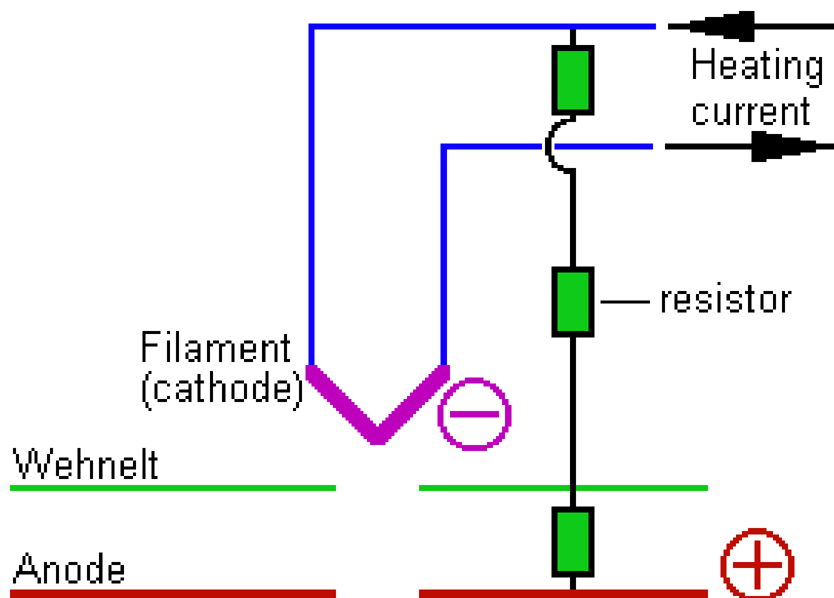
Source

- Tungsten, LaB_6 (Thermionic)
- Thermal Field Emitter
- Cold Field Emitter (Not normally used for Lithography)

Source Type	Brightness [amp/cm2/str]	Source Size	Energy Spread	Vacuum Required (Torr)
Tungeston	10^5	25um	2-3eV	10^{-6}
LaB_6	10^6	10um	2-3eV	10^{-8}
TFE	10^8	25nm	0.9eV	10^{-9}
Cold FE	10^9	5nm	0.22eV	10^{-10}

Electron Sources

- Thermionic emitters:
  - Electrons "boiled" off the surface by giving them thermal energy to overcome the barrier (work function)
  - Current given by Richardson-Dushman equatio



Schematic of Thermionic emission

$$J = A_G T^2 e^{\frac{-W}{KT}}$$

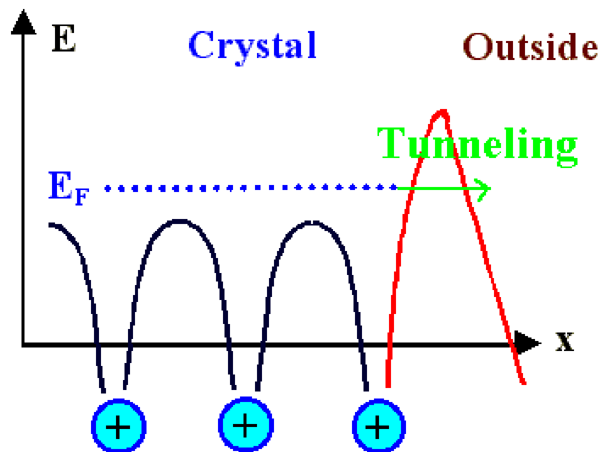
J : current density
A: constant
T: temperature
W: workfunction

Field emission

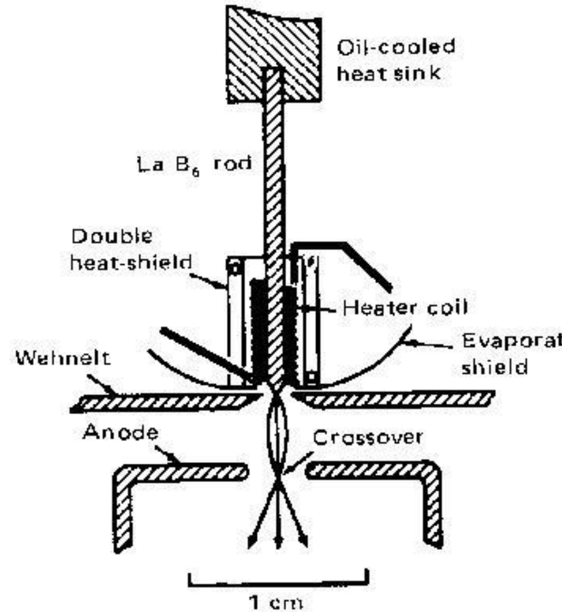
Field Emitters:

Takes advantage of the quantum mechanical properties of electrons. Electrons tunnel out when the surface barrier becomes very narrow

Current given by Fowler-Nordheim equation



Tunneling of electrons



Schematic of Thermal field emission

$$J = k_1 E^2 \exp(-\frac{k_2}{E})$$

J : emission current density

K1 , k2: constant related

To work function

E: field strength

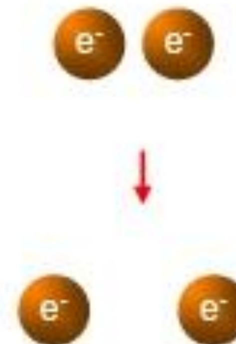
E-beam Movement

Coulomb Interaction

Boersch Effect

- Electrons repel each other in the beam direction
- Causes energy spread among electrons
- Result in chromatic aberration

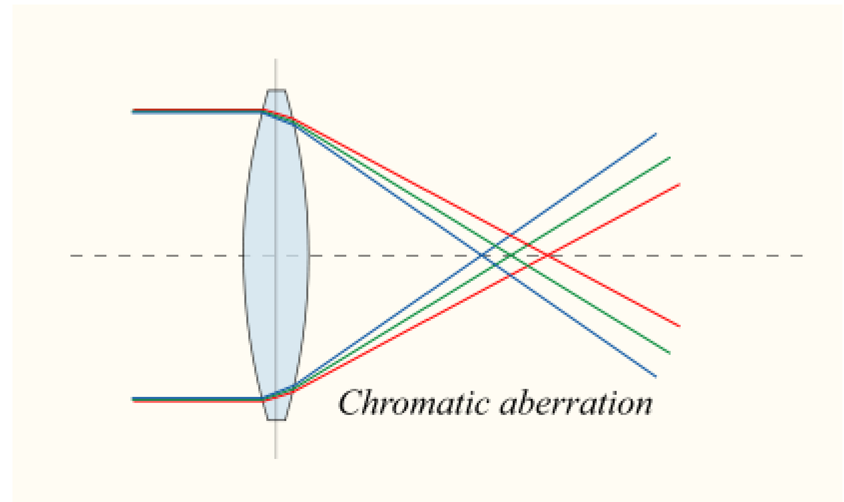
Loeffler Effect



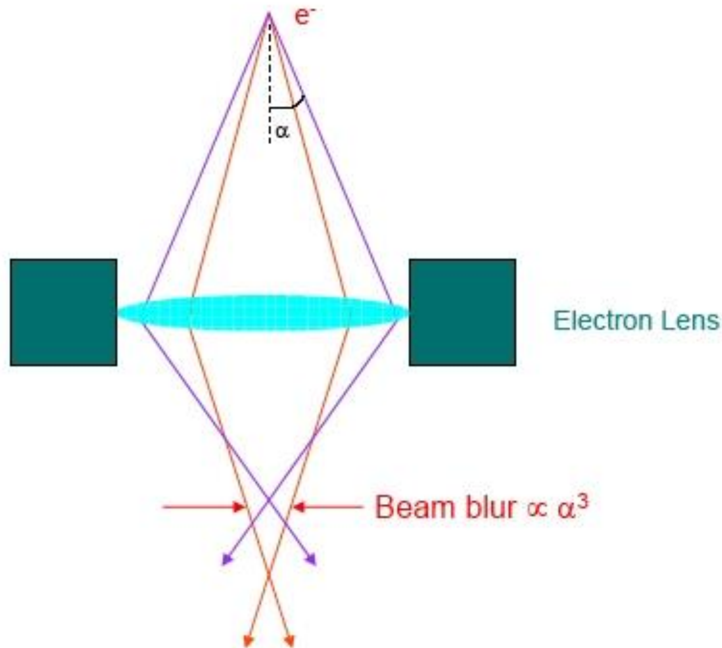
- Electrons repel/collide each other in the radial direction
- Causes trajectory change and energy spread among electrons
- Result in chromatic as well as spherical aberration

Chromatic Aberration

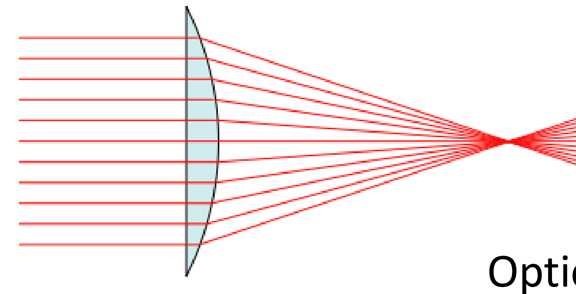
In optics, chromatic aberration is a type of distortion in which there is a failure of a lens to focus all colors to the same convergence point.



Spherical Aberration



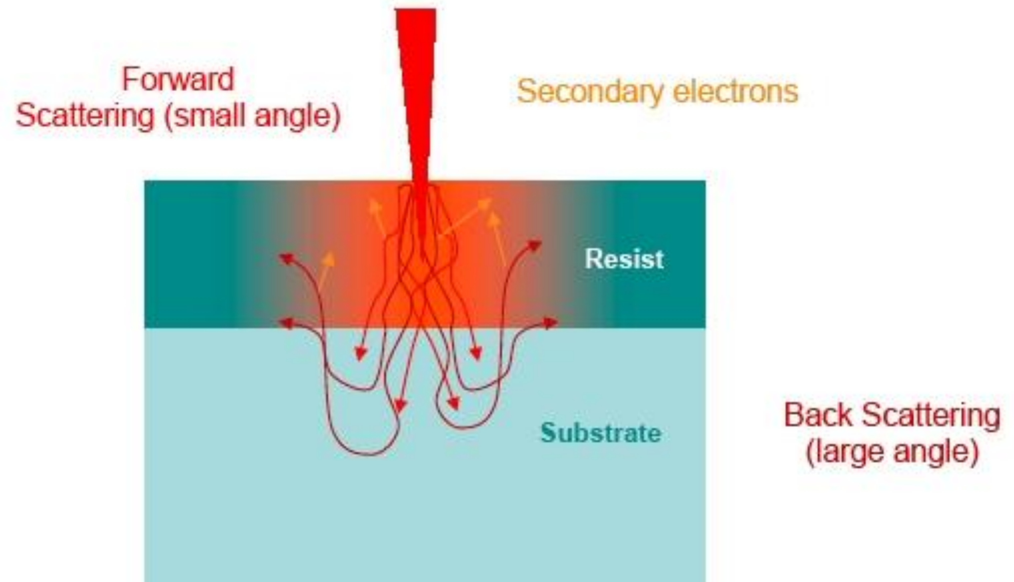
Spherical aberration. A perfect lens (top) focuses all incoming rays to a point on the optic axis.
A real lens with spherical surfaces (bottom) suffers from spherical aberration: it focuses rays more tightly if they enter it far from the optic axis than if they enter closer to the axis. It therefore does not produce a perfect focal point. (Drawing is exaggerated.)



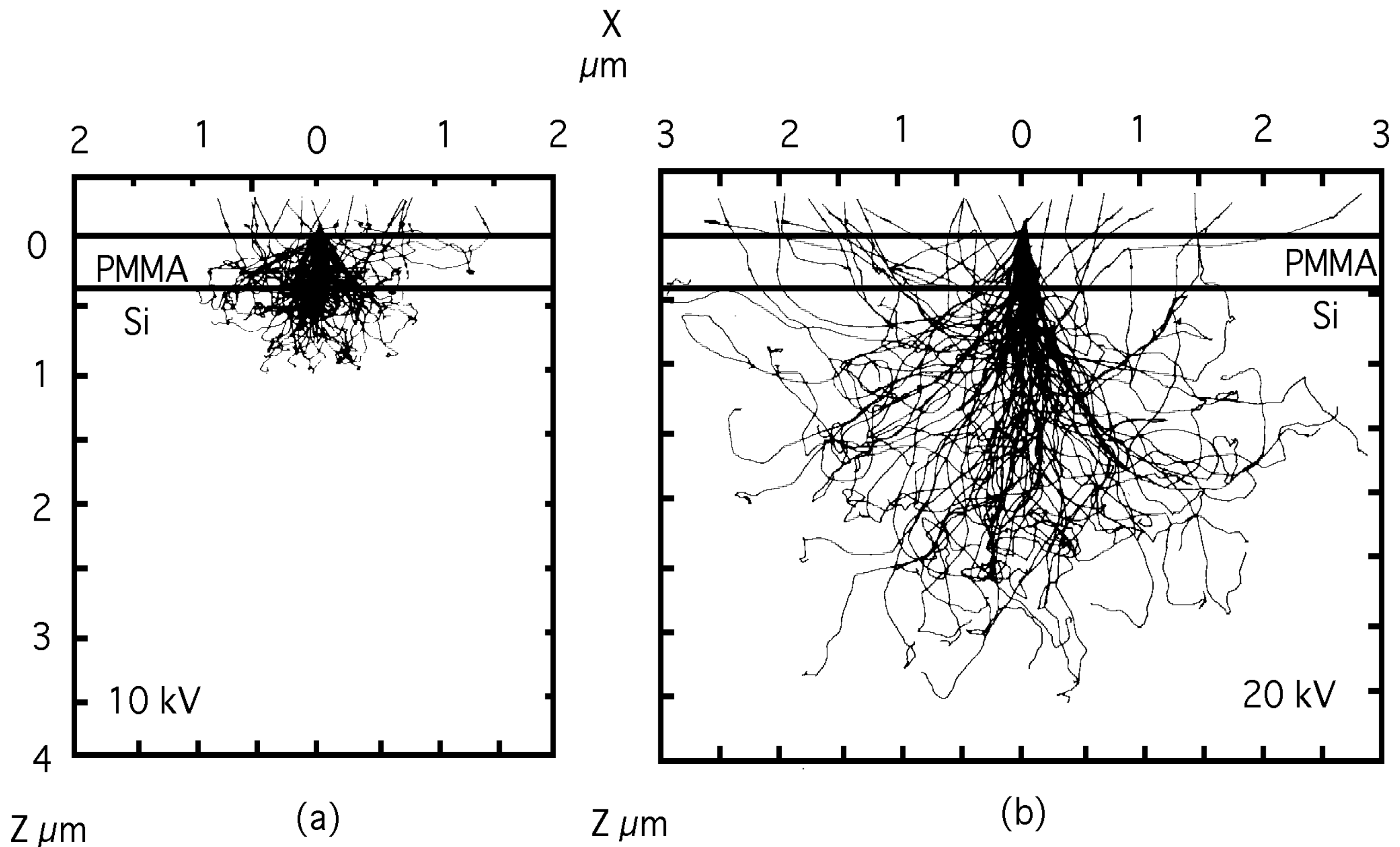
Optical lens

Electron Scattering

- Electron scattering in resist and substrate
- The scattered electrons also expose the resist
- Interaction of e-and substrate + resist leads to beam spreading
  - Elastic and in-elastic scattering in the resist
  - Back-scattering from substrate and generation of secondary e-
  - Reduce resolution



Electron Scattering Limits Resolution

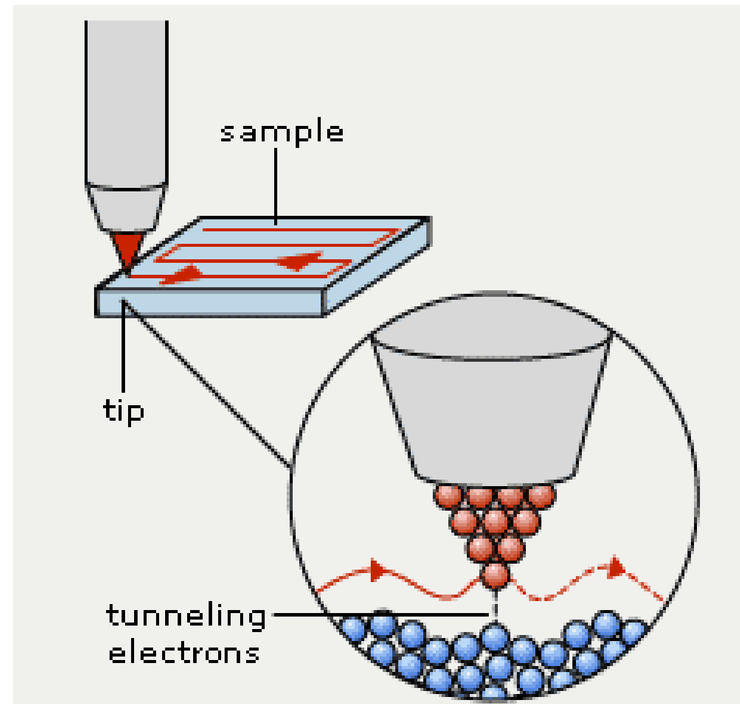


Higher energy electrons have larger back-scattering range

Nanofabrication by Scanning Probes

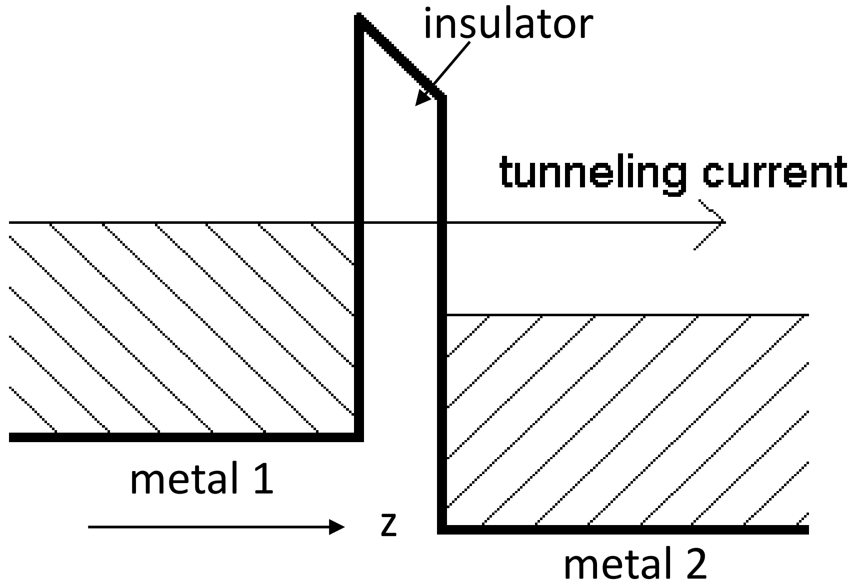
The Scanning Tunneling Microscope (STM)

The STM is an electron microscope that
uses a single atom tip to attain atomic resolution.



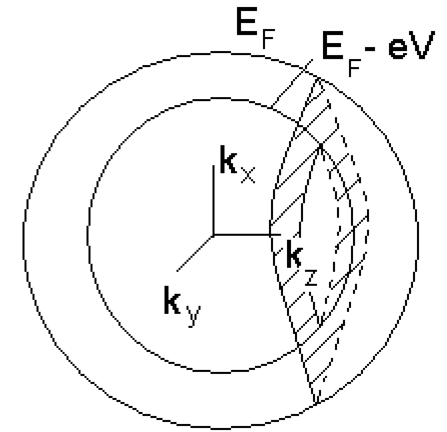
STM: limited to conducting materials

Tunneling Current



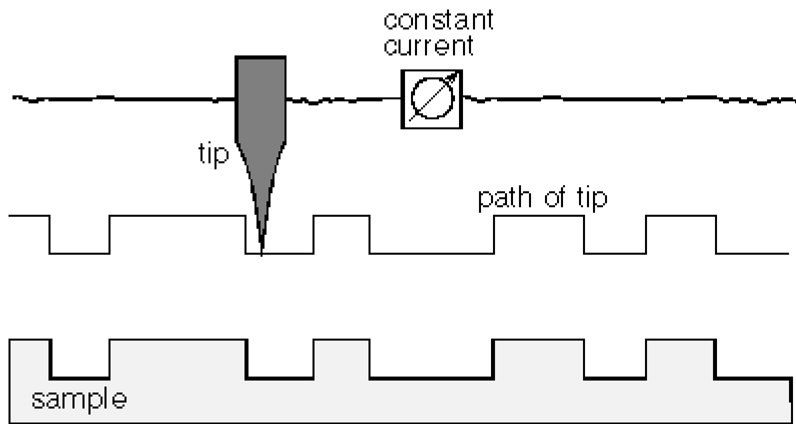
- Applied voltage bias, V
- Tunneling electron gains energy eV
- Number of electrons that can tunnel depends on occupation on each side

$$J \propto \int_{E_z} \int_{\substack{k-space \\ \text{constant} E_z}} P(E_z)\Big(f(E) - f(E+eV)\Big) dE_z$$



Modes of Operation

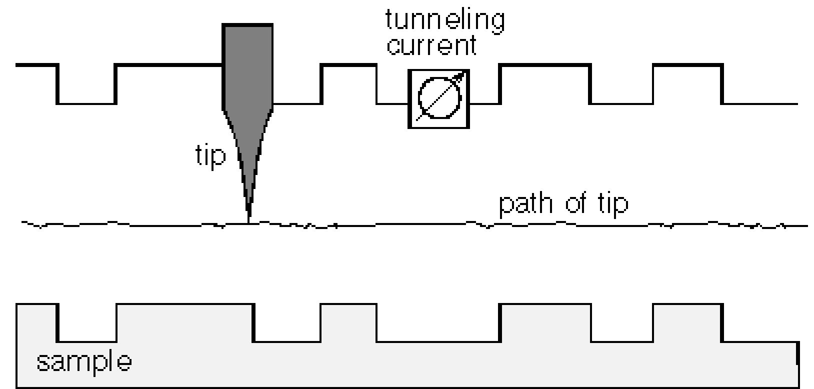
Constant-Current Mode



Tip height is ~constant: an x-y scan reveals a topographic ‘image’ of the surface.

- better vertical resolution
- slower scanning – may yield overall drift in x-y scan
- can be used for surfaces that aren’t atomically flat

Constant-Height Mode



Tip height is kept constant and tunneling current is monitored.

- very fast scans, reduces image distortion
- lower vertical resolution
- allows study of dynamic processes

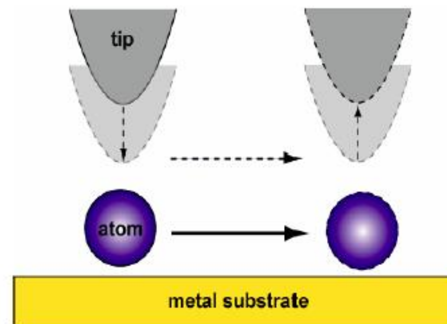
STM Lithography

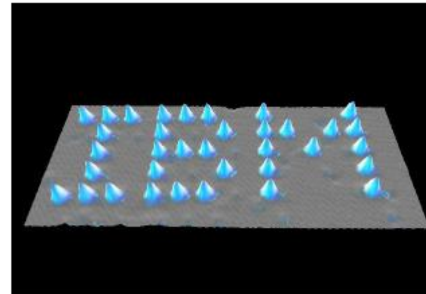
•Advantage of STM Lithography

–Information storage devices

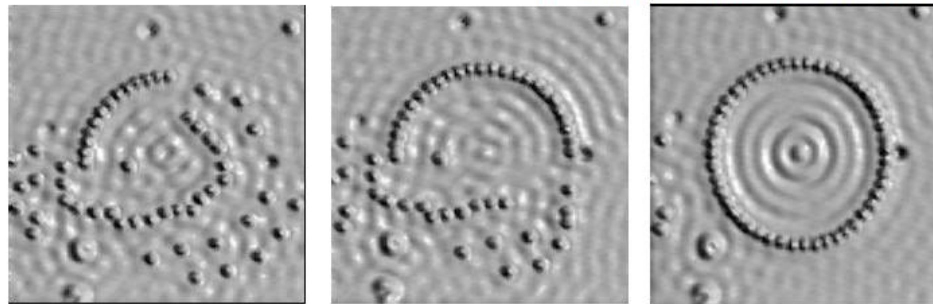
–Atomic scale patterning technique

–Manipulation of both single atoms or molecules





M. Crommie (UC Berkeley), *Science* 262, 218 (1993)

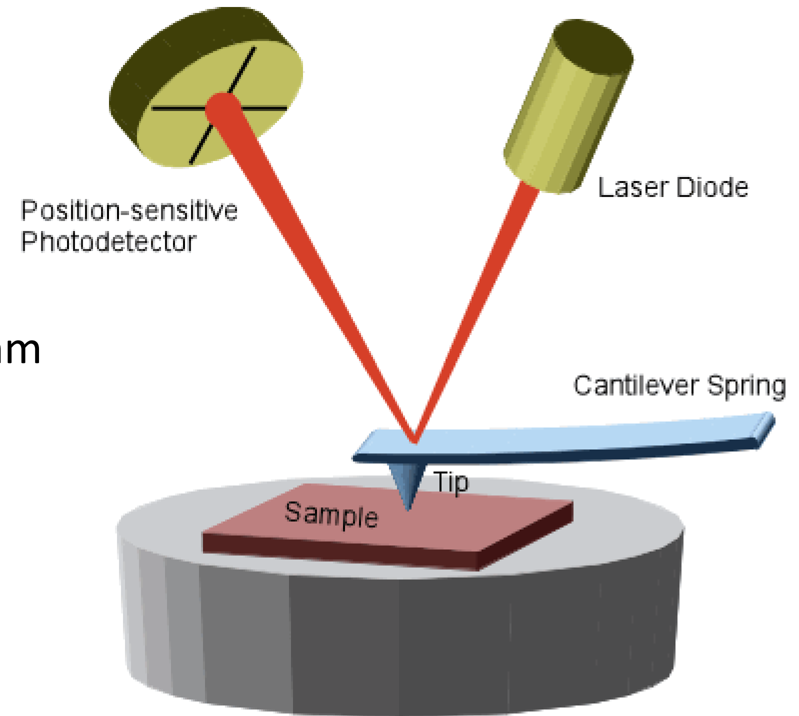


Iron atoms on the surface of Cu(111) IBM

Atomic Force Microscope Principle

AFM basic components:
Tip (<~10 nm diameter) on a cantilever
Detector (generally position)
Raster-scan (to drag tip)
Force/height control
Image processing software

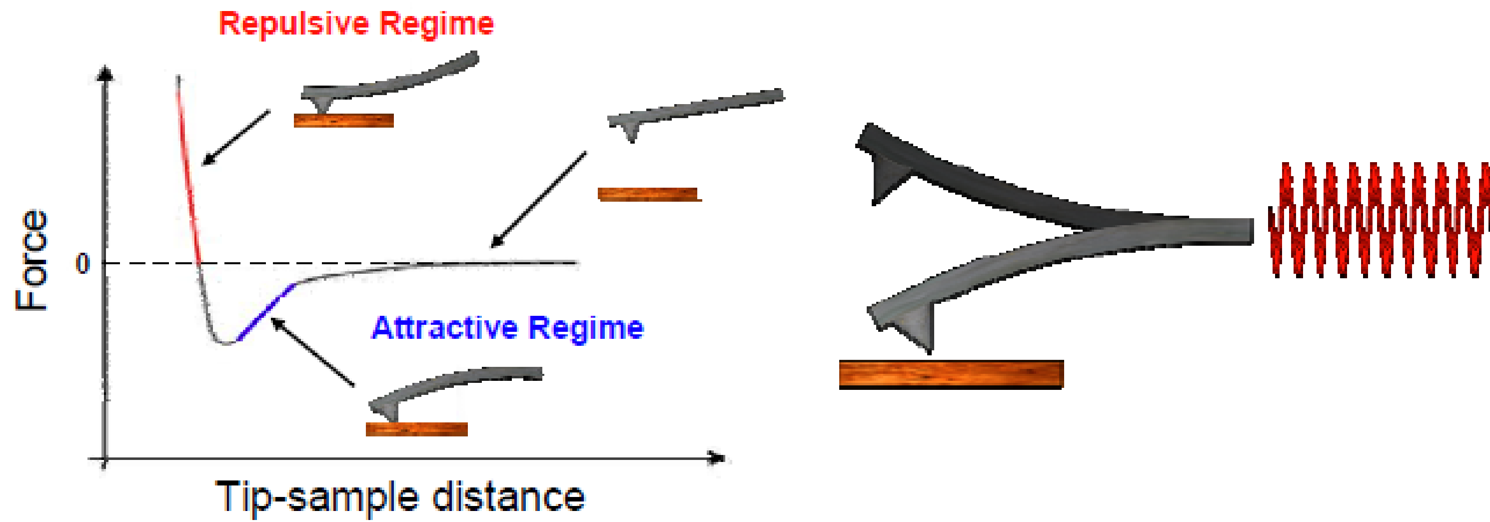
Lateral resolution 0.1 nm Vertical resolution 0.02 nm



Feedback ON: constant force mode
Feedback OFF: constant height mode

AFM: worse resolution but all types of surfaces compare to STM

Atomic Force Microscope



- Dynamic tip-sample interaction
  - Attractive Regime
    - van der Waals Forces, Magnetic Forces, Electrical Forces
  - Repulsive Regime
    - Elasticity

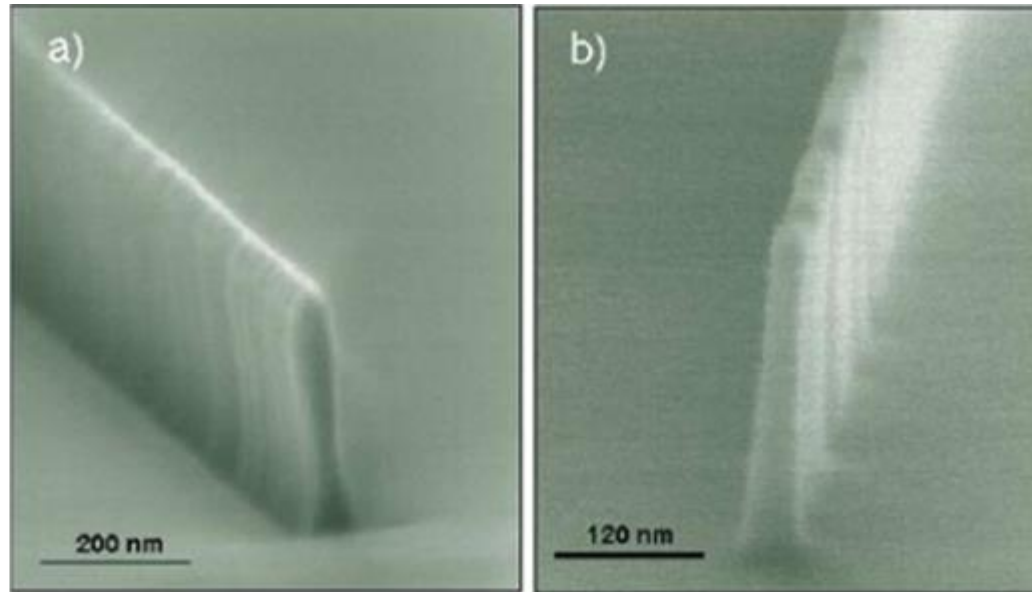
$$Force \sim Hrd^{-2}$$

H – material dependent constant
r– radius of the tip
d – tip to surface distance

Exposure of Resist by STM

STM tip closing to the substrate will induce a tunneling current, and this current can be Used to expose resist.

Feature sizes of patterns written determined by the exposure dose
Low energy expose is the key of STM lithography.
Can write 25nm size in 50-100nm thick resist.



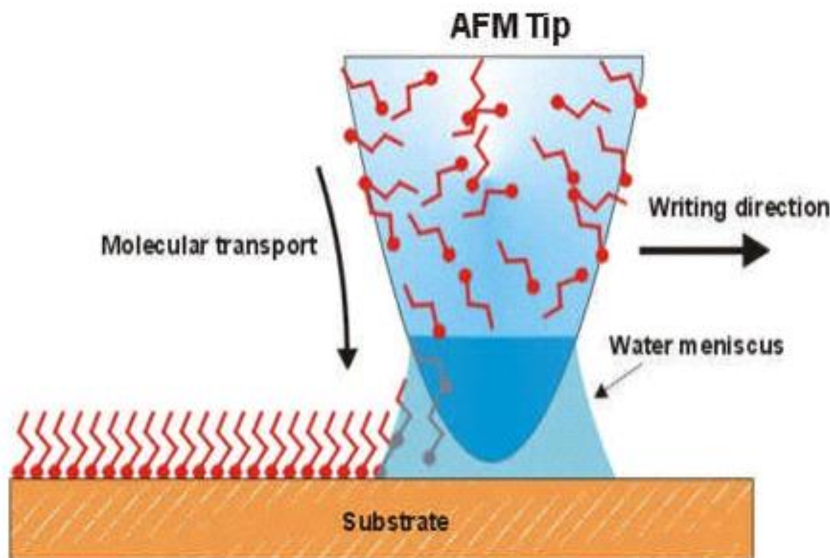
50 nm structure wrote by STML followed by RIE etching

Dip-pen Lithography

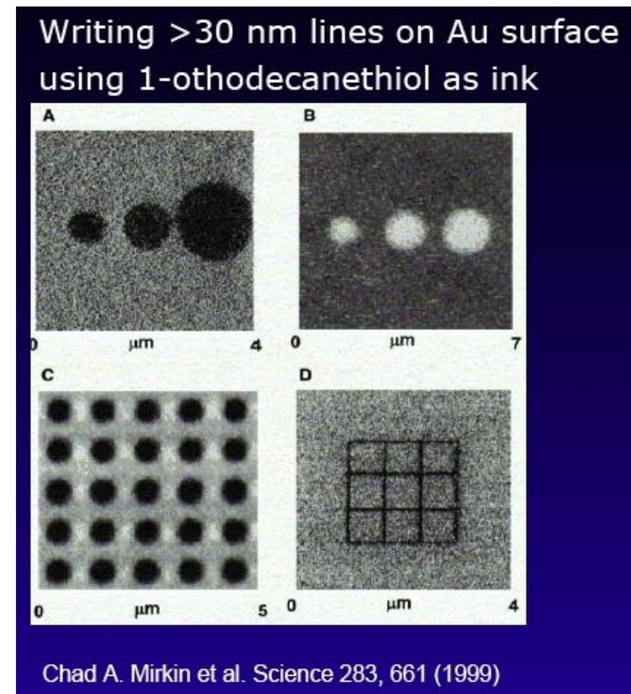
Dip-pen lithography: involves the use of a sharp tip which has been coated or dipped into a solution of molecules.

The tip is then brought into close proximity with a substrate to be patterned in a humid atmosphere.

Ambient humidity causes a tiny water droplet to be formed in the gap which serves as a conduit for the molecules transfer to the surface. The capillary forces leave the molecules on the surface, so the tip can be used to create patterns of self-assembled monolayers.



Northwestern University



Thermal Dip Pen Lithography

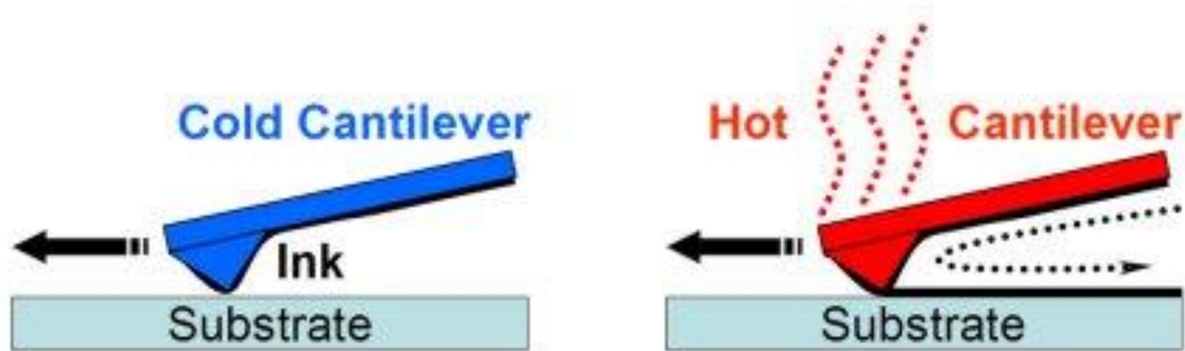


Diagram illustrating thermal dip pen nanolithography.

Cantilever is cold (left) no ink is deposited.

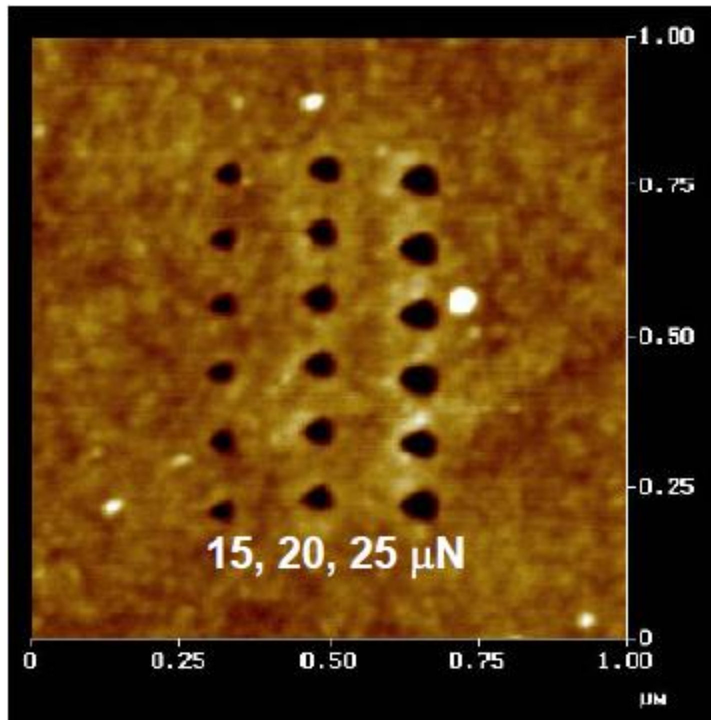
When the cantilever is heated (right), the ink melts and is deposited onto the surface.

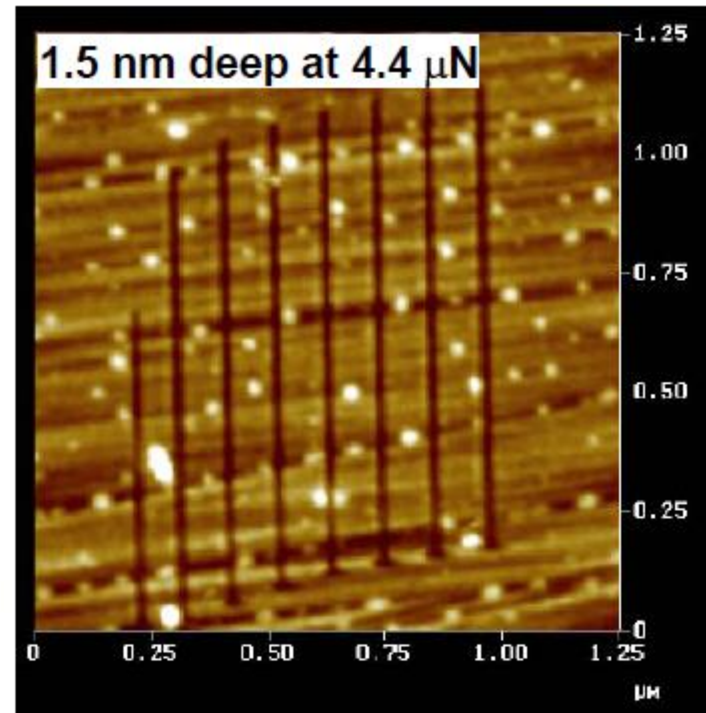
AFM Lithography Scratching

Directly scratch substrate leaving a trenches on the surface.

Advantage:

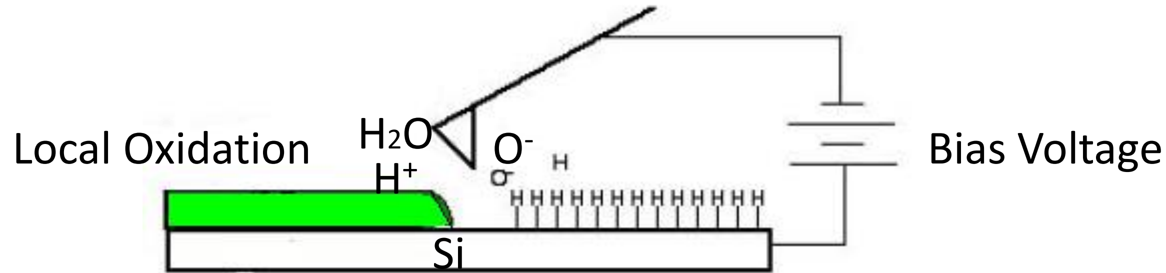
Precision of alignment and feature size controlling
The absence of additional processing steps, such as etching the substrate.





Diamond like Carbon

Electrical Field Enhanced Oxidation



Schematic illustration of field-induced local oxidation

$$Si + 2H^+ + 2(OH^-) \rightarrow Si(OH)_2 \rightarrow SiO_2 + 2H^+ + 2e^-$$

Voltage bias between a sharp probe tip and sample generates an intense electric field at the tip, electrical field is around $10^8 Vcm^{-1}$

Oxidization of silicon and metals
Oxidation depends on humidity
Can achieve sub-50nm feature sizes

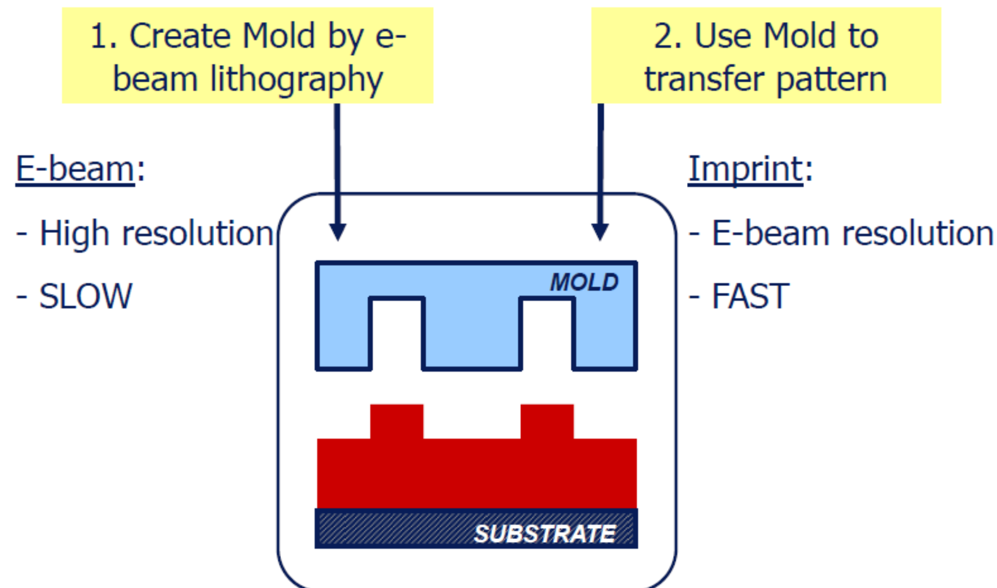
Nanoprinting lithography (NIL)

Nanoimprinting Definition:

Nanopatterning method differs from UV lithography and e-beam lithography in that the features are formed onto substrate using a **stamp** instead of light or electron beam. The minimum feature size is defined by the features on the stamp.

Stamps form an essential part in the NIL technology.

With nanoimprinting lithography is possible to produce sub-50-nm structures.



Nanoprinting lithography (NIL)

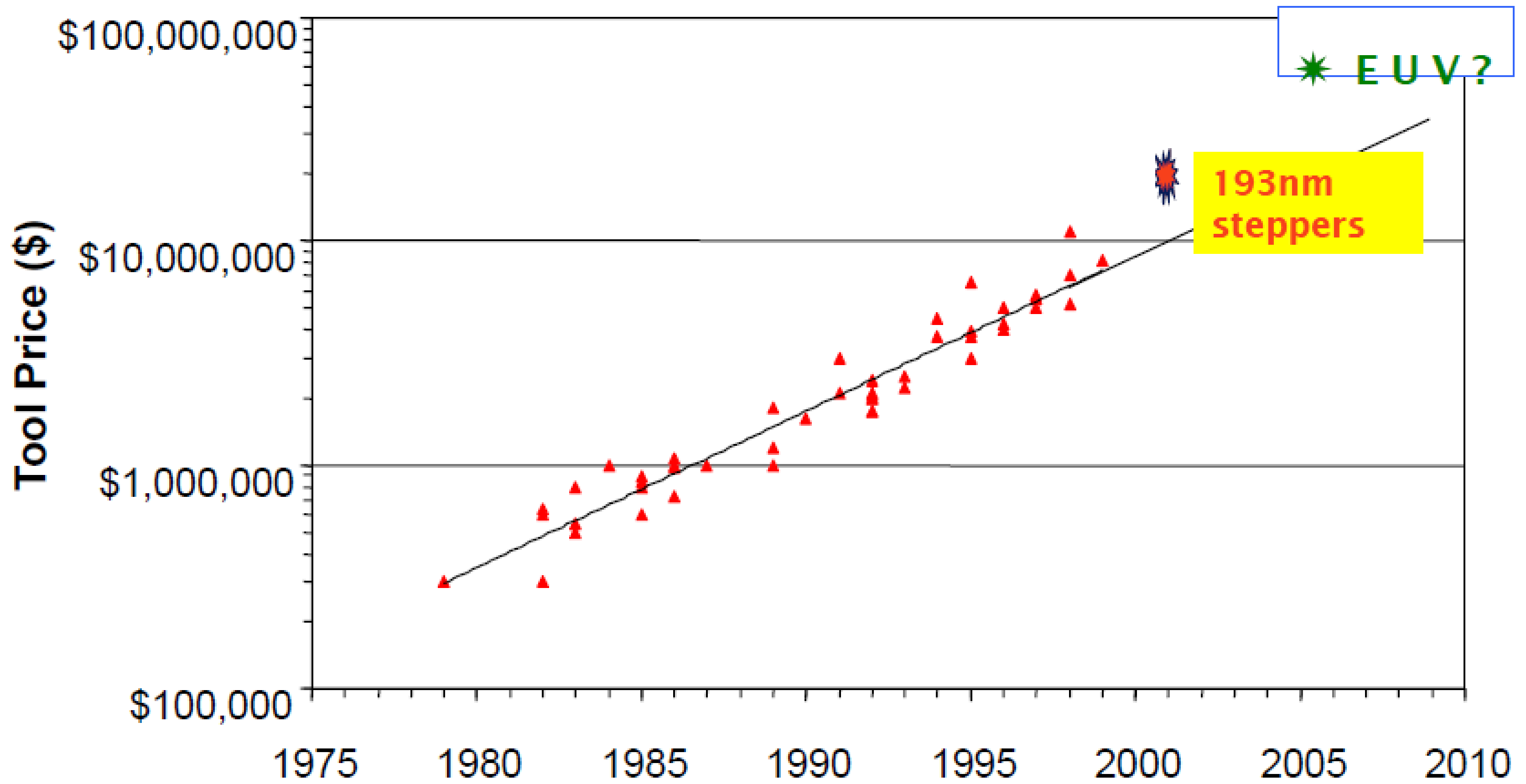
Advantages:

- High throughput, high resolution, low costs.
- No diffraction limit: features as small as 10 nanometers have been fabricated.
- Broad range of materials can be used, including polymers, metals, and ceramics.
- Easily performed technique -without need of specialized fabrication facility or clean room.

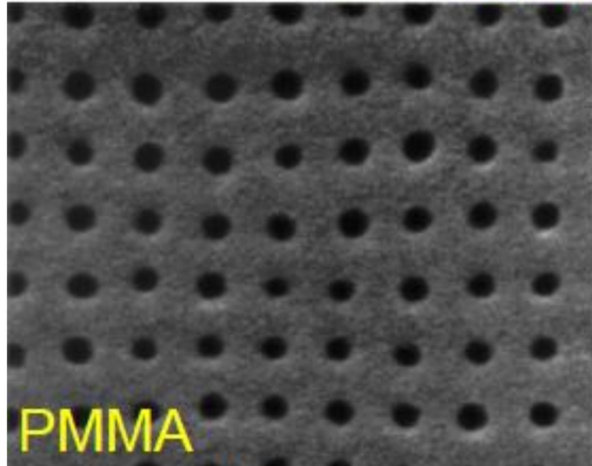
Disadvantages:

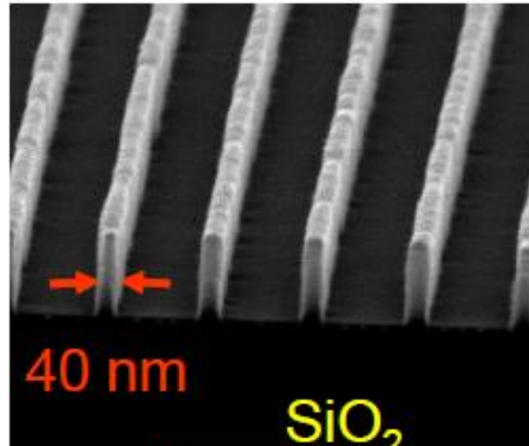
- Extremely difficult to build a 3-D structure-many steps needed for material deposition and removal. Accumulation of defects.
- Very high temperatures/pressures are needed to cause the viscosity to drop for the polymer to flow into channels, but, same high temperature causes polymers to degrade.

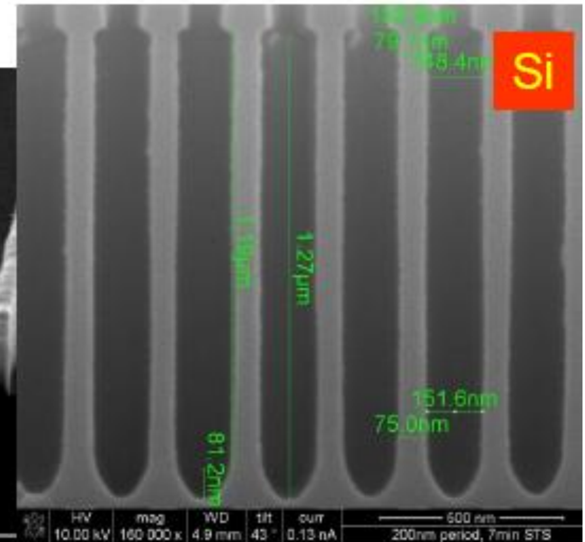
Exposure Tool Cost

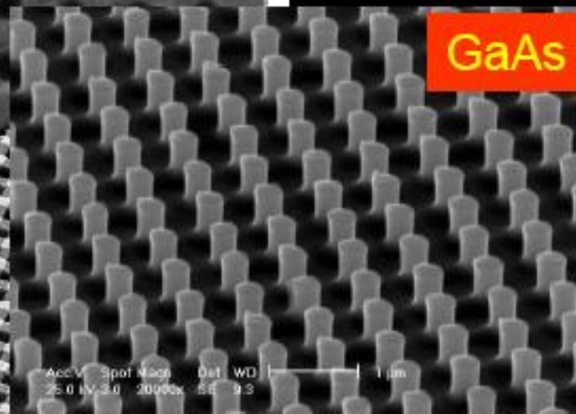


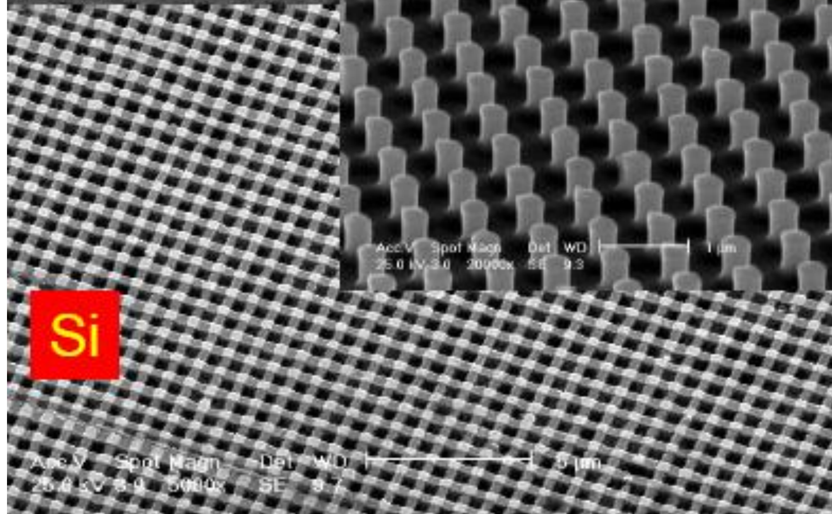
Structures Fabricated by Nanoprintting

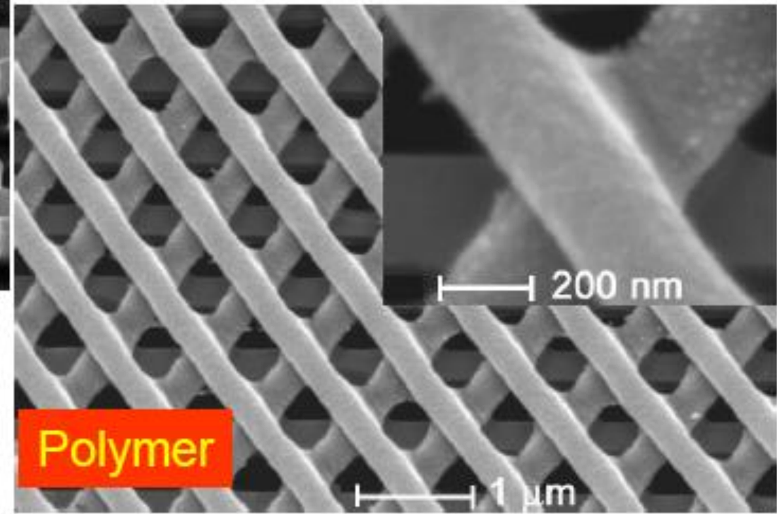






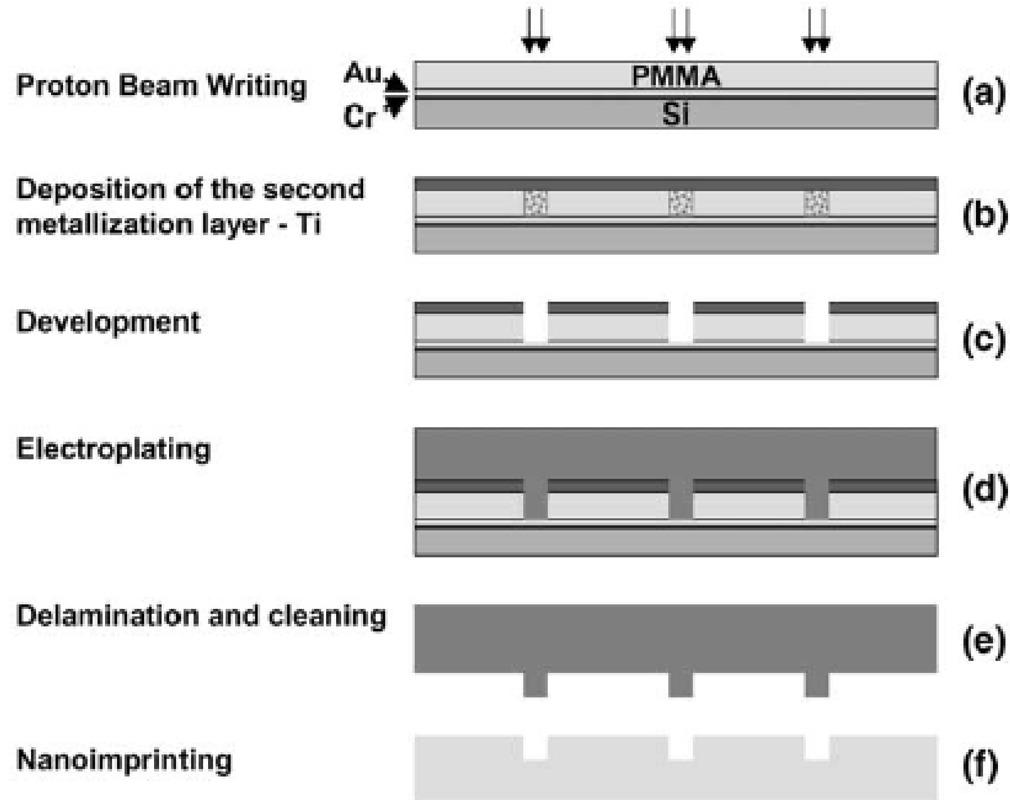






Versatile technology

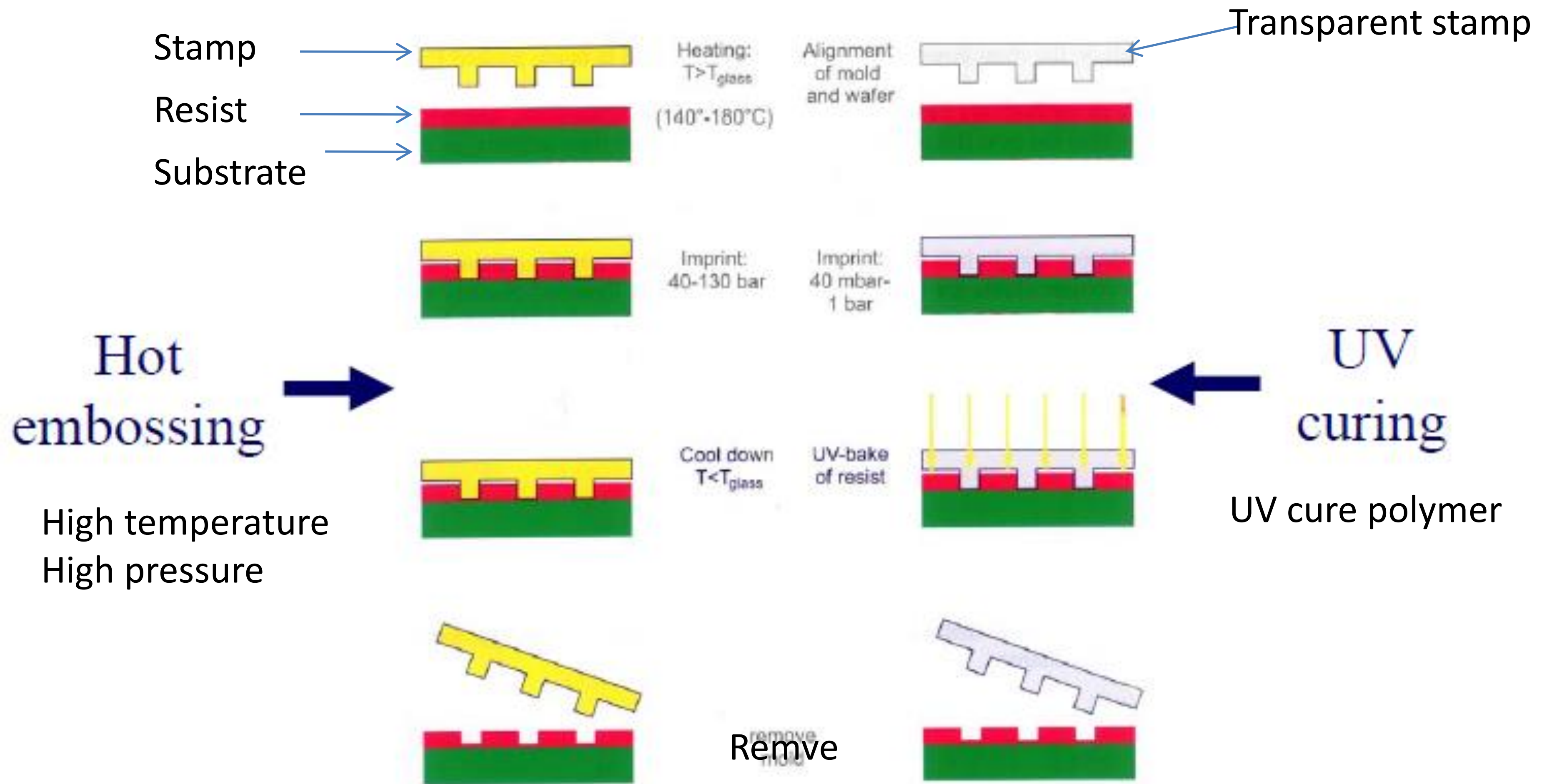
How to Make a Stamp?



Process for making nickel stamp

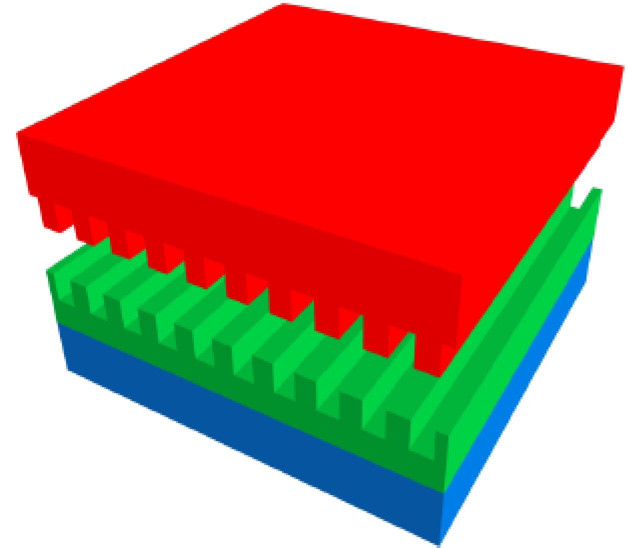
Stamp:
Working at high temperature
High pressure.
Nickel is a better choice

Process of Nanoprint lithography



Schematic of Nanoprint process

Critical Steps in Nanoimprint Lithography



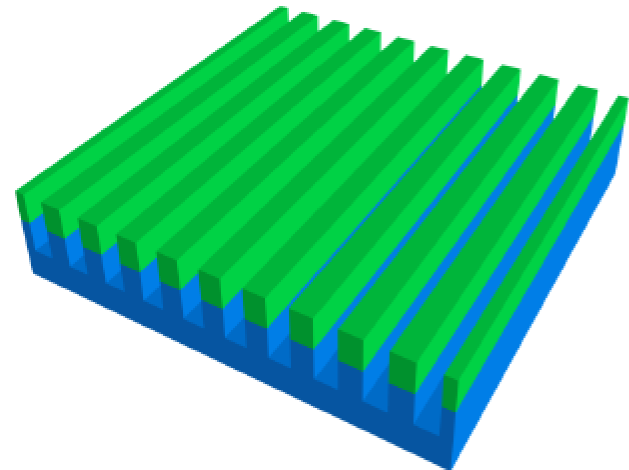
Mold Release

Large contact area

Resist shape integrity

Complete mold-resist separation

Resist remains on substrate.

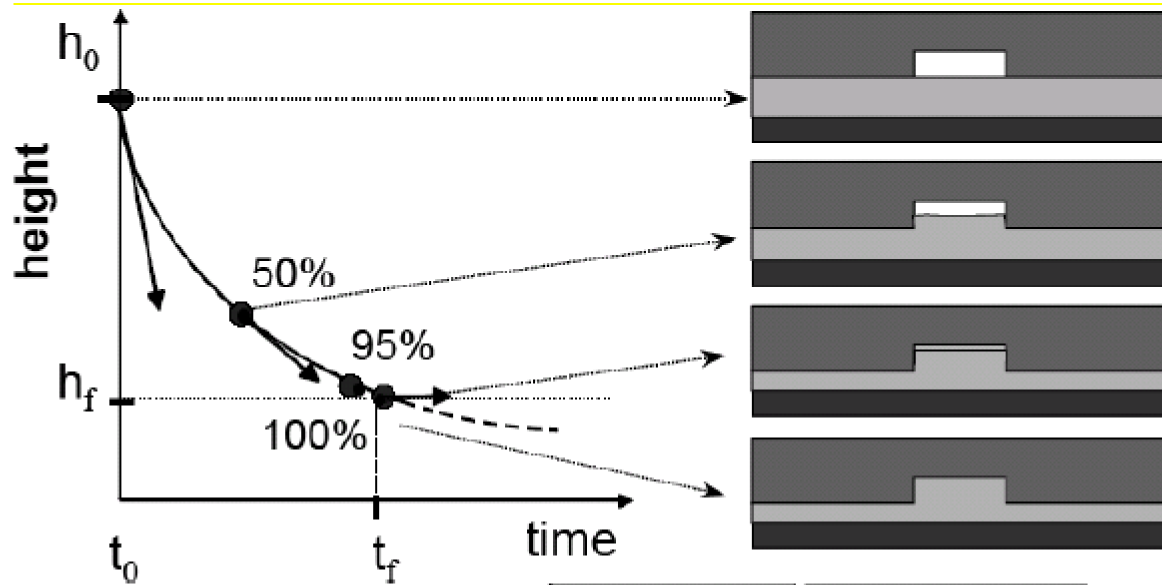


Pattern Transfer

Resist serves as an etch mask requiring good dry etching resistance

High requirement for resist

Squeezed Flow of Newtonian Fluid



Squeeze flow of polymer into one cavity, once the cavity is filled the polymer Continue to sink but at a very slow rate.

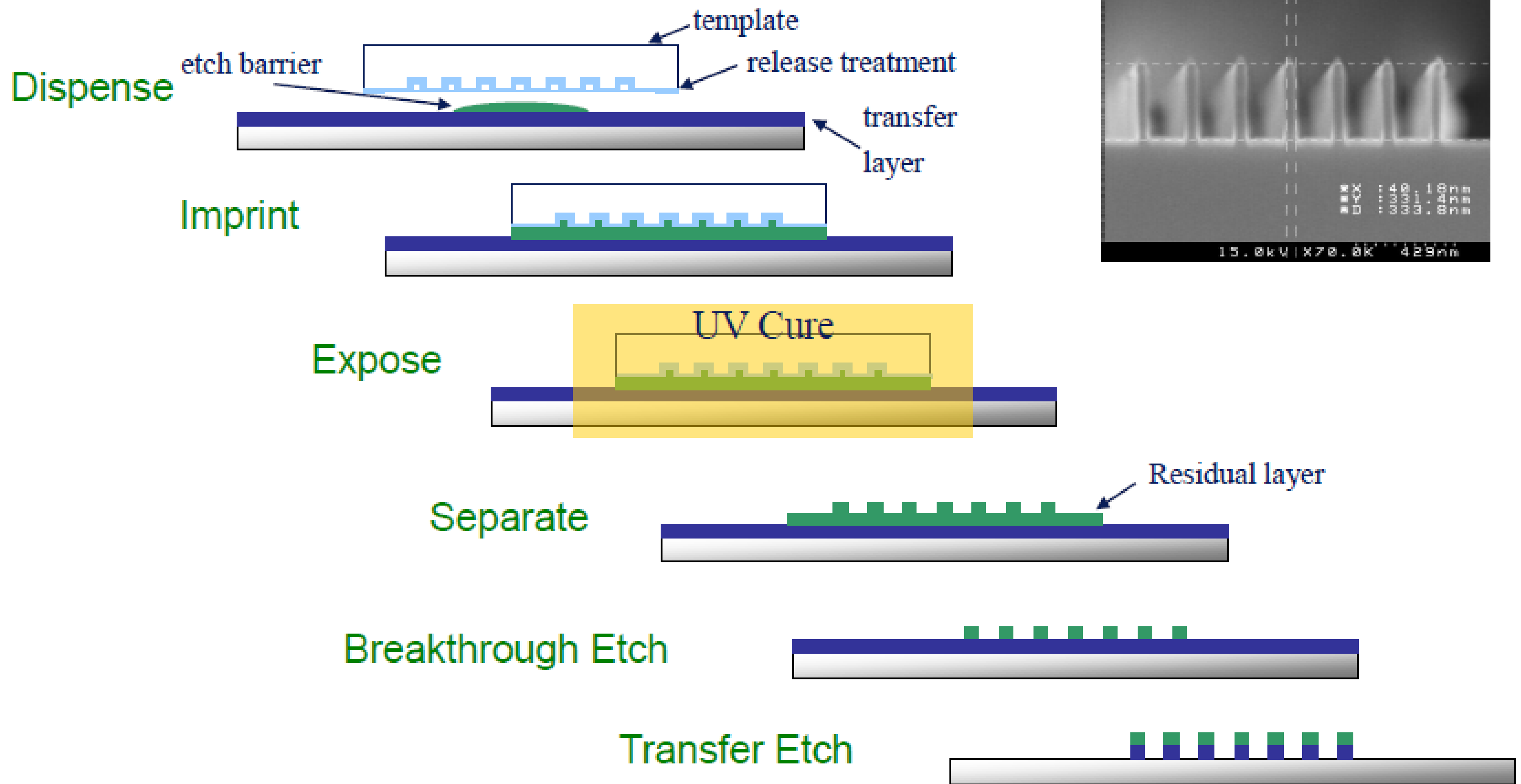
Force required for the squeeze flow:

$$F = -\frac{3\pi R^4 dh}{4h_0^3 dt}\eta_0$$

R: radial flow distance, h_0: initial thickness of the polymer, dh/dt: speed of the polymer under press.η_0: viscosity of polymer

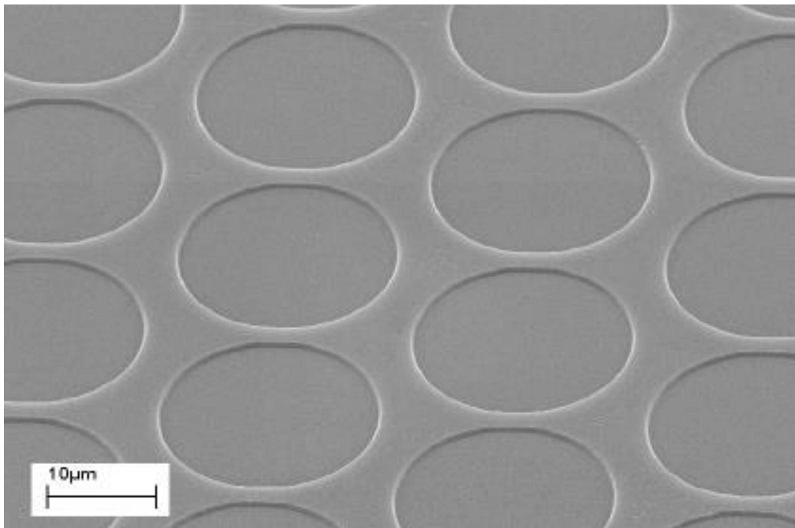
Step and Flash Imprint Lithography (SFIL)

Double-layer UV-NIL Process

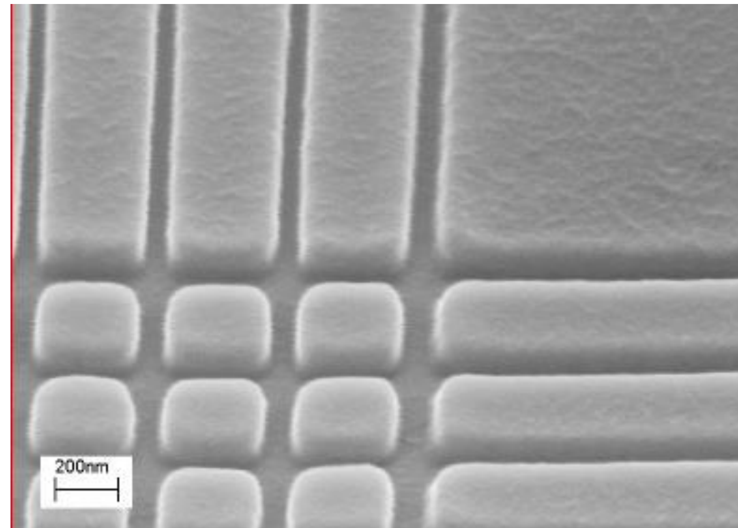


UV Imprint Using Contact Aligner

Low viscosity of the UV curable liquid enables easy patterning of large and nanoscale patterns at low pressure

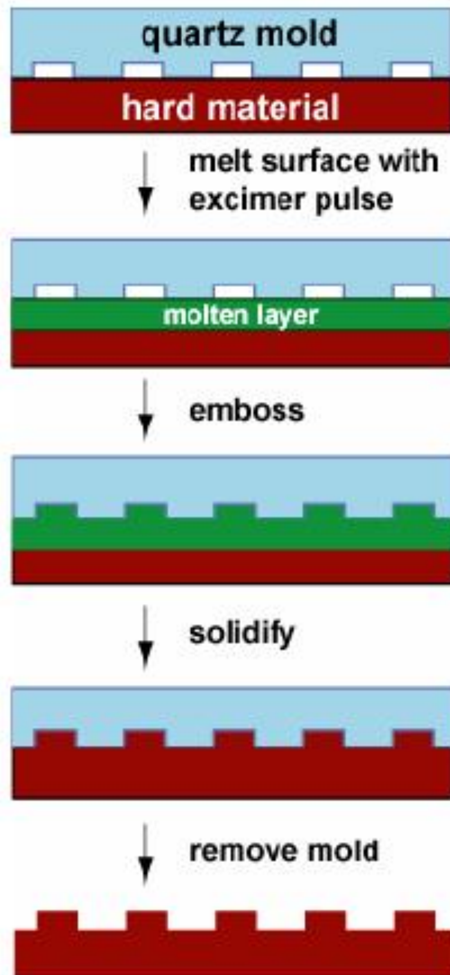


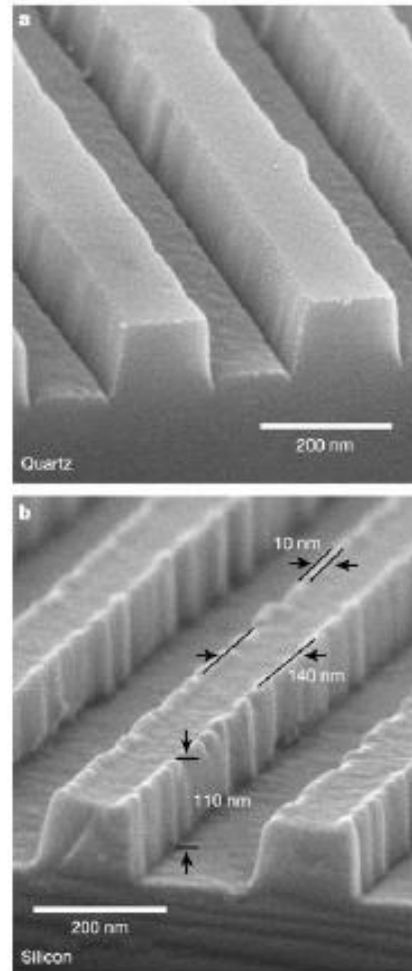
20um patterns



60 nanometer trenches

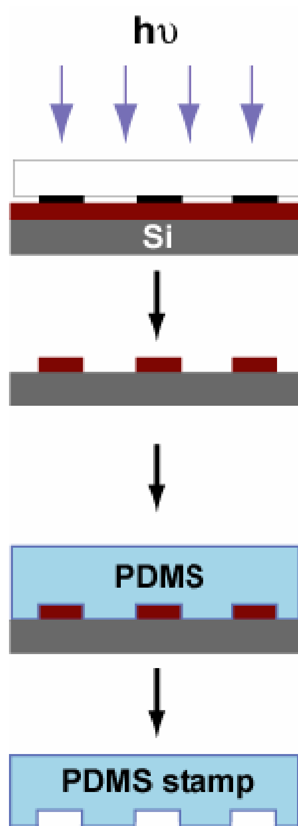
Laser-assisted Direct Imprinting





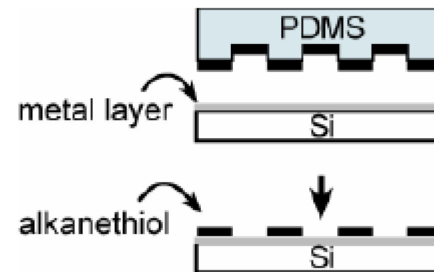
Zhou et. Al., Nature, 2002,417, 835

Soft Lithography



Preparation of PDMS Stamp

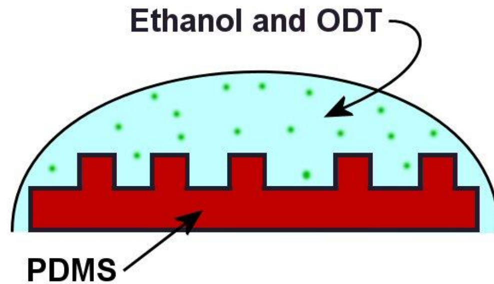
Microcontact printing (μCP)



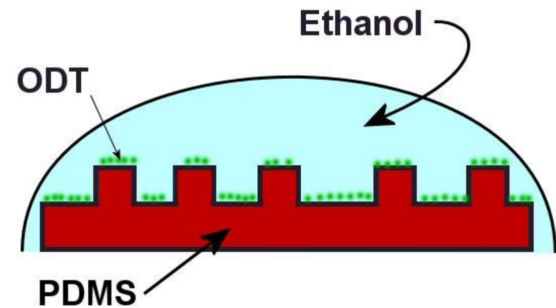
Basic elements of CP:
Stamp
- made of silicon based elastomer (poly-dimethylsiloxane, PDMS)
- conformal contact with substrate
Self assembled monolayers (SAMs) for different applications

Soft Lithography

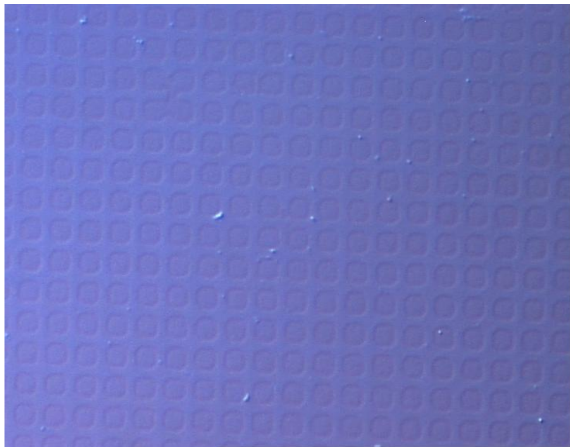
Transfer a liquid ink from the stamp to the substrate.



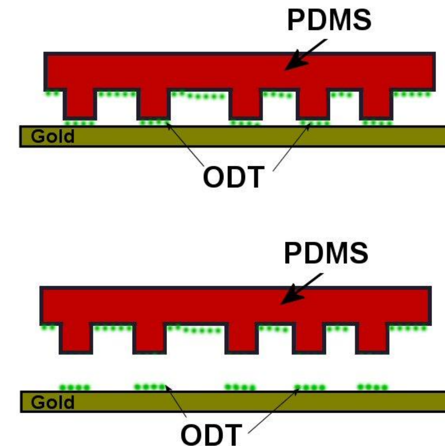
"Inking" a stamp. PDMS stamp with pattern is placed in Ethanol and ODT (**Octadecanethiol)**solution



ODT from the solution settles down onto the PDMS stamp. Stamp now has ODT attached to it which acts as the ink.



SEM image of structure made by ink stamp



The PDMS stamp with the ODT is placed on the gold substrate. When the stamp is removed, the ODT in contact with the gold stays stuck to the gold. Thus the pattern from the stamp is transferred to the gold via the ODT "ink."

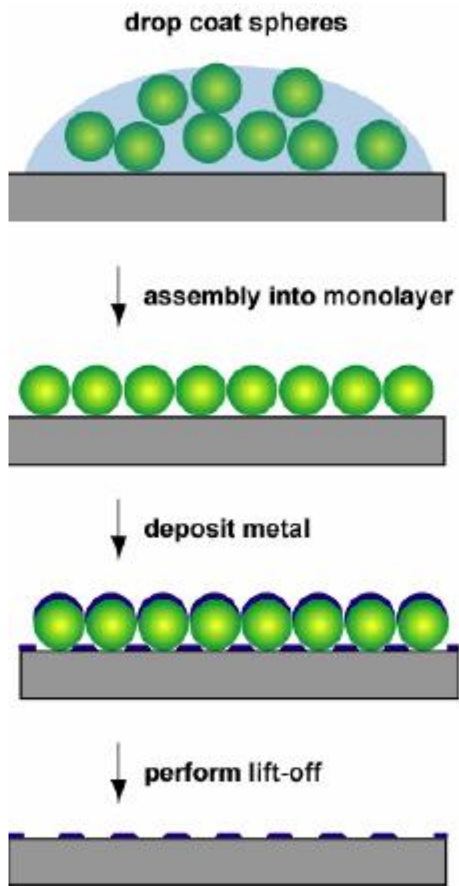
Advantage of Soft Lithography

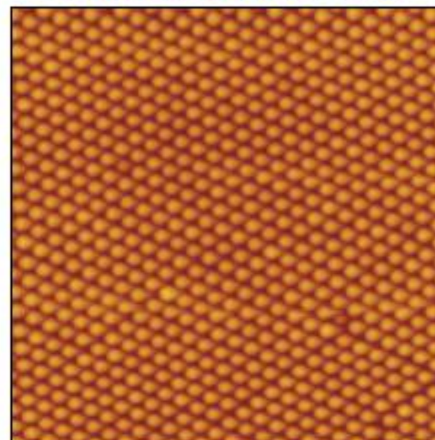
- Lower cost than traditional photolithography in mass production
- Well-suited for applications in biotechnology
- Well-suited for applications in organic electronics
- More pattern-transferring methods than traditional lithography techniques (more "ink" options)
- Does not need a photo-reactive surface to create a nanostructure
- The resolution depends on the mask used and can reach 6 nm

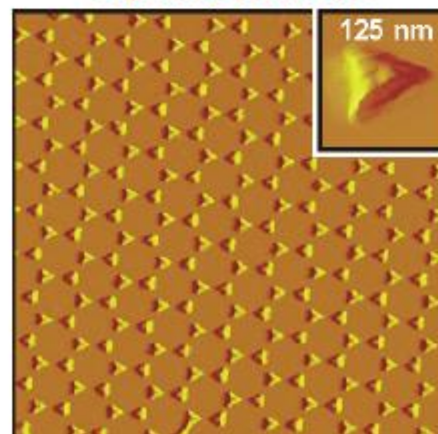
Other Lithographic Approaches

Nanosphere Lithography
Sidewall lithography
Size Reduction lithography
Organic Layers Reduce Feature Size
Template Method
……

Nanosphere Lithography

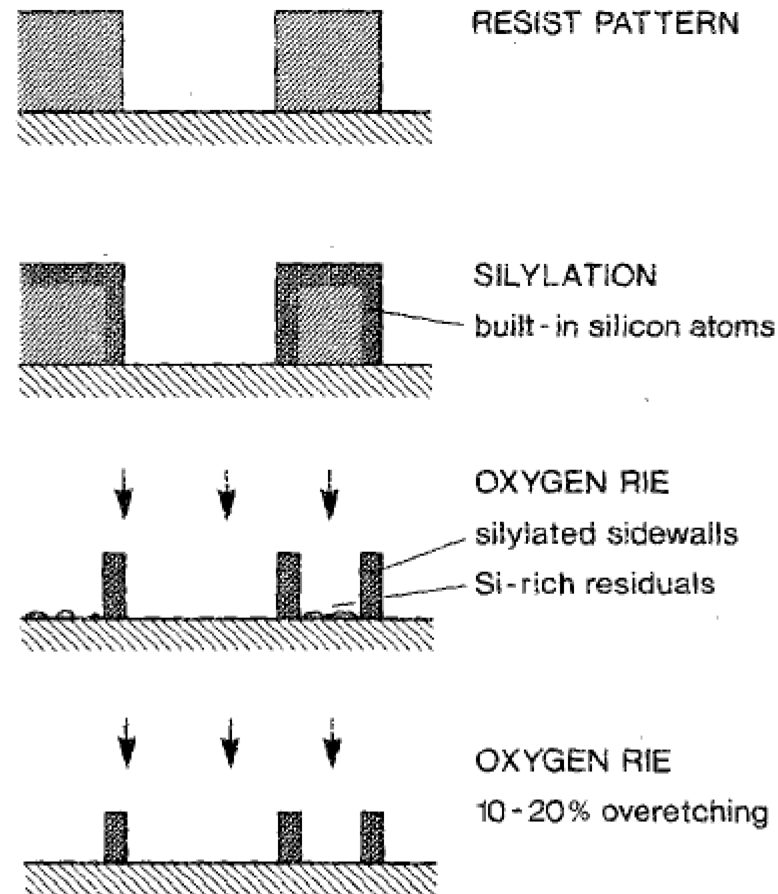






R.P. van. Duyne, Northwestern

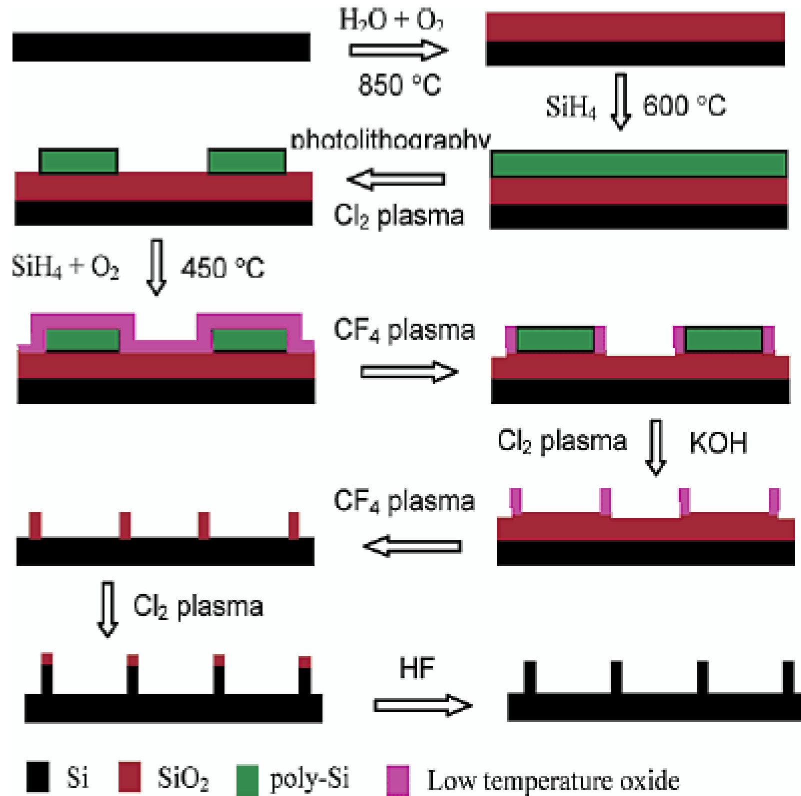
Sidewall Transfer Lithography

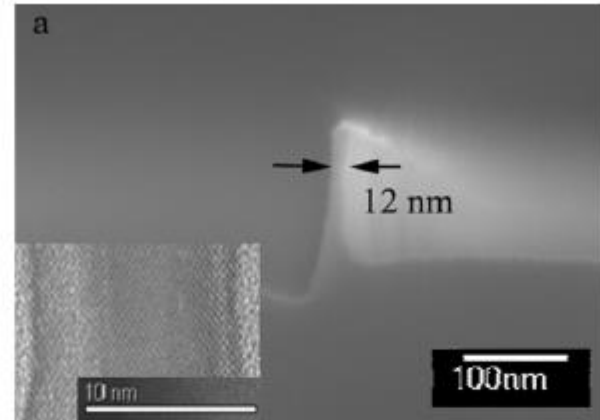


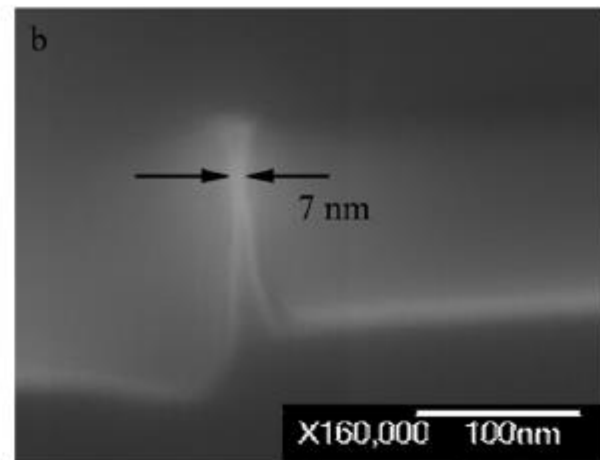
Sidewall formation process sequence

J. Vac. Sci. Technol. B 7 (6), 1989,1756

Size Reduction lithography

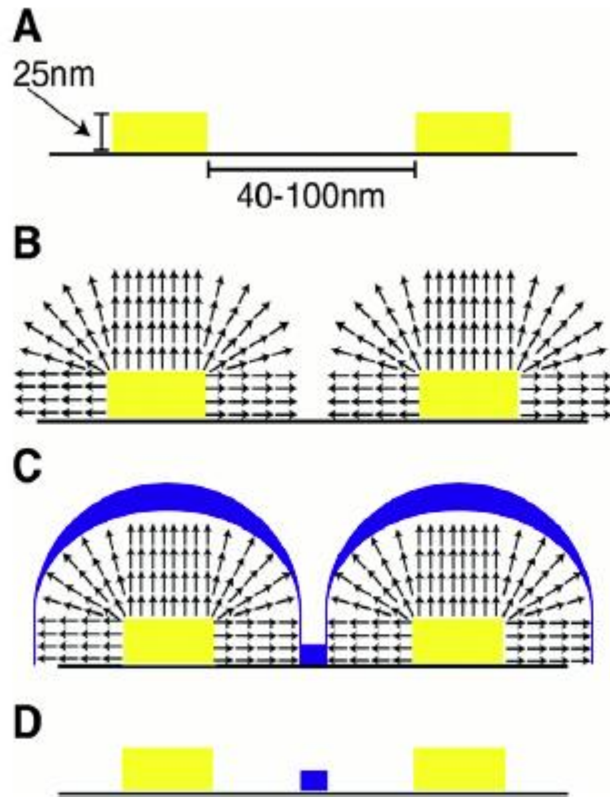


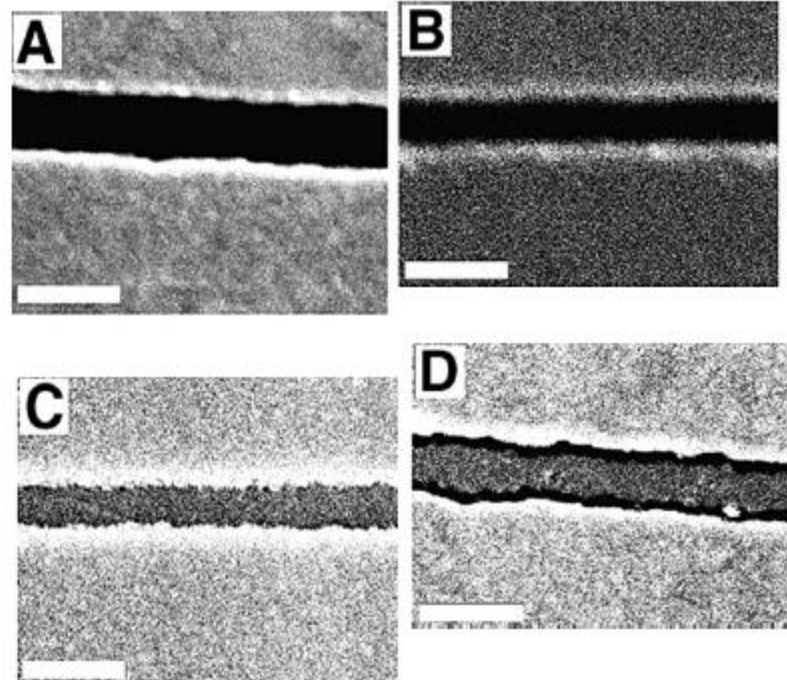




G. A. Somorjar J. Phys. Chem. B 2003, 107.3340,

Organic Layers Reduce Feature Size

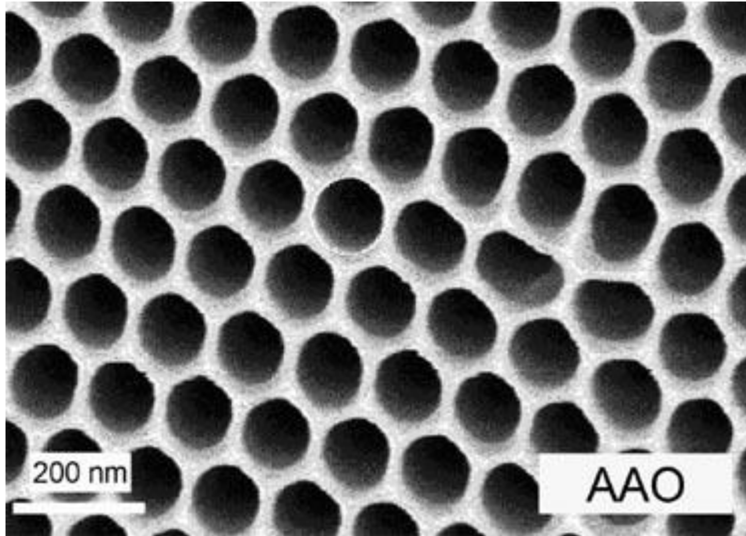


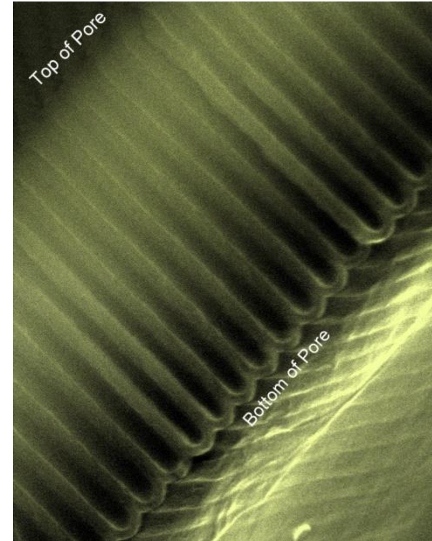


P. Weiss, Science, 2001, 291, 1019

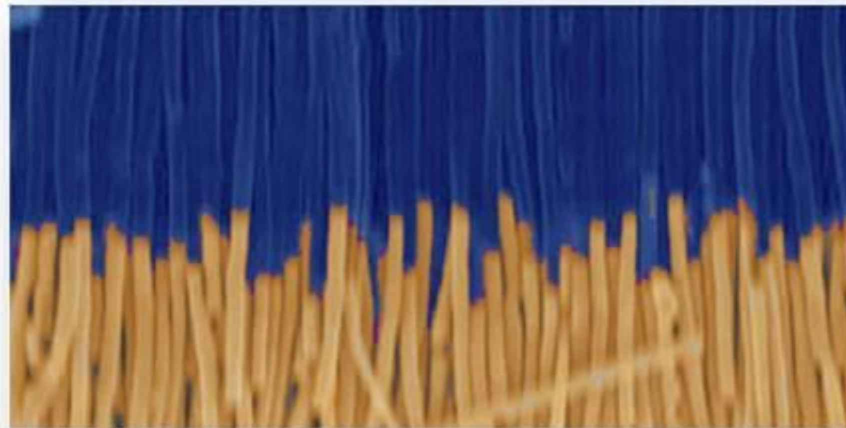
Template Method

Top View





Side view



Use template to fabricate Nanostructure

Carbon nanotube-gold hybrid structures

Appl. Phys. Lett. 89, 243122 (2006)

Nanoscale pattern Transfer

The lithography process is not finished until a functional pattern structure has been on or into a substrate ……….

Deposition or etching

Additive Pattern Transfer

Thin film deposition
Pattern transfer by lift off
Pattern transfer by plating

Subtractive Pattern Transfer

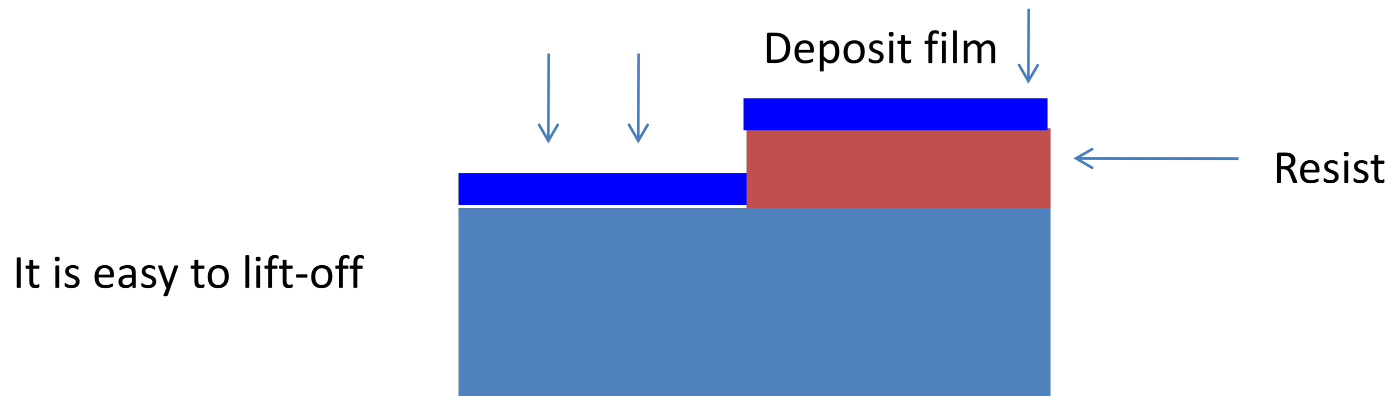
Wet Etching
Dry etching

Thin film deposition techniques

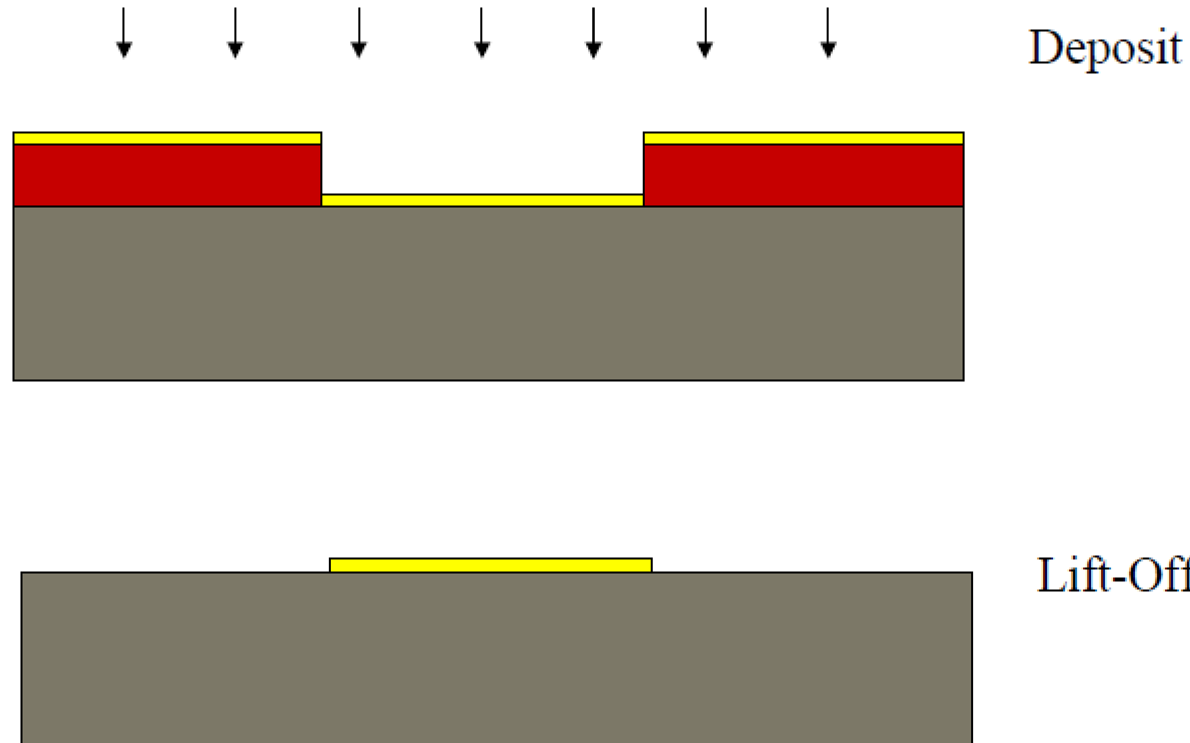
- Vacuum deposition Methods
  - Sputtering
  - CVD
  - Laser Oblation
  - Thermal deposition
  - Epitaxy

Deposition Issues in Pattern Transfer

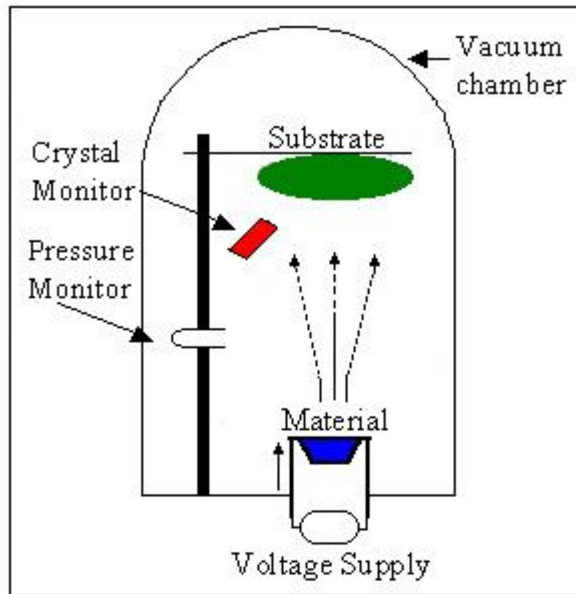
- Thermal compatibility
  - Compatible with polymers,
- Topographic compatibility
  - Can not cast over large step heights



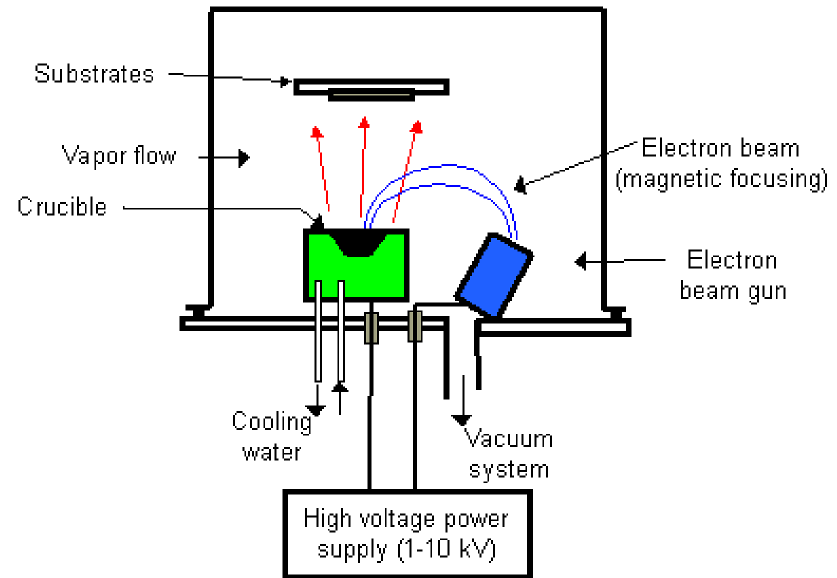
Deposition and lift-off



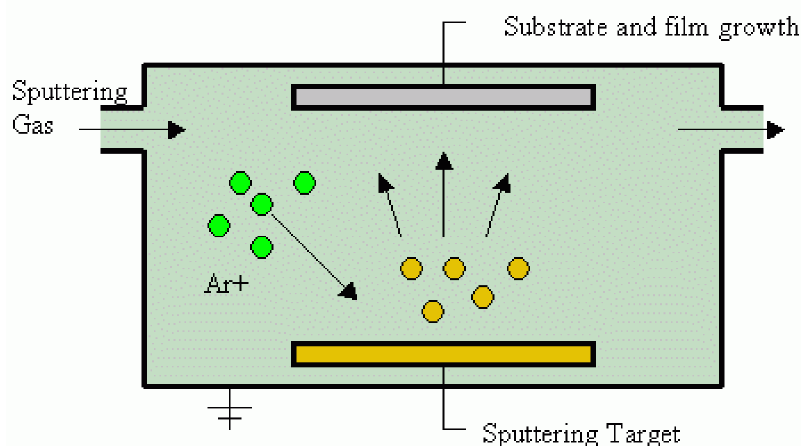
Physical vapor deposition (PVD)



Thermal Evaporation



Electron Beam Evaporation



Sputtering

The physical vapor deposition technique is based on the formation of vapor of the material to be deposited as a thin film. The material in solid form is either heated until evaporation (thermal evaporation) or sputtered by ions (sputtering).

Subtractive Pattern Transfer

- **Wet etching**

  Isotropic wet etching

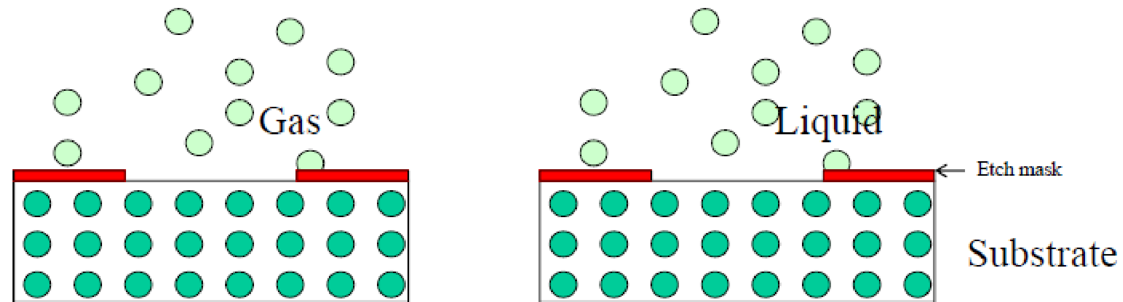
  Anisotropic wet etching

- **Dry etching**

  Reactive-Ion etching

  Ion milling

Etching Issues – Anisotropy and selectivity

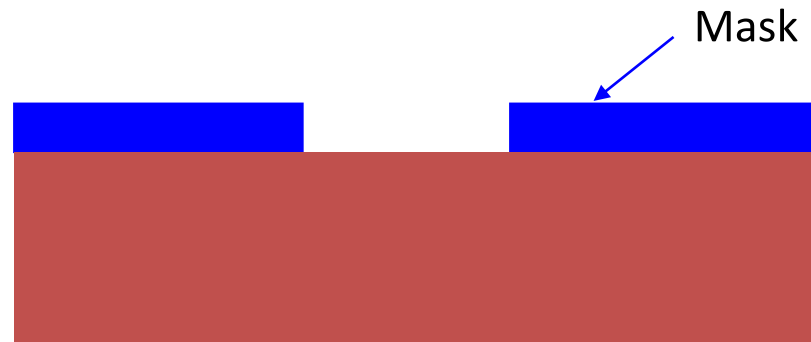


Gas Phase Etching (Dry Etching)

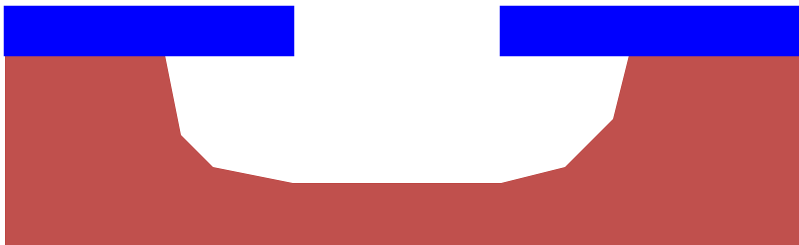
Liquid Phase Etching (Wet Etching)

Etching Issues - Anisotropy

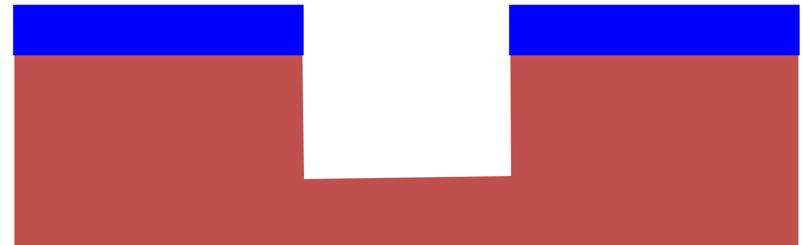
Isotropic etchants etch at the same rate in every direction



Isotropic

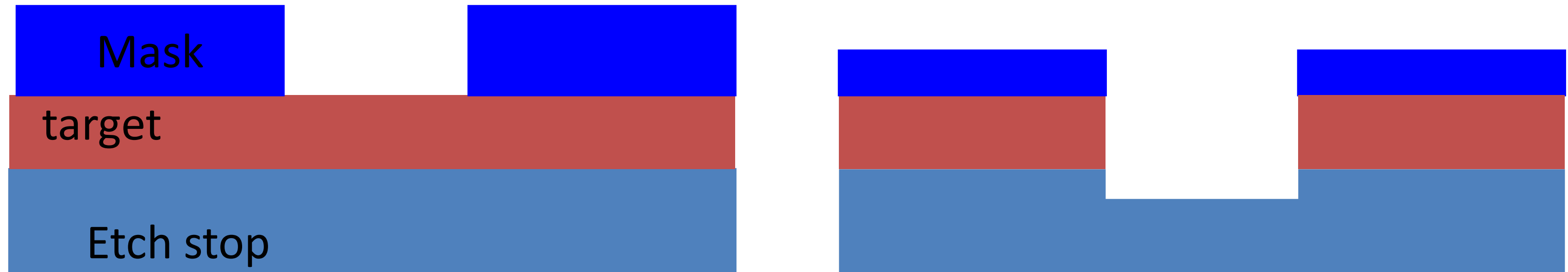


Anisotropic



Etching Issues - Selectivity

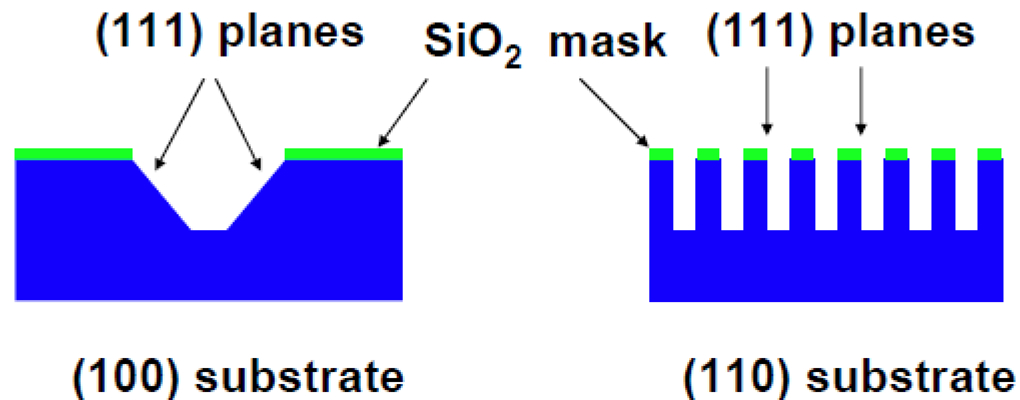
- Selectivity is the ratio of the etch rate of the target material being etched to the etch rate of other materials
- Chemical etches are generally more selective than plasma etches
- Selectivity to masking material and to etch-stop is important.



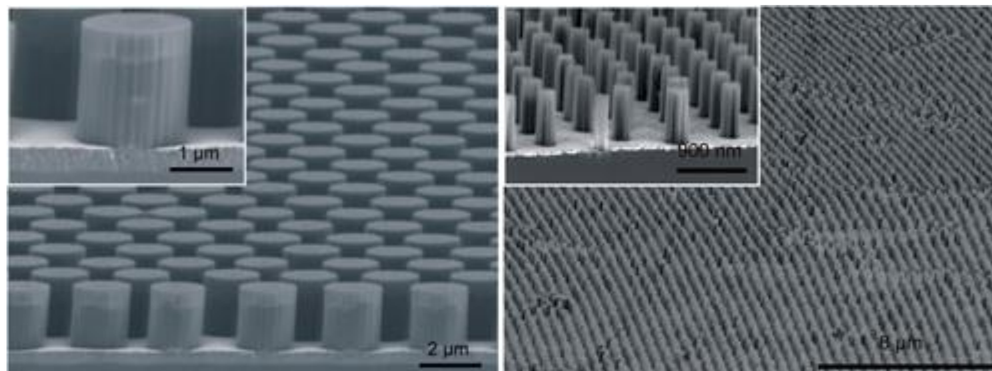
A highly selective etch leaves the underlying material unharmed

Anisotropic Wet Etching of Si

Some wet etchants etch crystalline materials at very different rates depending upon which crystal face is exposed. In single crystal materials (e.g. silicon wafers), this effect can allow very high anisotropy.



KOH (1μm/min at 60°C) Etching stops on (111) planes



Si nanopillar

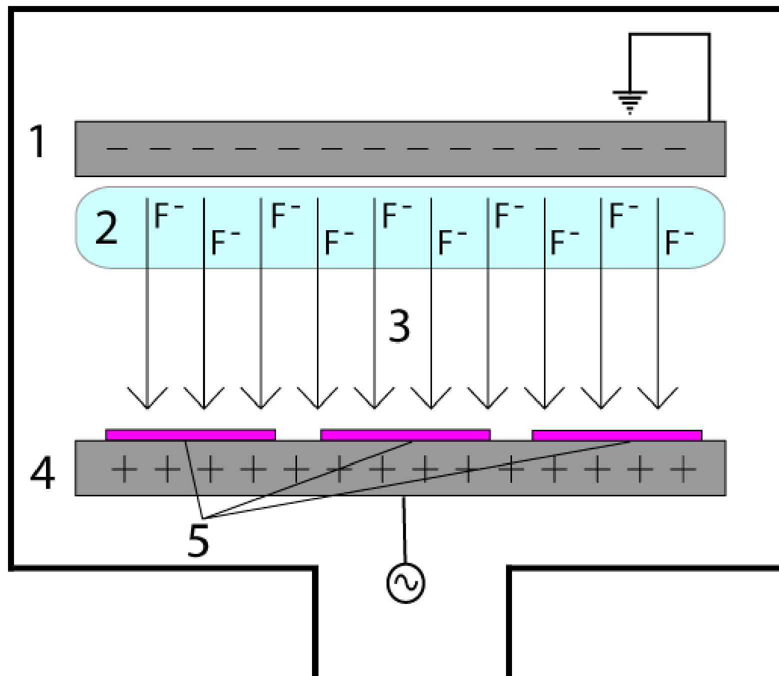
Plasma Etching

Plasma etching can be divided into:
– Physical (sputtering, milling)
– Physical + chemical = ion enhanced etch (RIE)

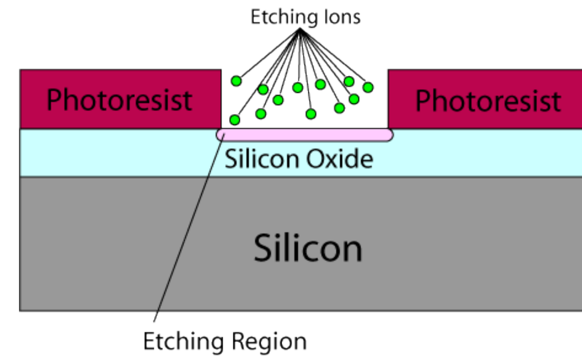
- Reactive component is **selective**
- Ionic component is **directional**
- RIE uses both **selectivity and directionality**

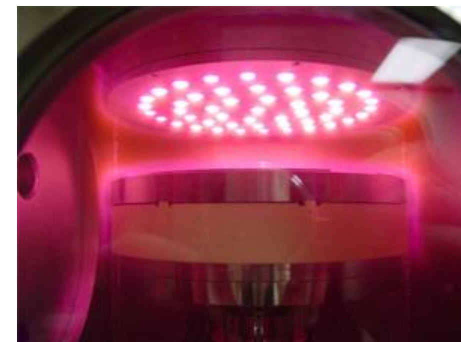
Reactive-Ion Etching

Reactive ion etching (**RIE**) is an etching technology used in microfabrication. It uses chemically reactive plasma to remove material deposited on wafers. The plasma is generated under low pressure (vacuum) by an electromagnetic field. High-energy ions from the plasma attack the wafer surface and react with it.



An RIE consists of two electrodes (1 and 4) that create an electric field (3) meant to accelerate ions (2) toward the surface of the samples (5).



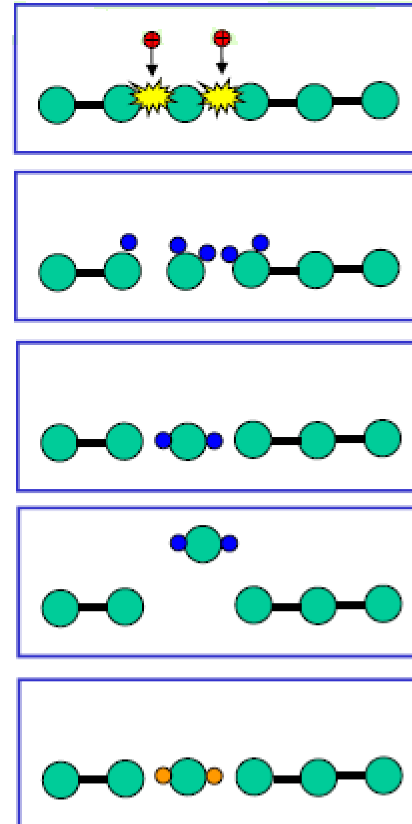


a plasma shower head over a silicon wafer

Plasma Etching Process

Creation of free radicals from flow gas

- Dissociation of the substrate bonds with ion bombardment
- Adsorption of free radicals on the surface
- Reaction of free radical + substrate atoms
- Desorption of volatile by products
- Non-volatile byproducts remain

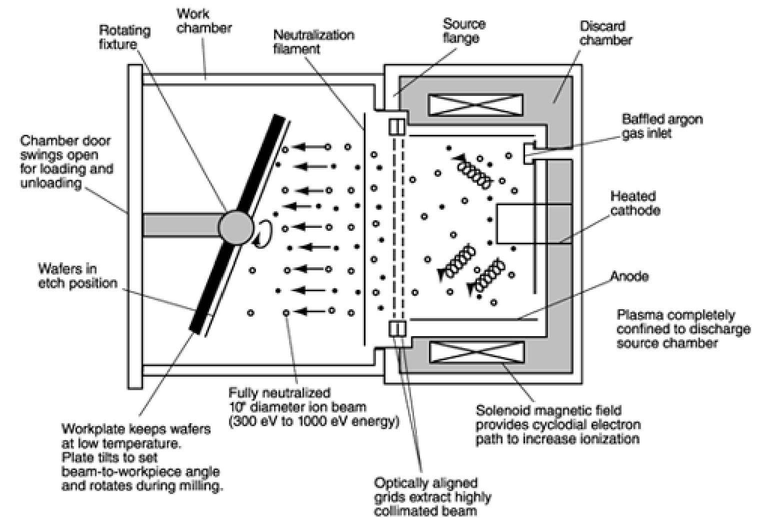


Etch Chemistries of Different Etch Processes

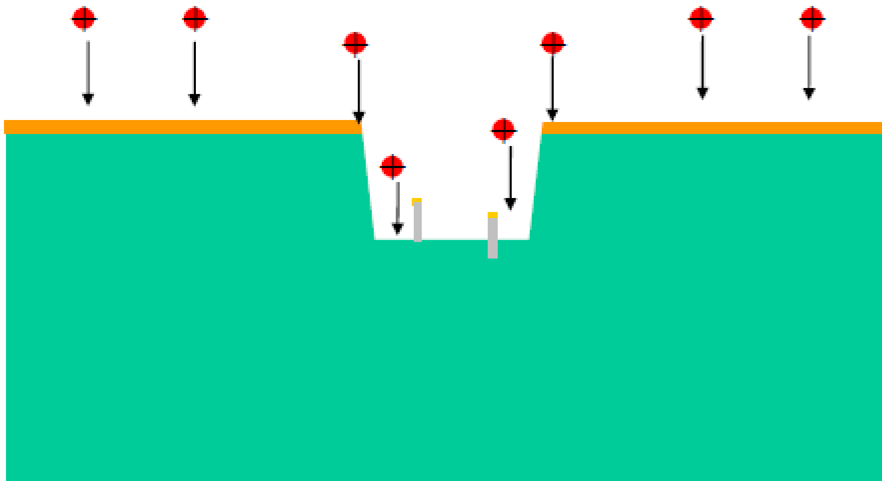
Material Being Etched	Etching Chemistry
Deep Si trench	$HBr/NF_3/O_2/SF_6$
Shallow Si trench	$HBr/Cl_2/O_2$
Poly Si	$HBr/Cl_2/O_2$, HBr/O_2, BCl_3/Cl_2, SF_6
Al	BCl_3/Cl_2, $SiCl_4/Cl_2$, HBr/Cl_2
AlSiCu	$BCl_3/Cl_2/N_2$
W	SF_6 only, NF_3/Cl_2
TiW	SF6 only
WSi_2, $TiSi_2$, $CoSi_2$	CCl_2F_2/NF_3, CF_4/Cl_2, $Cl_2/N_2/C_2F_6$
$Si0_2$	CF_4/O_2, $CF_4/CHF_3/Ar$, C_2F_6, C_3F_8,C_4F_8/CO, C_5F_8, CH_2F_2
Si_3N_4	CF_4/O_2, $CHF_3/0_2$, CH_2F_2, CH_2CHF_2

Ion Beam Milling (Sputter Etch)

- Inert gas (Ar)
- No selectivity (mask erosion is faster)
- Highly directional (anisotropic)
- Redeposition of sputtered material can mask additional etching (micromasking).
Use a mask with low sputtering yield.
- Typically used for complex films that don't have good chemistries (InAlGaAs, YBaCuO)



Ion Beam Milling system



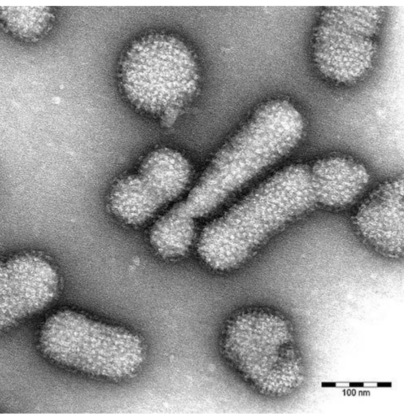
Characterization

- **SEM,TEM**, AFM, STM- Morphology analysis
- XRD, XPS, **EDS**- Element analysis
- UV, IR, **Raman**- Vibrational analysis

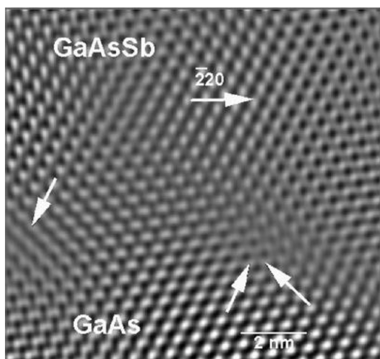
History of the Microscope

- In the late 17th century Robert Hooke added a third lens, greatly improving contrast issues and comfort.
- Over the next two hundred years optical microscopy revolutionizes science, especially biology.
- During this time improvements are continually made, including corrections for chromatic spherical aberrations.
- In the late 19th century, Ernst Abbe showed that the improvement of the magnification of optical microscopes was fundamentally limited by the wavelength of light.
- 1931- Ernst Ruska co-invents the electron microscope.
  - 1938- 10nm resolution reached.
  - 1940- 2.4 nm resolution.
  - 1945- 1.0nm resolution achieved.
- 1981- Gerd Binning and Heinrich Rohrer invent the scanning tunneling electron microscope (STM).
- 1986- The Atomic Force Microscope was developed in collaboration between IBM and Stanford University.

Resolution of Microscope



Flu virus SEM



TEM image

Vertical scale (Å)

10^6

10^4

10^2

1

SEM

TEM

OM

STM

1 10^2 10^4 10^6

Lateral scale (Å)

100 × Cell OM

STM Image of Si

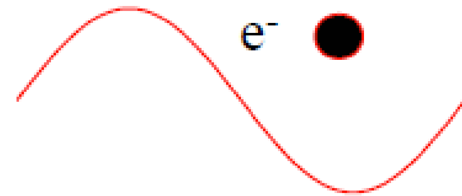
Electron microscopy : aims and means

• Microscopies: morphologies in small scales (micrometer or nanometer)
Optical microscopy, Electron microscopy, Ion microscopy, Scanning probe microscopy….., offer images only.

• Microanalyses: composition and/or structures in small scales (micrometer or nanometer)
Energy Dispersive Spectroscopy, Wave-length Dispersive, Spectroscopy, Electron Energy Loss Spectroscopy, Auger Electron Spectroscopy, Convergent Beam Electron Diffraction, Select Area Diffraction….., offer spectra and/or diffraction patterns

Wave Behaviors
– images and diffraction patterns
– wavelength can be tuned by energies

Charged Particle Behaviors
– strong electron-specimen interactions
– chemical analysis is possible



Vc=120KV, λ=0.00336 nm

Scanning Electron Microscopy (SEM)

- Scan sample with a high-energy beam of electrons in a raster scan pattern.
- The electrons interact with the atoms that make up the sample producing signals.
- secondary electrons for image.
- Back-scattered electrons (BSE), intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen - EDS

Scanning Electron Microscopy

•Beam size: a few – 30 A

•Beam Voltage: 1-30kV

•Resolution: 10-100 A

•Magnification: 20x-650,000x

•Imaging radiations: Secondary electrons,
  backscattering electrons

•Topographic contrast: Inclination effect,
  shadowing, edge contrast,

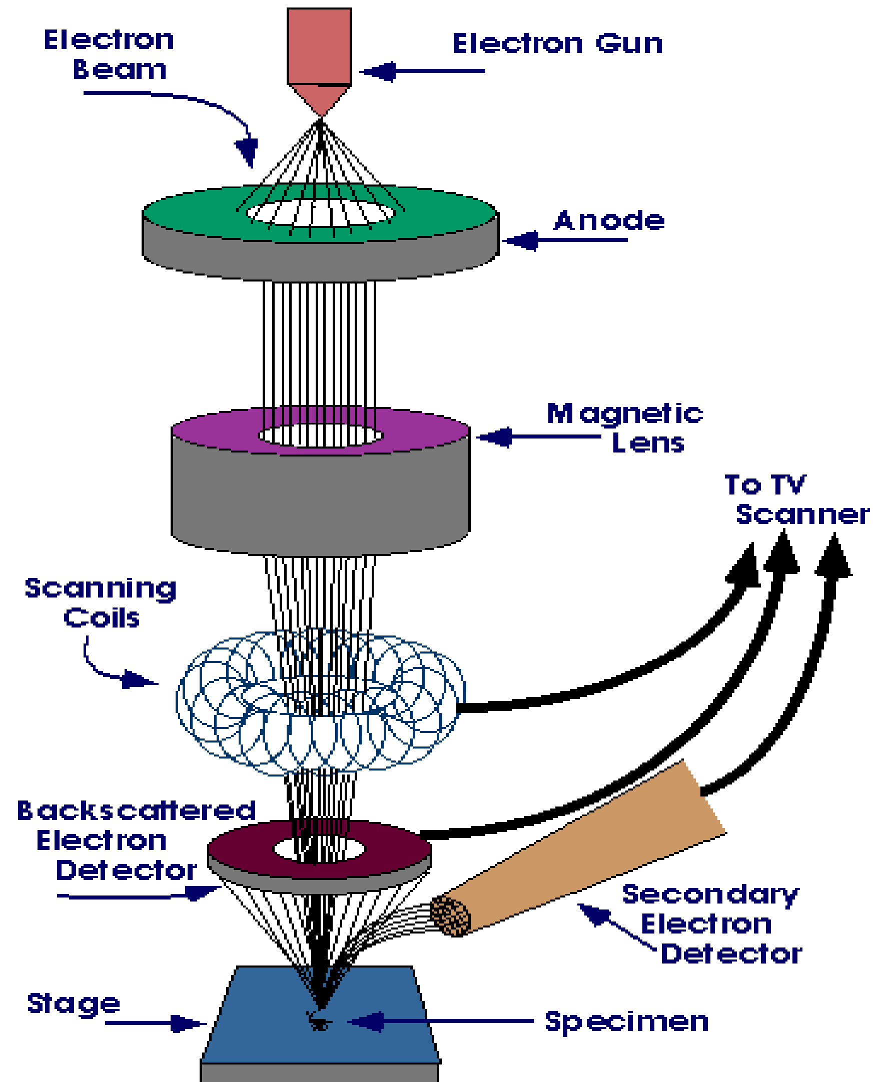
•Composition contrast: backscattering
  yield ~ bulk composition

•Detections:

 - Secondary electrons: topography

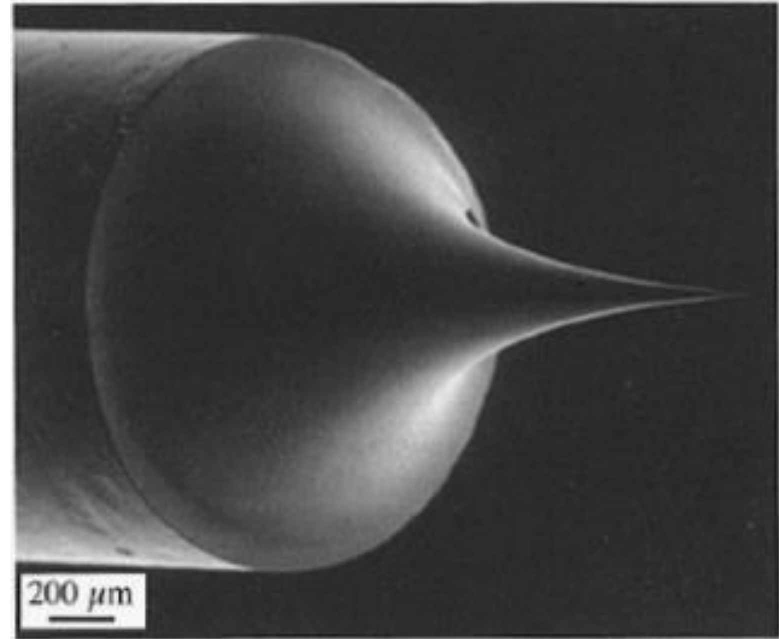
 - Backsactering electrons:
   atomic # and topography

 - X-ray fluorescence: composition



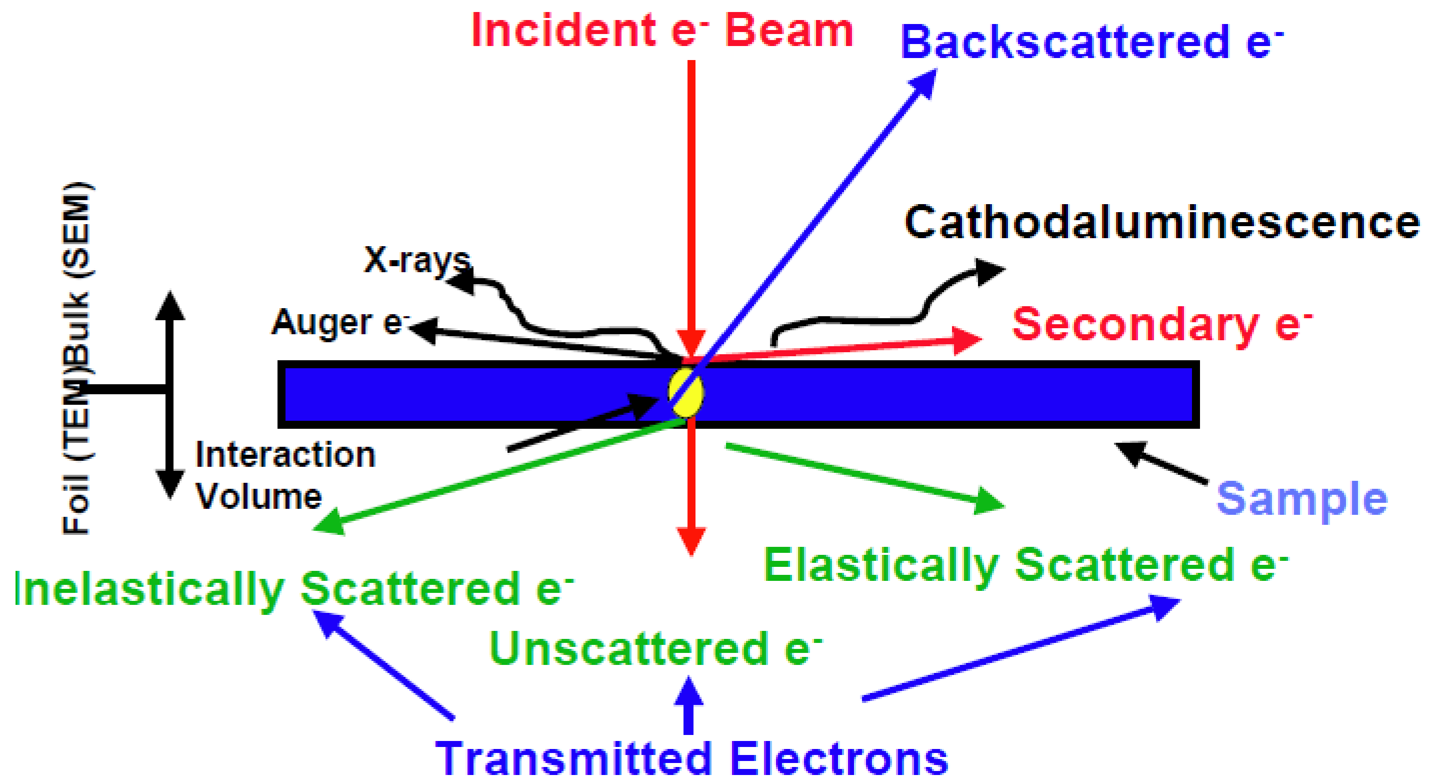
Electron Source (Field Emission)

LaB_6



Tungsten needle

Interaction of Electrons with Sample



Signals has two categories:

1) Electron signals, 2)photo signals

Electron scattering

• Two primary classes of electron scattering:

– **elastic scattering –**

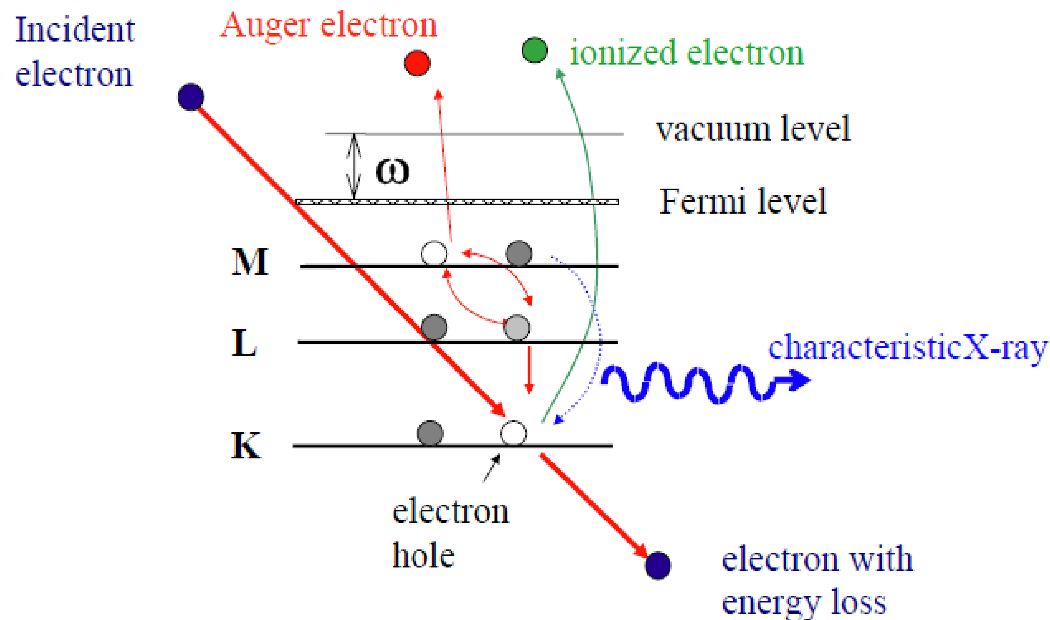
incident electron will change direction, but not kinetic energy

– **inelastic scattering –**

incident electron will change direction, but also give up some kinetic energy to the sample

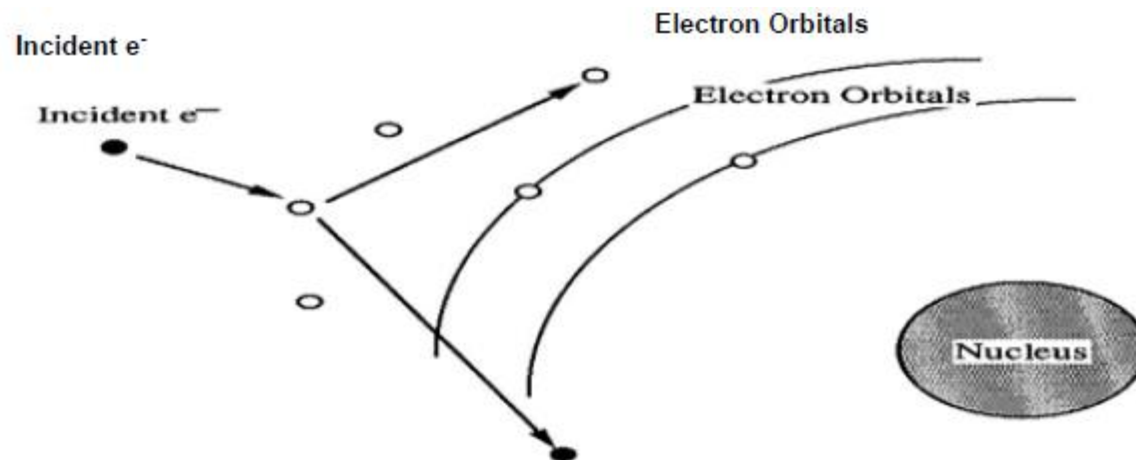
• will allow for elemental analysis

• Ultimately, scattering will lead to the image contrast



Inelastic Scattering – Secondary Electron Emission

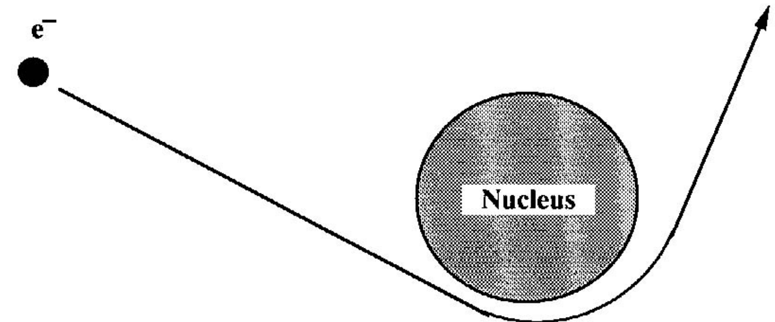
Secondary electrons
– Main signal used in the SEM for imaging
– Due to interactions between the e- beam and weakly bound conduction band e- (metals) or valence band e- (semiconductors or dielectrics)
• Secondary e- energies are typically 2-10eV, but can range up to 50eV
• Since the scattering cross section increases with decreasing e- energy, lower accelerating voltages generally give more SE signal



Backscattered Electrons

Backscattered electrons (BSE) arise due to elastic collisions between the incoming electron and the nucleus of the target atom (i.e. Rutherford scattering). Higher Z, more BSE emitted.

As the name implies, elastic scattering results in little (< 1 eV) or no change in energy of the scattered electrons, although there is a change in momentum (p). Since p = mv and the mass of the electron doesn't change, the direction of the velocity vector must change. The angle of scattering can range from 0 to 180°.



Backscattered electrons (BSE) relate to the atom numbers, so BSE can be used to Detect the element.

Inelastic scattering - other processes

Auger e- emission
– 2e- process similar to the X-ray scenario, but instead of emitting an X-ray, a weakly bound outer shell e- is emitted (typically from the first 2nm of the surface)
– outer shell e- can give bonding information about the samples!! –

very useful in surface science
• Cathodoluminescence
– again similar to X-ray and Auger,
but energy is conserved by the emission of a photon in the IR / Visible / UV range

Resolution of SEM

Resolution is the ability to resolve two closely spaced points. While you may have to be at a high magnification to see small features, resolution is NOT the same as magnification

One way to improve resolution is by reducing the size of the electron beam that strikes the sample:

$$d_{min} = 1.29 C_s^{1/4} \lambda^{3/4} [7.92\,(iT/J_c) x 10^9 + 1]^{3/8}$$

at low current: $d_{min} = 1.29 C_s^{1/4} \lambda^{3/4}$

J_c = current density of the source, λ = electron wavelength
C_s = spherical aberration, i = current, T = temperature,

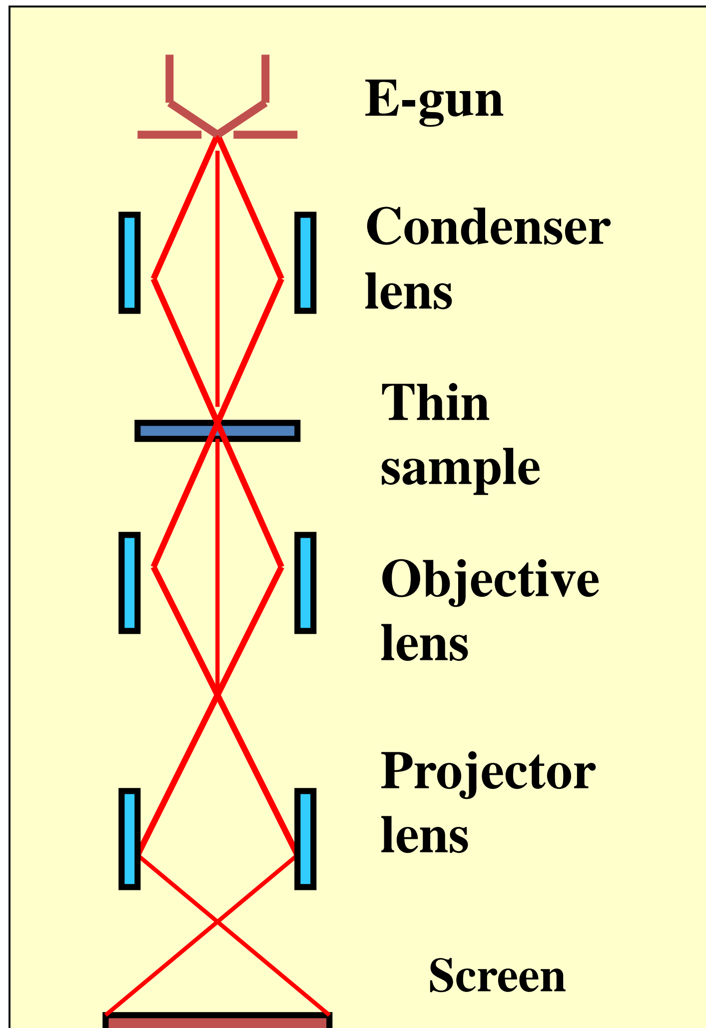
We can also improve the resolution by:

- Increasing the strength of the condenser lens
- Decreasing the size of the objective aperture
- Decreasing the working distance (WD = the distance the sample is from the objective lens)

Transmission Electron Microscopy (TEM)

- **Transmission electron microscopy** (**TEM**) is a microscopy technique whereby 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 a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

Principle: Transmission Electron Microscopy (TEM)

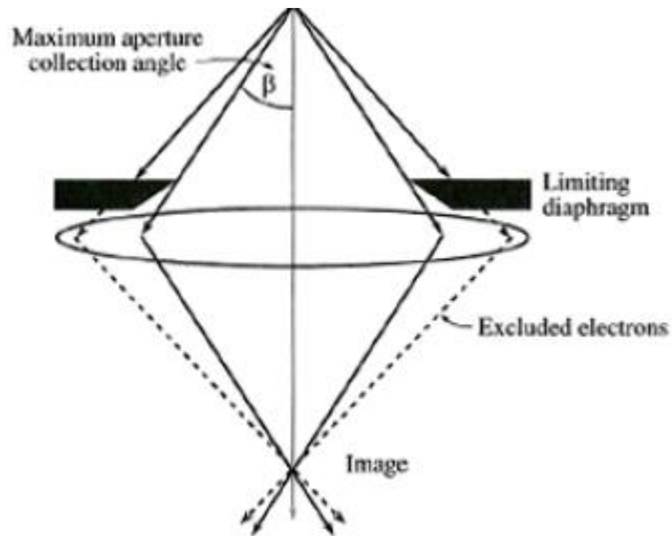


- Beam size: a few – 30 A
- Beam Voltage: 40kV- 1MV
- Resolution: 1-2A
- Imaging radiations: transmitted electrons,
- Imaging contrast: Scattering effect
- Magnification: 60x-15,000,000x
- Image Contrast:

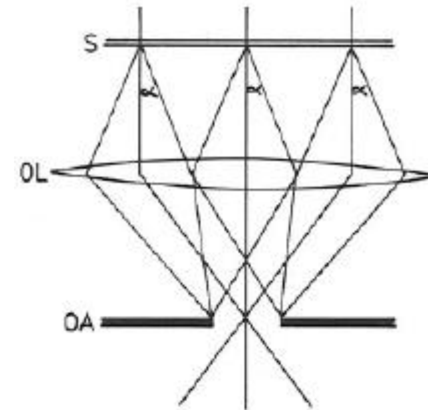
1) Amplitude (scattering) contrast
   - transmitted beam only (bright field image)
   - diffraction beam only (dark field image)

2) Phase (interference) contrast
   - combination of transmitted and diffraction beam
   - multi-beam lattice image: atomic resolution (HRTEM)

Condenser aperture and Objective aperture

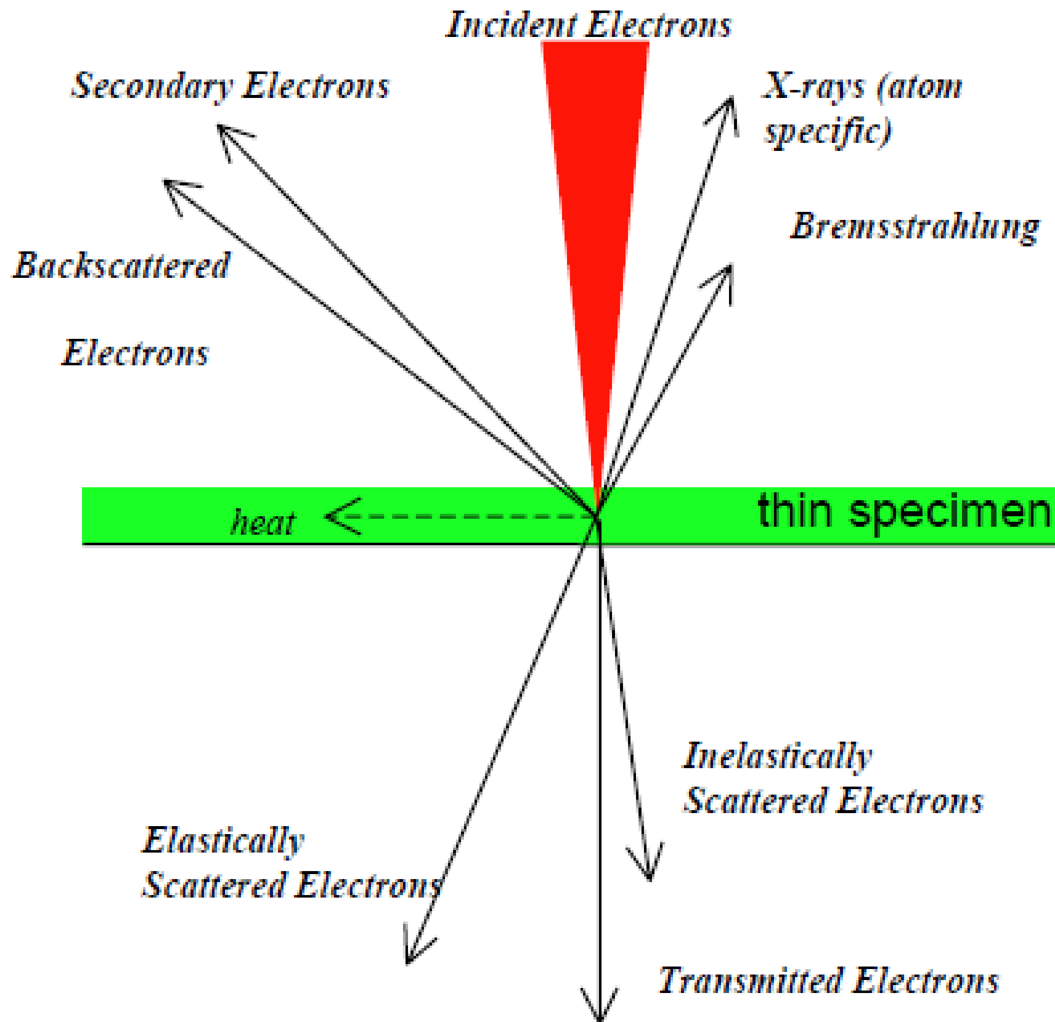


Ray diagram illustrateing how a diaphragm restricts the angular spread of electrons entering the lens. Only electron paths less than a semi-angle β subtended by the aperture at the object are allowed through the lens.

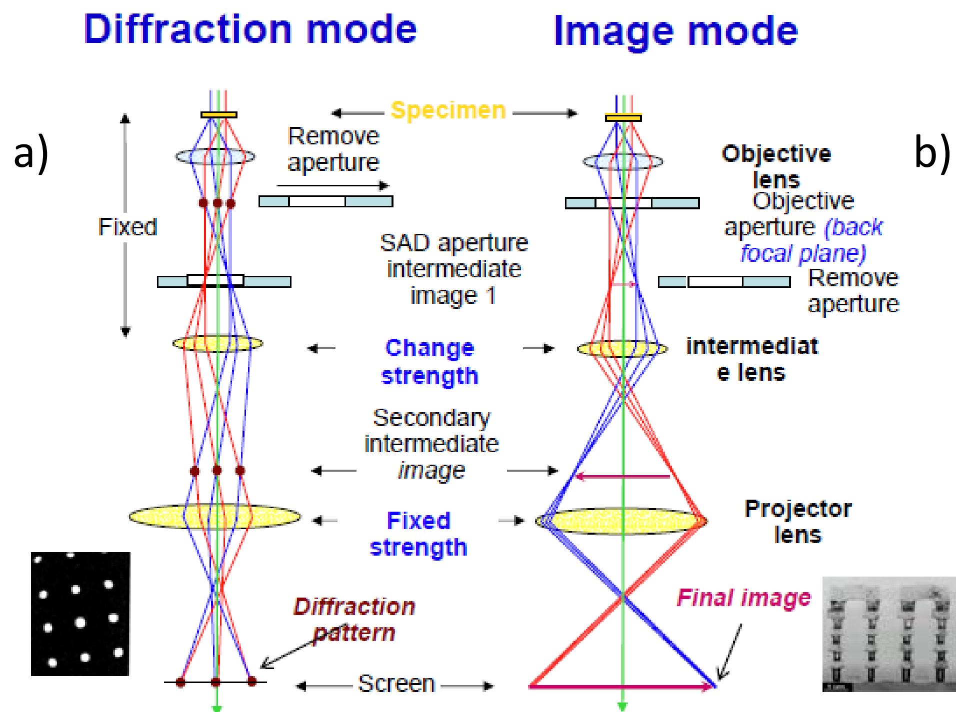


The objective aperture (OA), located at the Back focal Plane

Interaction of Electrons with Sample



Formation of the diffraction pattern and the image in the TEM



the *magnification* of the image is controlled by the projection lenses (3-4 lenses)

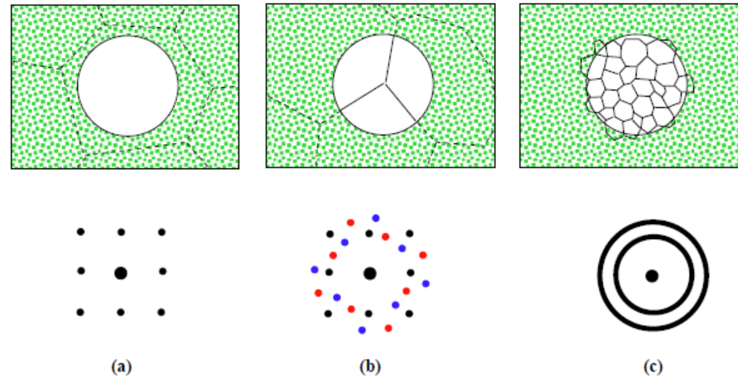
- $M = M_{obj.} \times M_1 \times M_2 \times M_3 \ldots$
- Obj: 50-100x
- Proj: ~ 20x for each
- The image is finally projected on the fluorescent screen

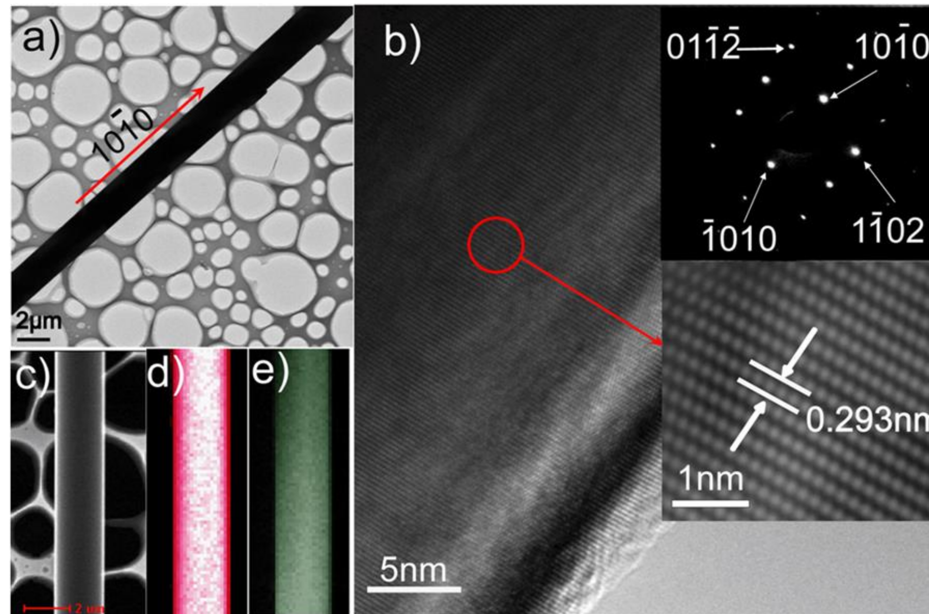
The objective and first intermediate lenses. The objective lens (OL) is focused on the specimen and form an intermediate image as shown in (b).

In order to make the diffraction pattern visible, *in diffraction mold* the intermediate lens is refocused on the back focal plane of the objective lens (BFP) and the diffraction pattern is passed to the projector system (a).

In imaging mold the intermediate lens (IL) magnifies this image further and passes it to the projector lens for display.

Electron Diffraction Pattern--Spot to Ring and Examples of the TEM in characterization



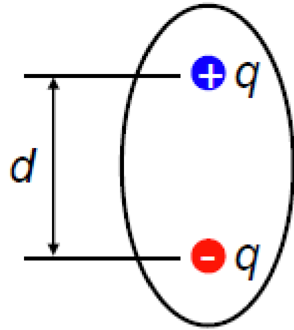


TEM image of a single ZnO microwire; (b) HRTEM image of the microwire. Inset images are the SAED pattern and Fourier filtered HRTEM; (c) a typical TEM image of the ZnO microwire; (d)-(e) the distribution maps of Zn (red) and Na (green) by EDX, respectively.

Raman

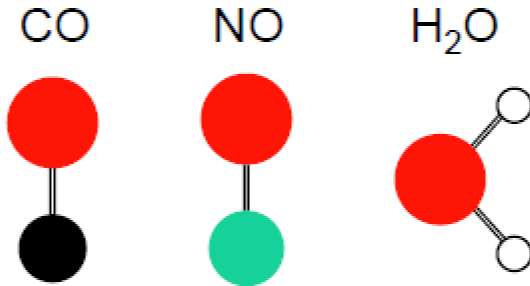
- Raman spectroscopy is concerned with radiation scattering from a sample.
- Scattering occurs when an incident photon interacts with the electric dipole of a molecule.
- This scattering process can be either elastic or inelastic.
- Most incident photons are elastically scattered by the molecule (Rayleigh scattering).
- In Rayleigh scattering the energy of the incident photons equals the energy of the scattered photons.
- A small fraction of light is scattered at energies different than that of the incident photons (Raman effect).
- The Raman effect is an inelastic process and was first observed in 1928.
- Chandrasekhara Venkata Raman awarded Nobel prize in 1930.

Electric Dipole Moment



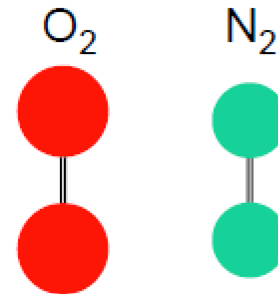
For a single dipole with a distance, d, between charges –q and +q, the dipole moment is: $p = qd$

Heteronuclear diatomics and asymmetric triatomics:



Have permanent dipole moment

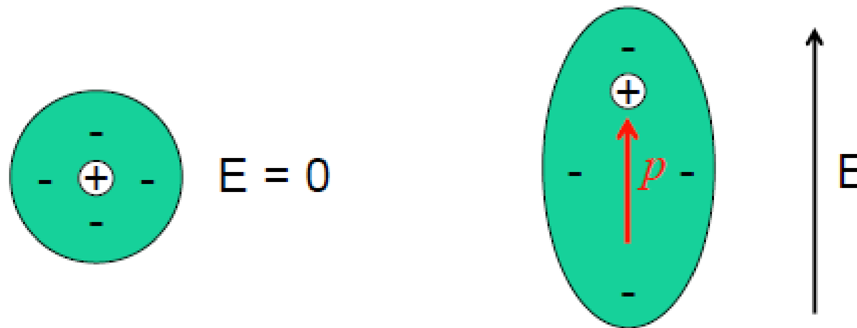
Homonuclear diatomics:



No permanent dipole moment

Induced Dipole Moment

A dipole moment may be created through:
- electronic excitation
- the polarizability of the molecule in the presence of an electric field (e.g. from a light wave of a laser)



Induced dipole moment: p

α: molecular polarizability
E: electric field

$$\vec{p} = \alpha \vec{E}$$

(polarization = vector sum of the dipole moments per unit volume)

Rayleigh scattering

Incident oscillating electric field: $\vec{E}_i(t) = \vec{E}_0 \cos \omega_0 t$

⇒ Induced oscillating dipole moment: $\vec{p}(t) = \alpha \vec{E}_i(t)$

Accelerating charges can emit radiation

⇒ the oscillating dipoles will **radiate at the same frequency as the applied field.**

This is the **Rayleigh scattering.**

However, considering the polarizability, α, to be a fixed constant is just an approximation, sufficient to describe the elastic Rayleigh scattering. In fact, α may change as the molecule vibrates and rotates ⇒ **vibrational and rotational Raman scattering**

Assume that Q is a function describing the motion of a particular vibrational mode:

$$Q = Q_0 \cos \omega_{vib} t \qquad \alpha(Q) = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q}\right) Q + \ldots$$

(ω_{vib}: vibrational frequency of the molecule)

$$\vec{p}(t) = \alpha(Q)\vec{E}_i(t) = \left(\alpha_0 + \left(\frac{\partial \alpha}{\partial Q}\right) Q_0 \cos \omega_{vib} t\right) \vec{E}_0 \cos \omega_0 t$$

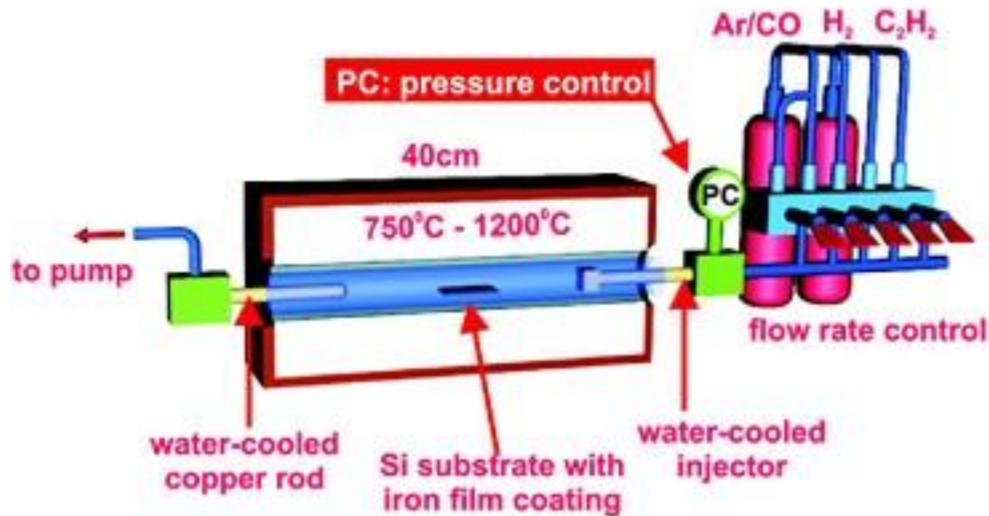
$$= \underbrace{\alpha_0 \vec{E}_0 \cos \omega_0 t}_{\text{Rayleigh}} + \frac{Q_0 \vec{E}_0}{2}\left(\frac{\partial \alpha}{\partial Q}\right)\{\underbrace{\cos[(\omega_0 + \omega_{vib})t]}_{\text{anti-Stokes}} + \underbrace{\cos[(\omega_0 - \omega_{vib})t]}_{\text{Stokes}}\}$$

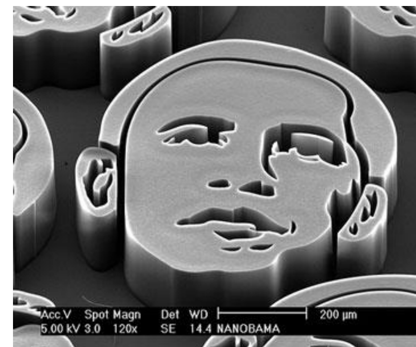
Carbon Nanomaterial Fabrication and applications of the Nano Characterization

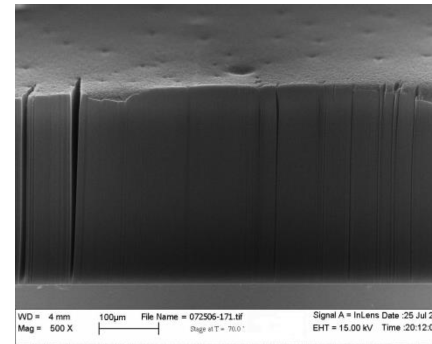
1.CNT fabrication and characterization
2. Graphene fabrication and characterization

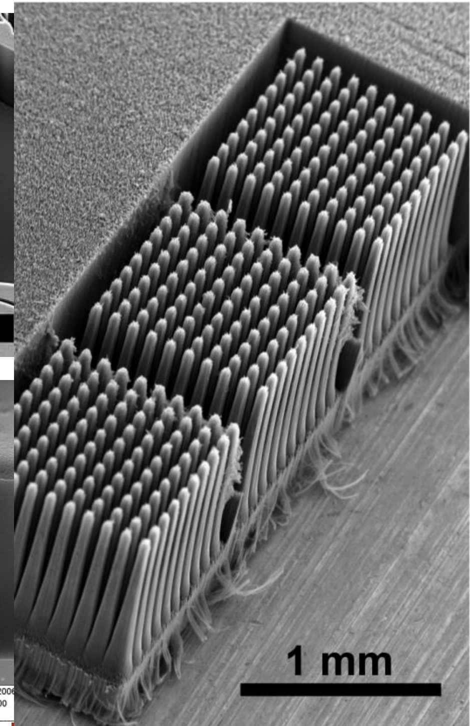
CNT Synthesis

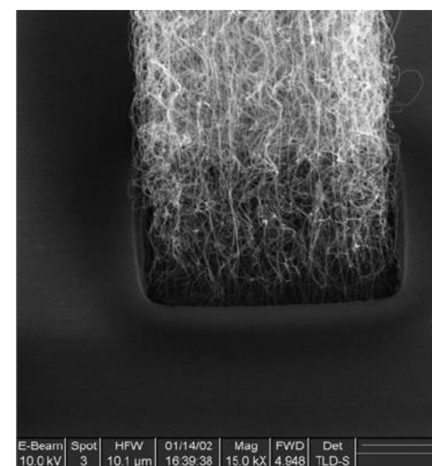
Schematic of a CVD System





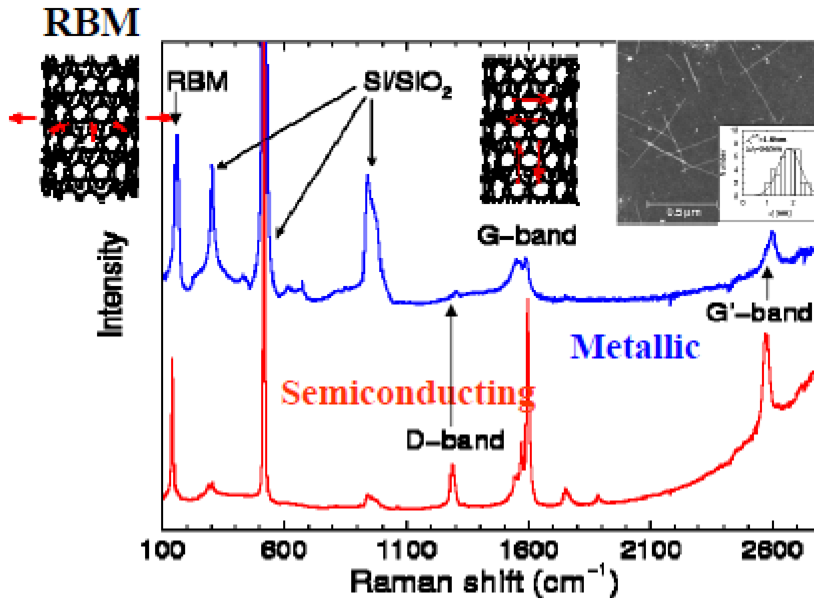






Catalyst nanocluster: Fe, Ni or Co and a reducing gas (H2 or NH3)
Carbon containing compound (gas): CH4, C2H2, CH3CH2OH….
Energy (Temperature): 400-1400 ^{0}C

Single Nanotube Raman



Information from Raman spectra:

Metal / Semiconducting nature: *G Band lineshape*

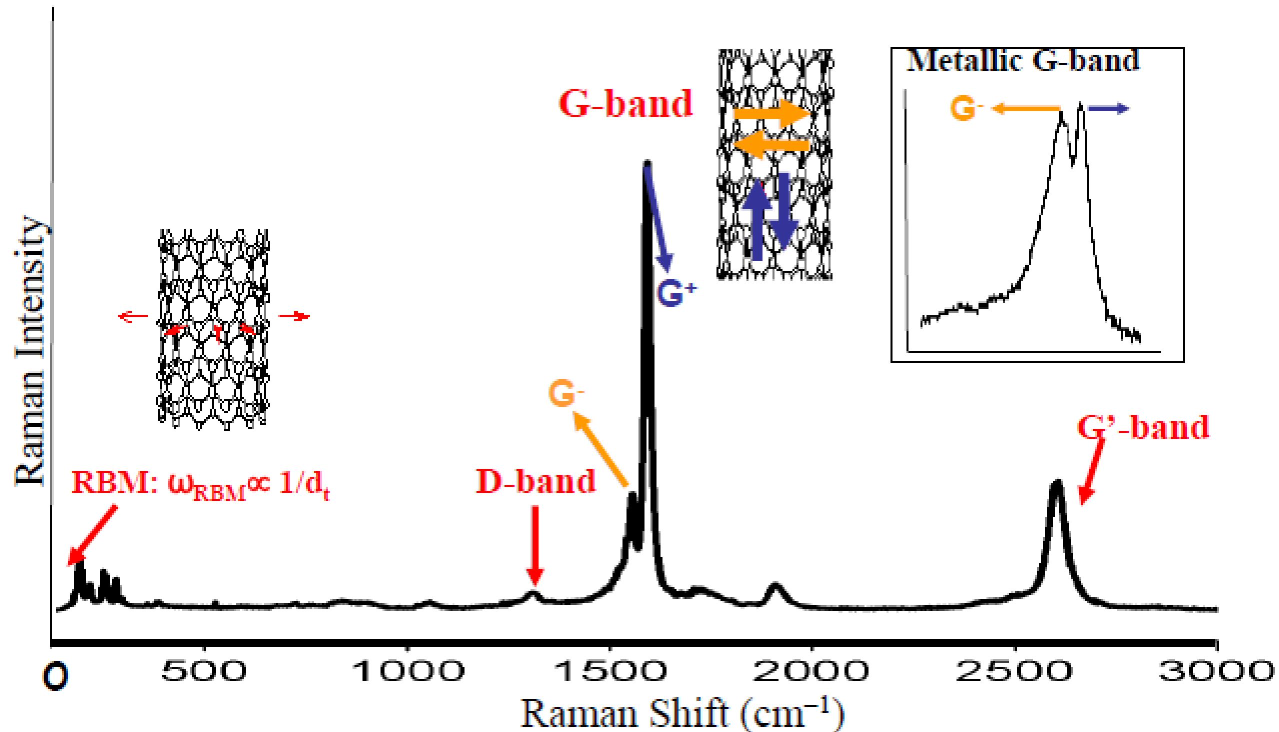
- Diameter (±5%): Inverse to RBM
- Rough chirality *(n,m): Eii and ω_{RBM}*
- Orientation of a nanotube: Polarized Raman Intensity
- Defect concentration: *D Band Intensity*
- Strain / Temperature effects :*G band frequency shift*

The large density of states at resonance enables single nanotube spectroscopy

- The geometrical structure of an individual carbon nanotube can then be found

A. Jorio et al., Phys. Rev. Lett. 86, 1118 (2001)

Raman Spectra of SWNT Bundles

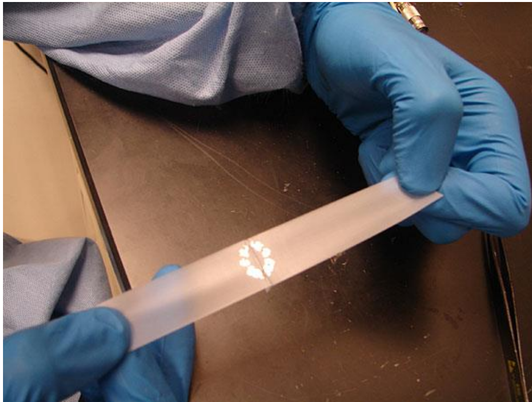


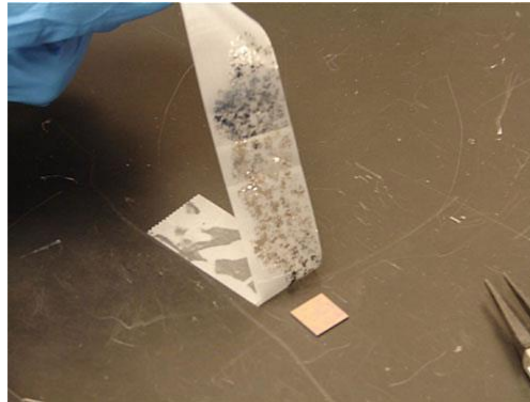
RBM gives tube diameter and diameter distribution

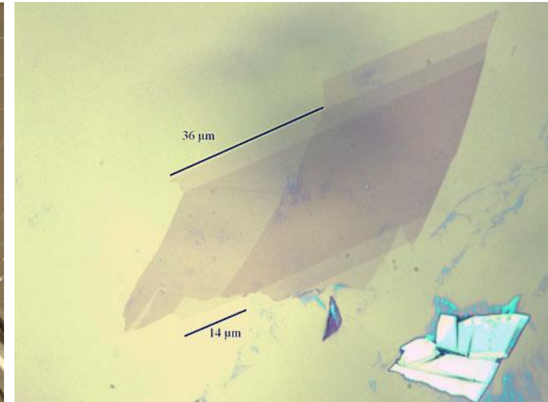
- Raman D-band characterizes structural disorder
- G- band distinguishes M from S tubes and G+ relates to charge transfer
- G' band at ≈ twice the D-band frequency provides connection of phonon to its wave vector
- Each feature in the Raman spectra provides complementary information about nanotubes

How to make graphene? Approach 1: Scotch Tape

High quality and
High Mobility

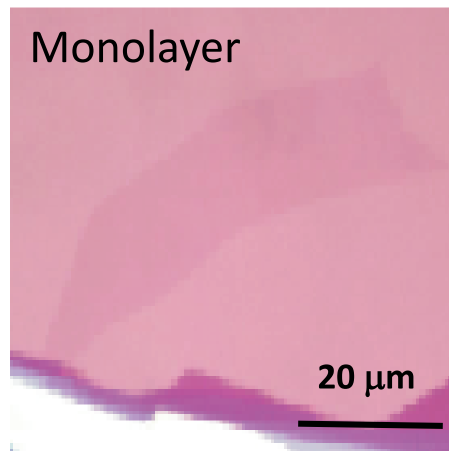


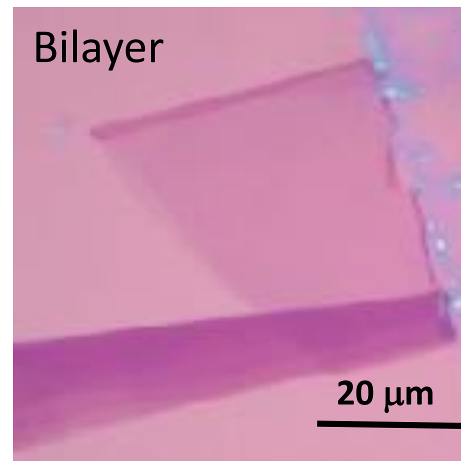




Peel off HOPG   Transfer to substrate   OM image on ssubstrate

Exfoliated Graphene Monolayer and Bilayers

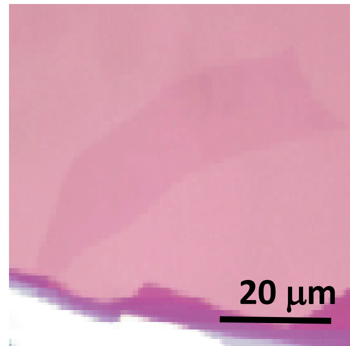




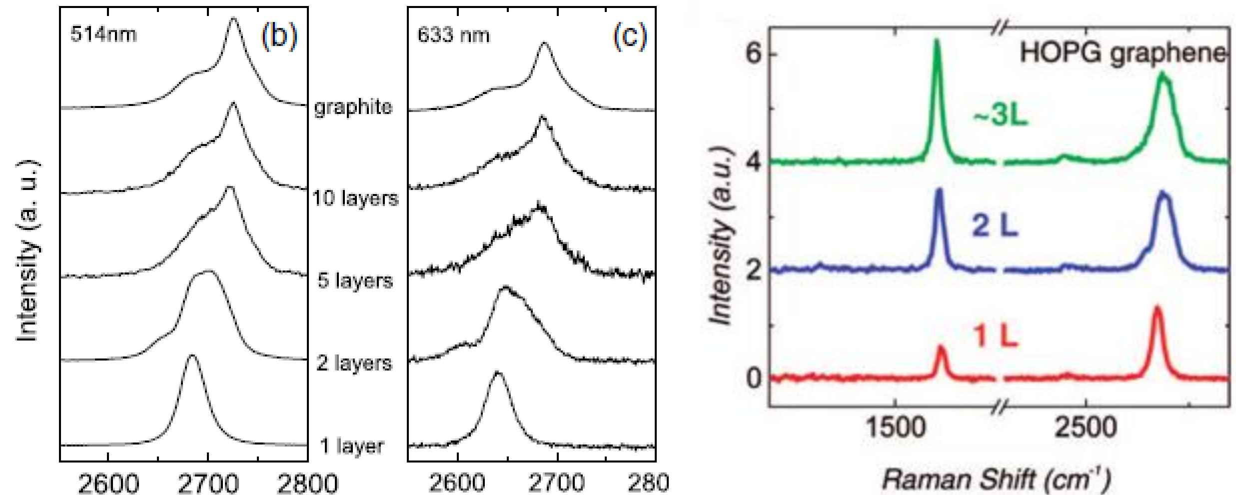
K. S. Novoselov *et al.*, *Science* **306***,* 666 (2004).

Application of Raman: Thickness Estimation of Graphene

Raman spectra



Graphene

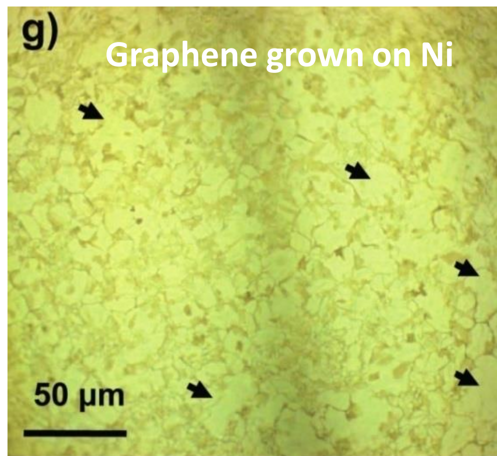


Ferrari et al., *Physical Review Letter* 2006

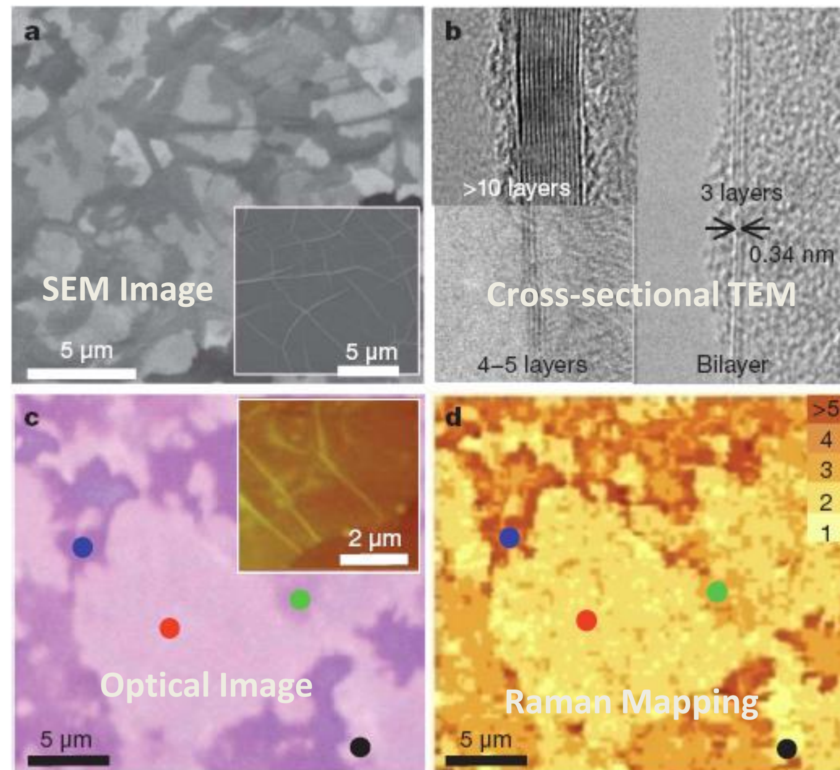
Raman scattering is sensitive to the number of layers

- Ratio of 2D/G
- Position of 2D and G peak
- Full width at half maximum (FWHM)
- Fast and reliable detection

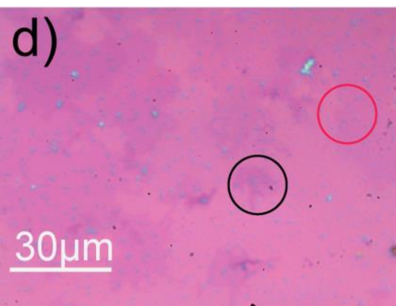
Graphene Growth on Ni film using CVD

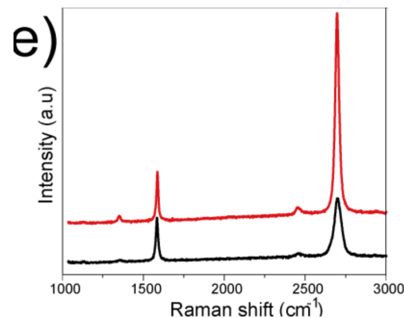


A. Reina et al., *Nano lett.*, 2009



K.S, Kim et al., *Nature* 2009



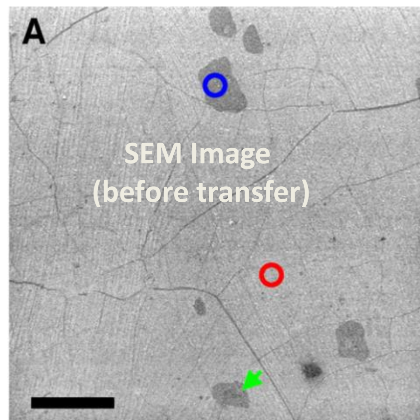


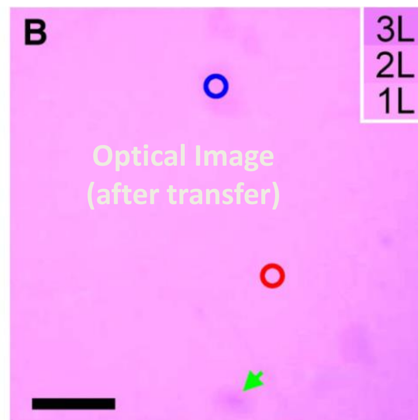
W. Liu et al., *Thin Solid Film* 2010

Current Status :

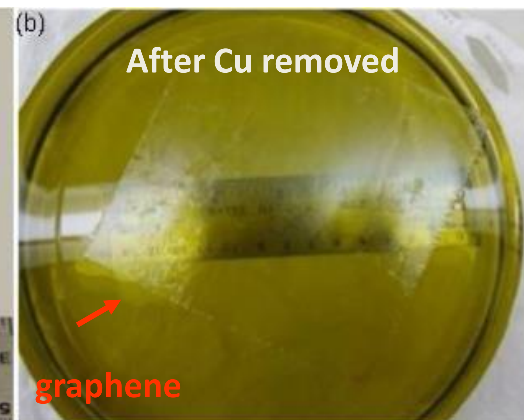
- Thermal CVD, high temperature, hard to control number of layer due to high temperature growth.
- Uniforminat y lower than Copper.
- Low quality due to the low cooling rate, H_2 etching .

Graphene Growth on Cu-foil using CVD





X. S, Li et al., *Science* 2009



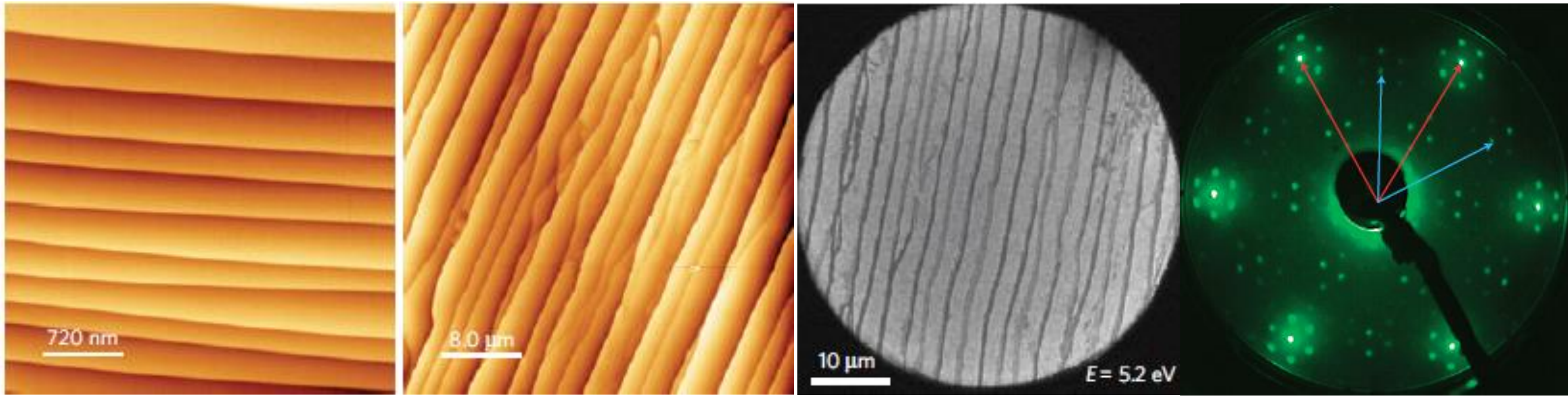
H. L, Cao et al., Arxiv/0910.4329

Mechanism

- Solubility of carbon in Cu is nearly zero @1000C, carbon atoms diffuses on Cu surface
- Cu grain size is larger than Ni

- **Pros: Larger grain with high graphene quality**
- **Cons: Due to low melting point of Cu, need to use thick Cu foil rather than thin Cu film**

How to produce graphene? Approach 3: SiC



AFM SiC

AFM Graphene

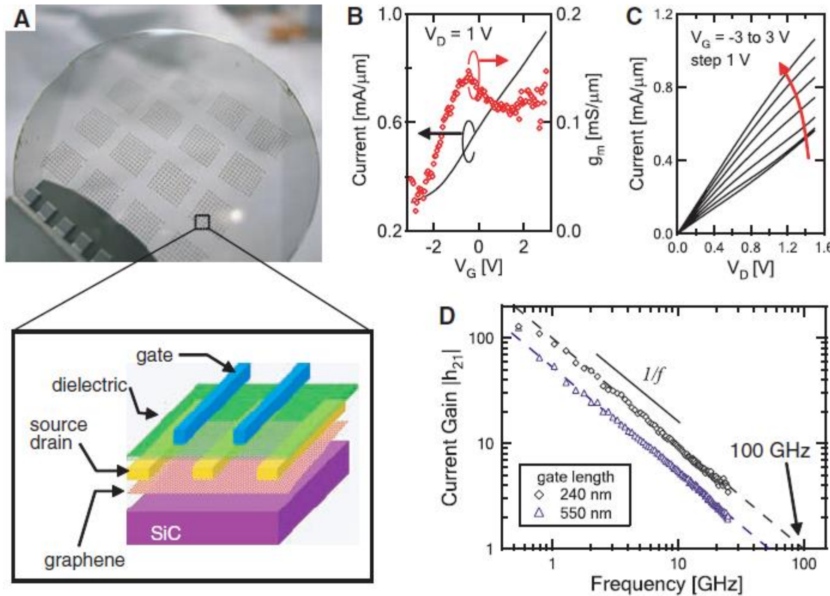
LEEM image

LEED pattern

Emtsev et al., *Nature Mat*. 2009

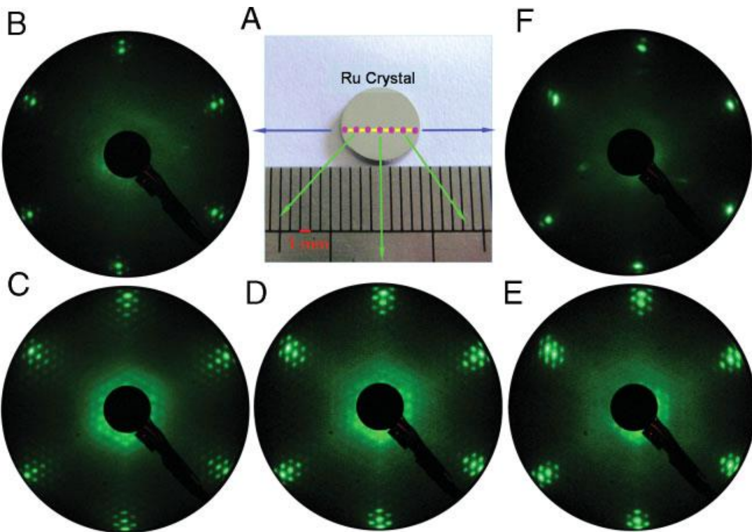
High temperature annealing

High temperatures (>1100 ° C)



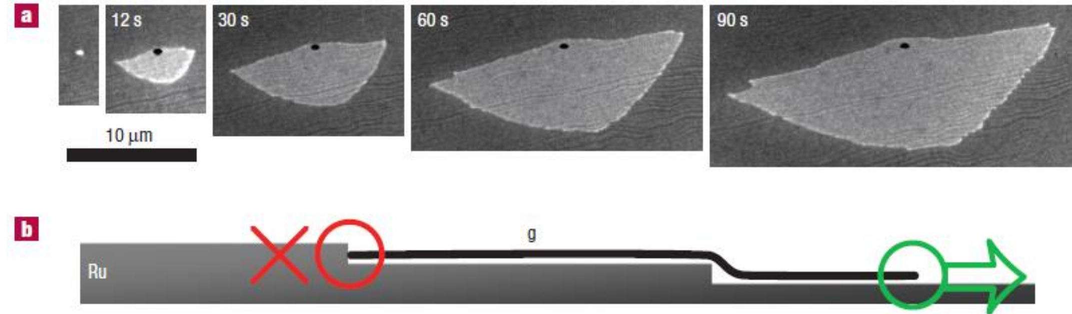
Lin et al., *Science, 2010*

How to make graphene?



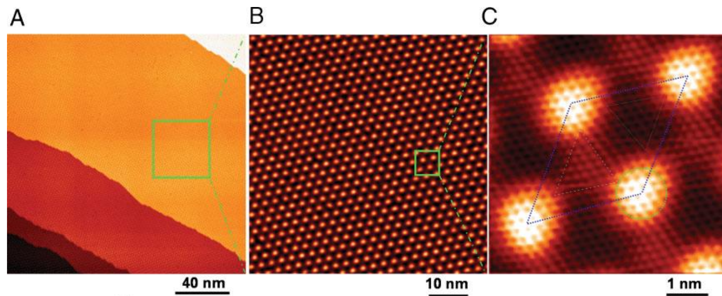
LEEM Pattern of the graphene on Ru

Approach4: single Crystalline metal



In situ microscopy of graphene epitaxy on Ru(0001).

Sutter et al., *Nature Materials*, 2008



STM image

Annealing at high temperature 1100-1500C
UHV needed
Expensive Singlecrystalline
Hard to transfer graphene to diltric substrate.

Pan et al., *Advanced Material* **2009**

How to make graphene?

Approach 2: Reduce GO

H_2SO_4

K_2MnO_4

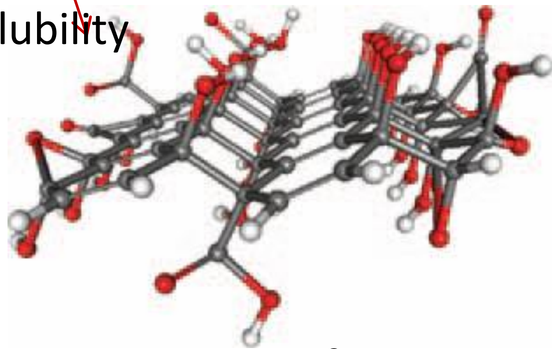
Graphite

Reaction

Graphite Oxide

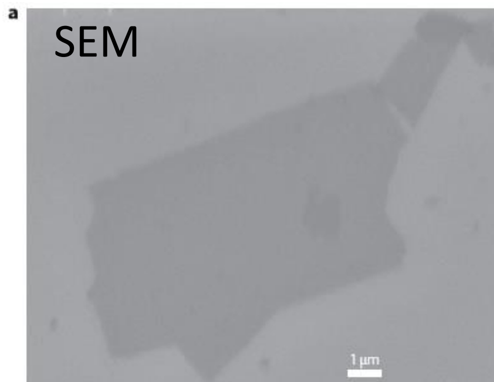
Water-solubility

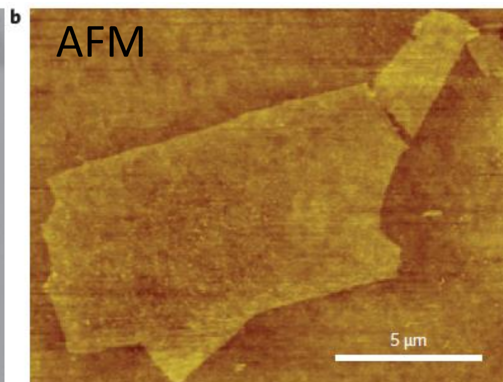
Graphene

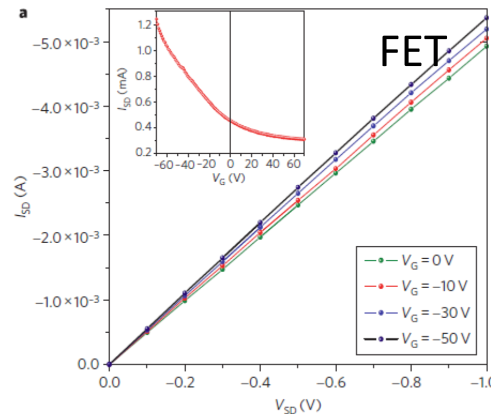


Structure of GO

N2H4





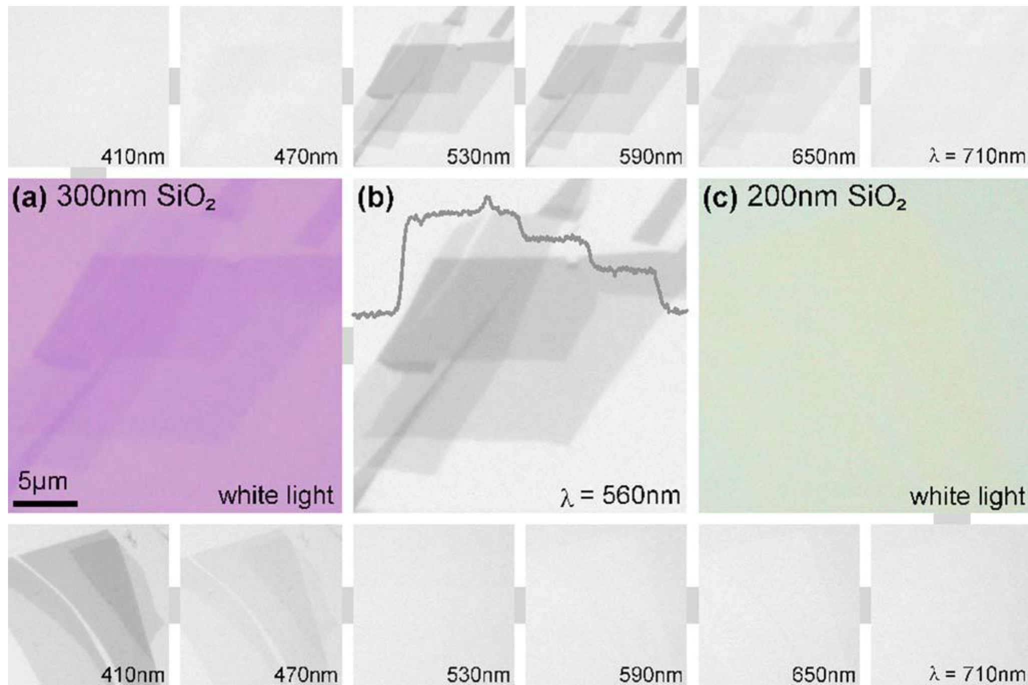


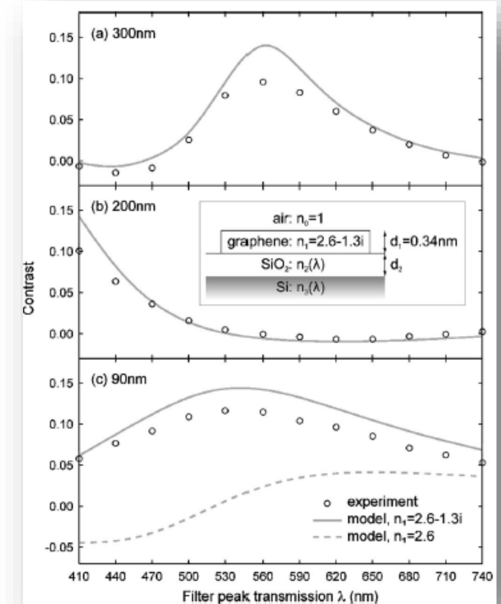
Huge mount defects

Poor Mobility

Tung et. al., *Nature nano* 2009

Visualization of Graphene



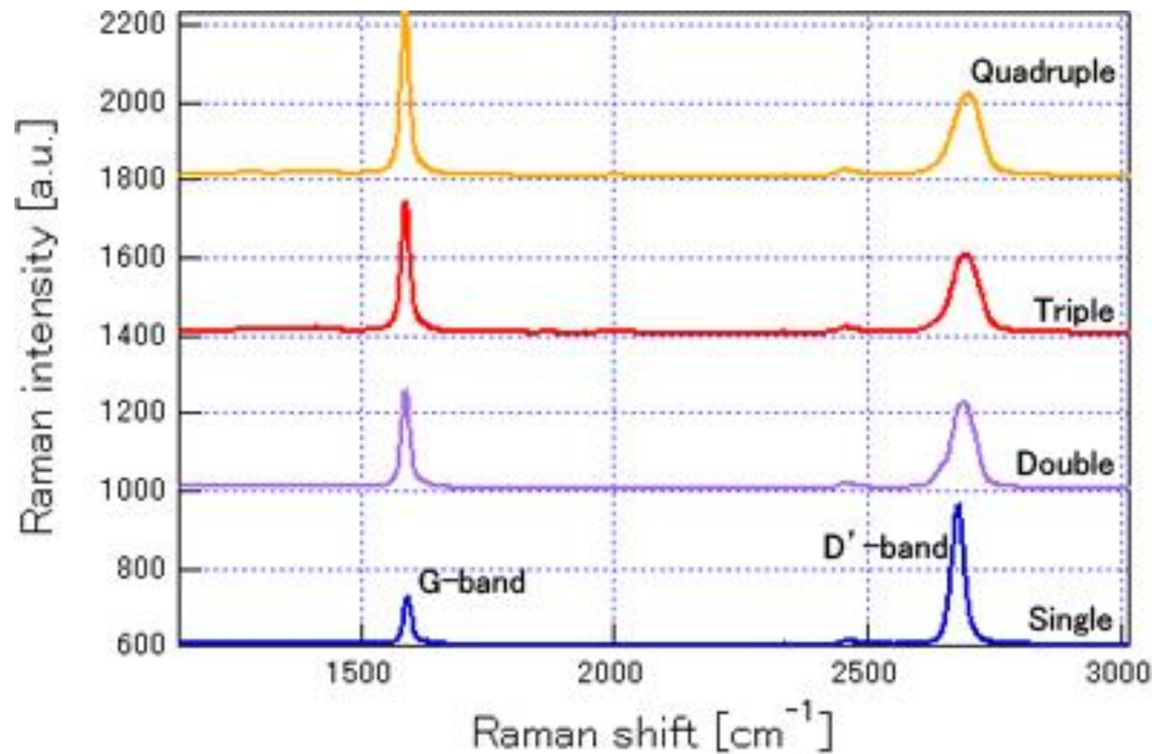


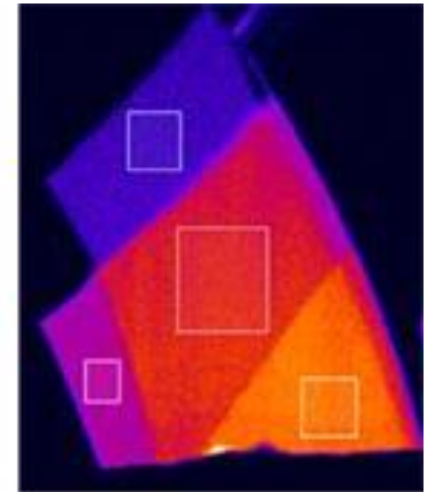
Contrast in optical image strongly depends on the thickness of oxide as well as the wavelength of illuminating light.

The best thickness
(SiO_2): 90nm,300nm

Blake et.al., *Applied Physics Letter*, 2007, 063124,

Thickness Estimation of *Graphene*



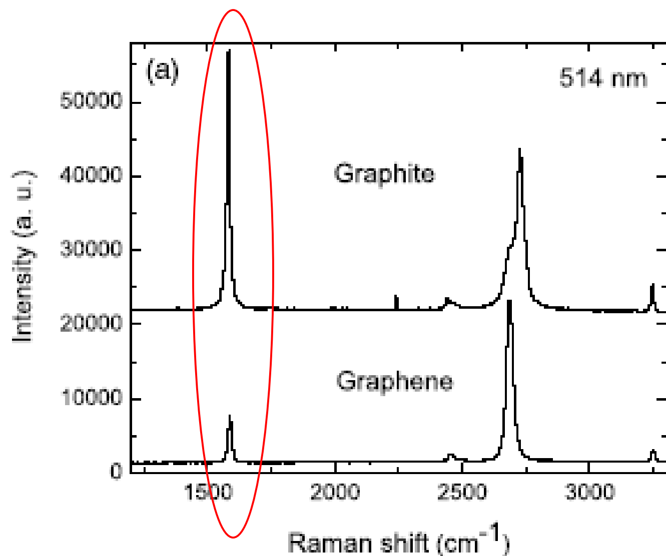


HOPG graphene

Raman scattering is found to be sensitive to the number of layers .

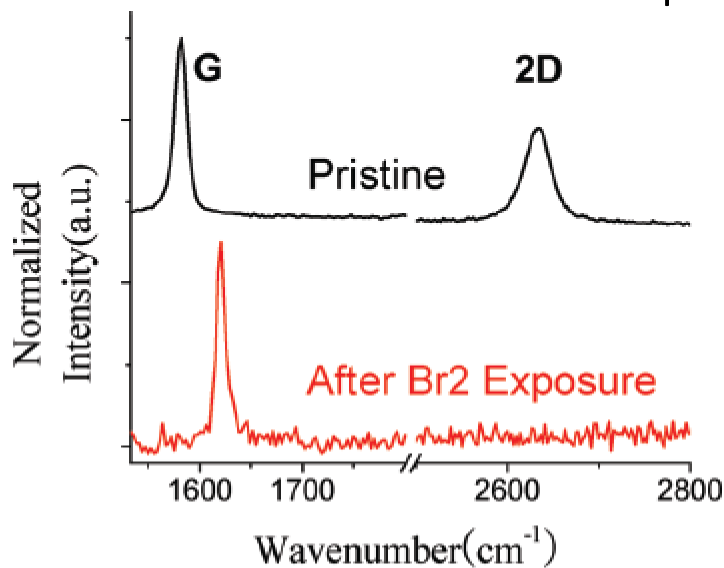
1. Ratio of 2D/G
2. Position of 2D and G peak.
3. The H of the 2D peak.

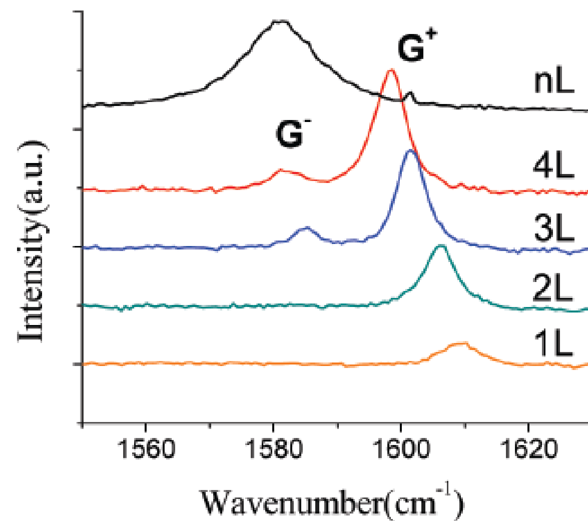
G-Band



- Most prominent line around 1580 cm-1
- Relative Intensity enhances with the number of layers
- Shift :chemical doping.

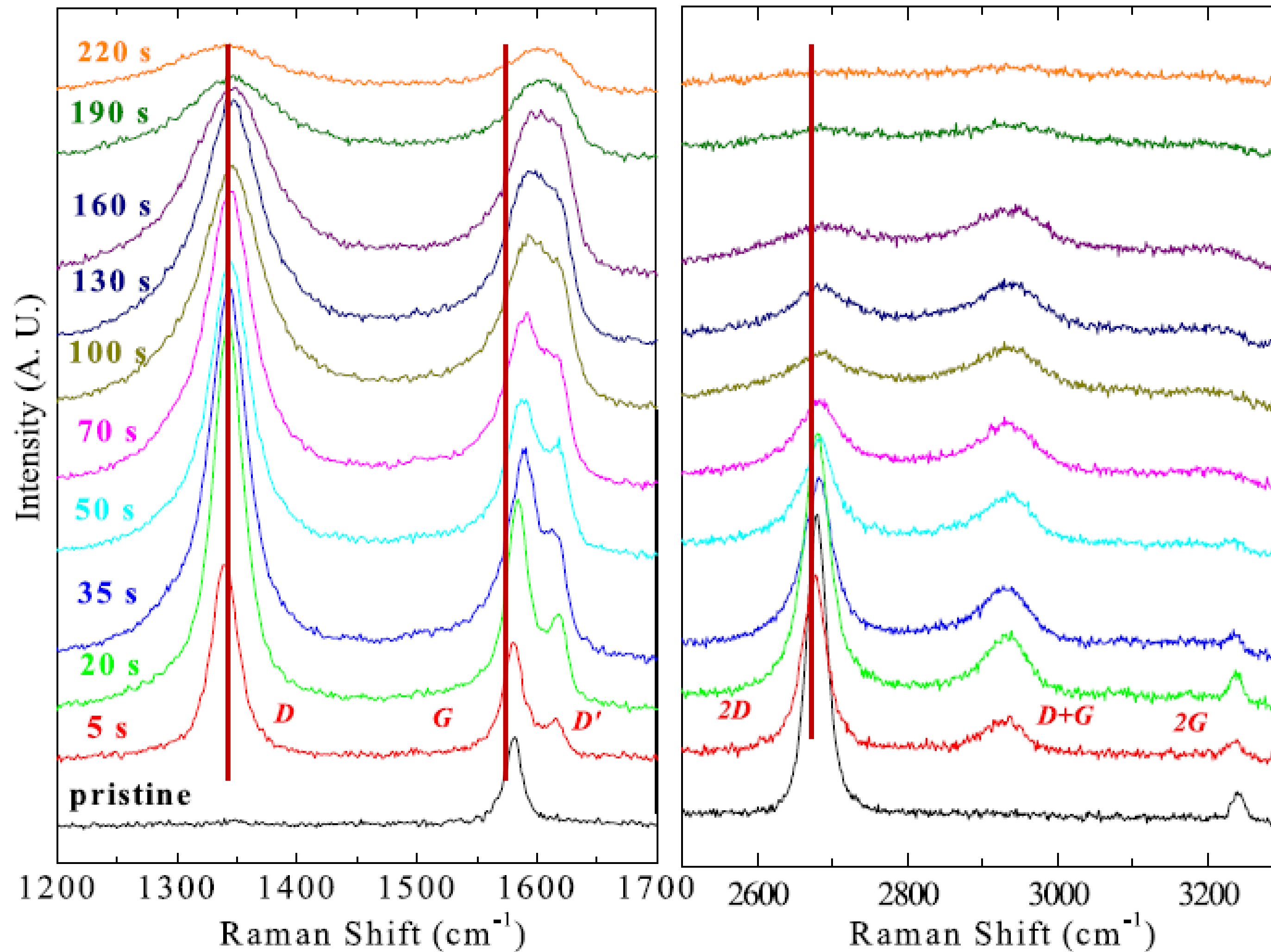
Br dope Grpahene





*Nano Lett., Vol. 9, No. 12, **2009***

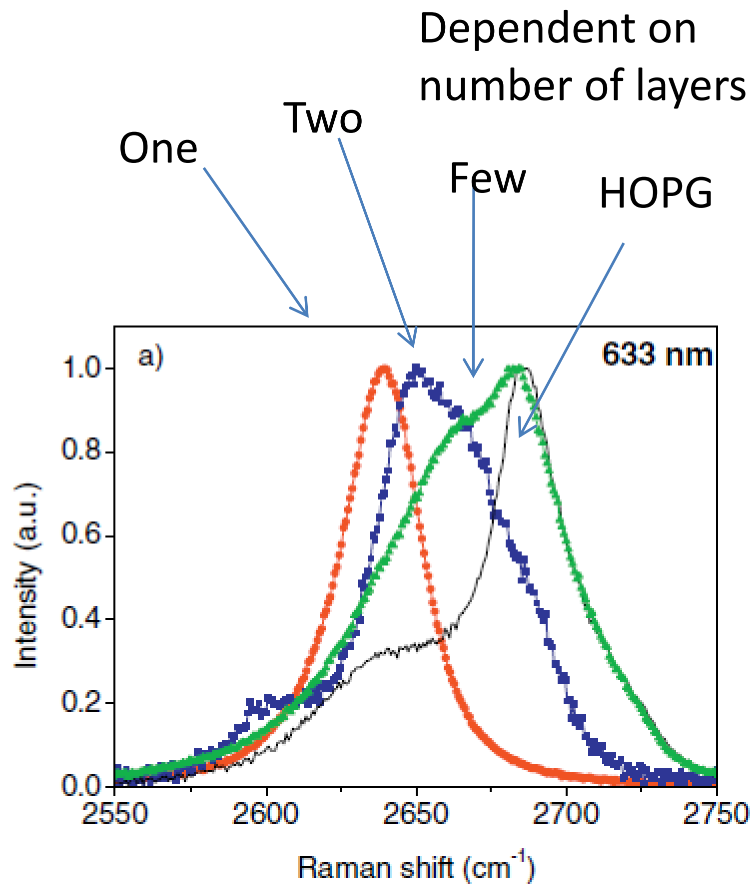
Raman spectra of Oxygen Doping

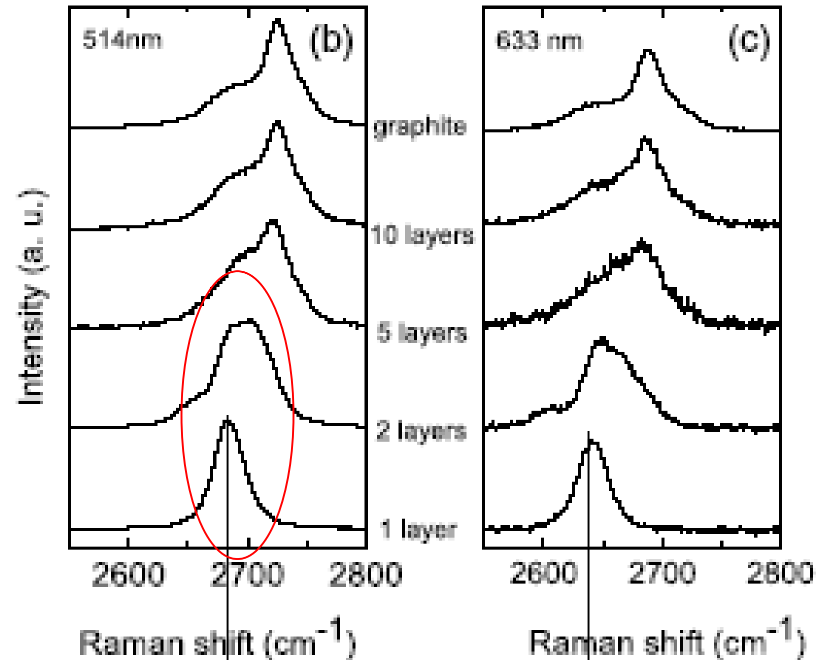


G band is sensitivity to doping than D and 2D

Nanotechnology 20 (2009) 375703

2D-Band

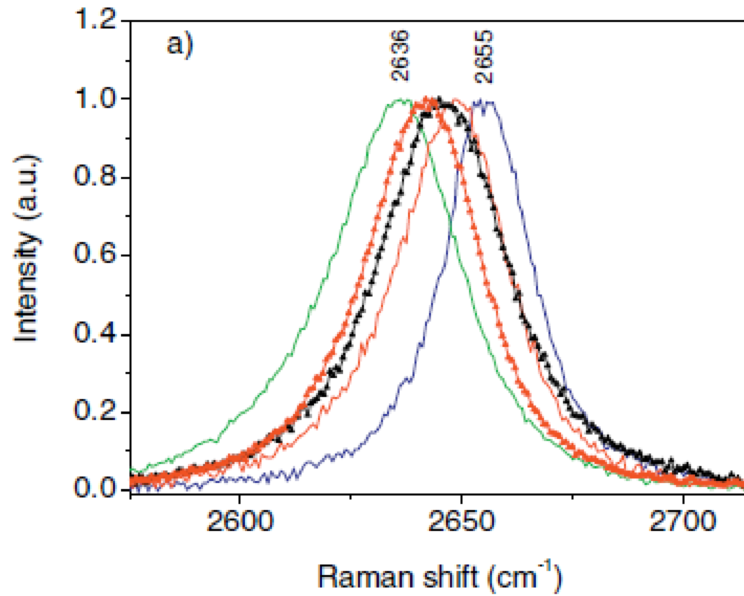


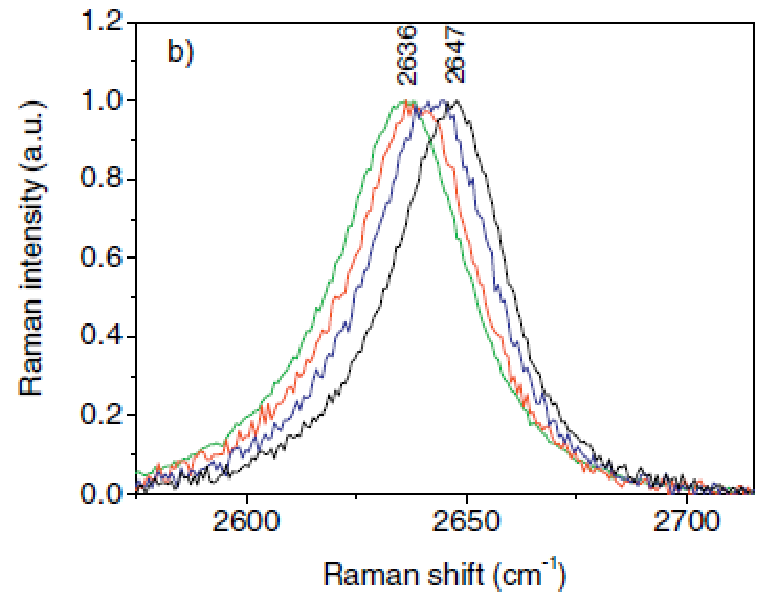


Wavelength dependent

- Line shape and position sensitive to the number of layers

Raman Shift of 2D

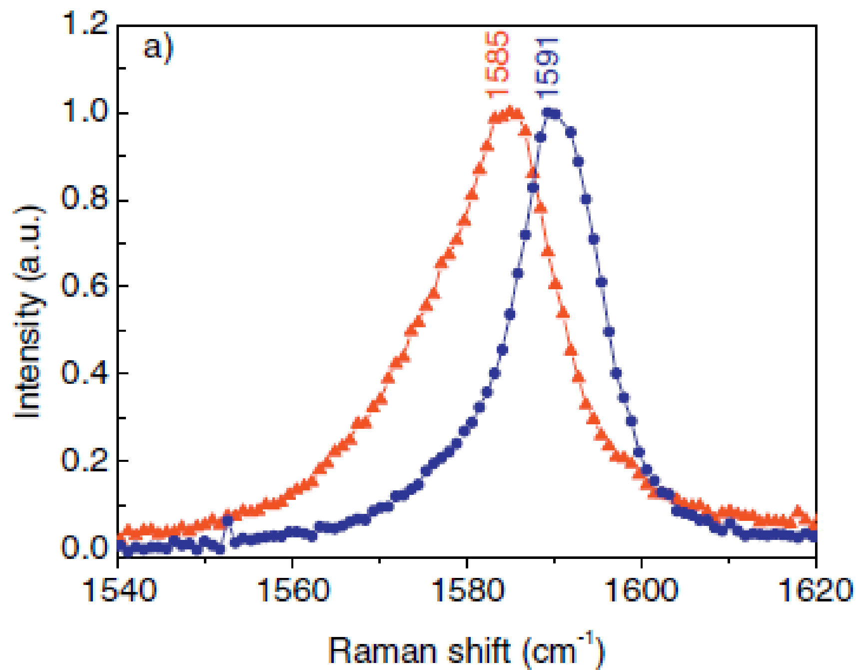


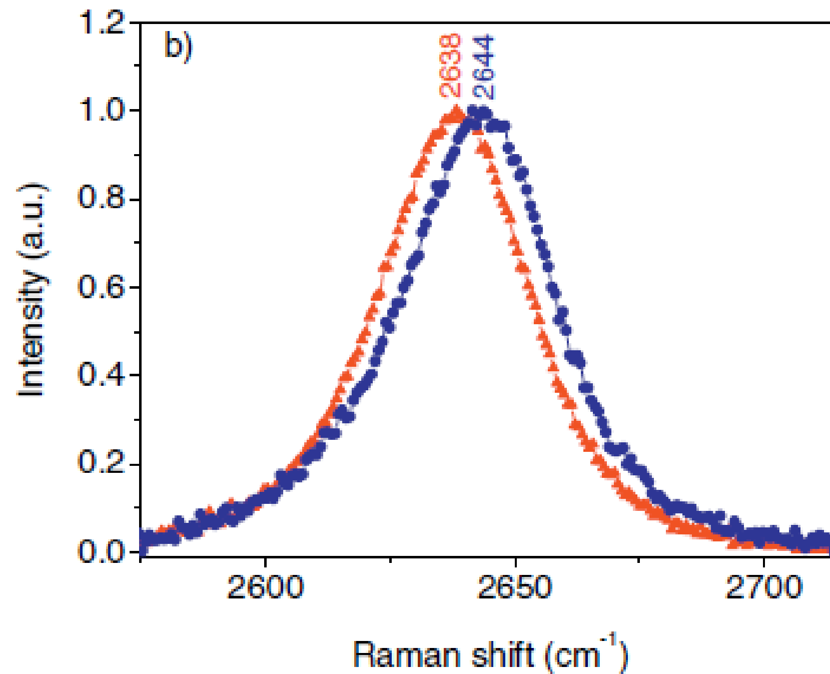


a)continuous lines indicate flakes on SiO_2 and lines with triangles correspond to flakes on Al_2O_3.
b) The same as in a) but for different sites within one long graphene flake.

shifts of Raman modes are not predominantly determined
by different types of surfaces

Raman Shift of 2D

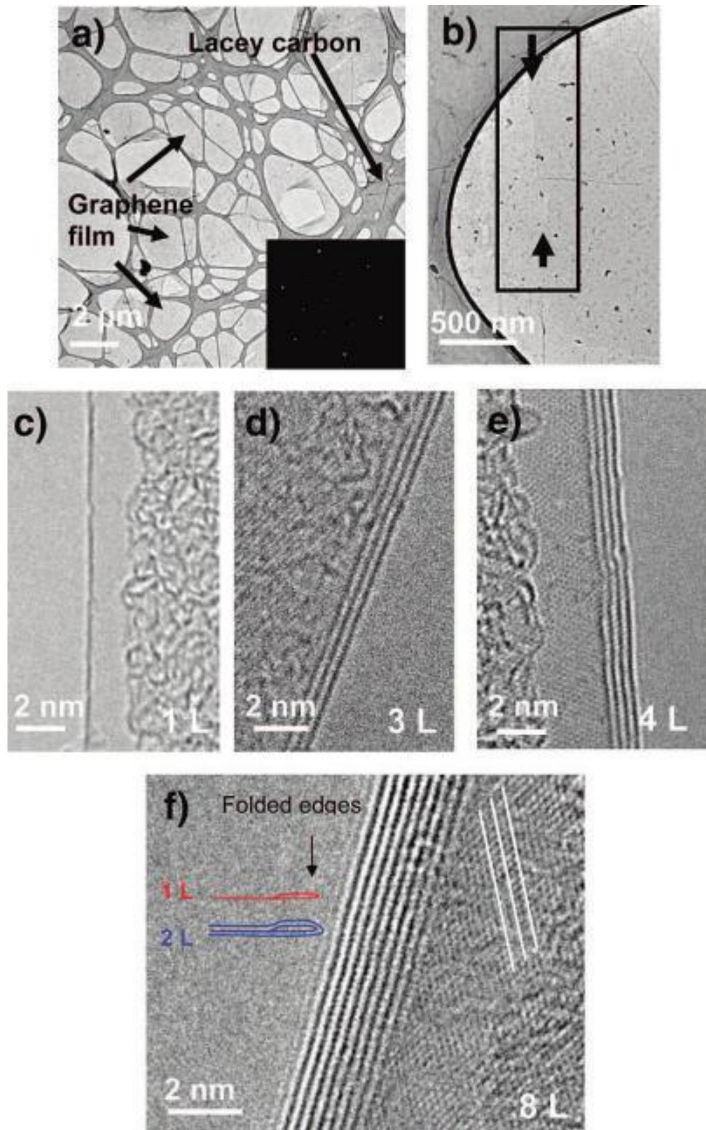




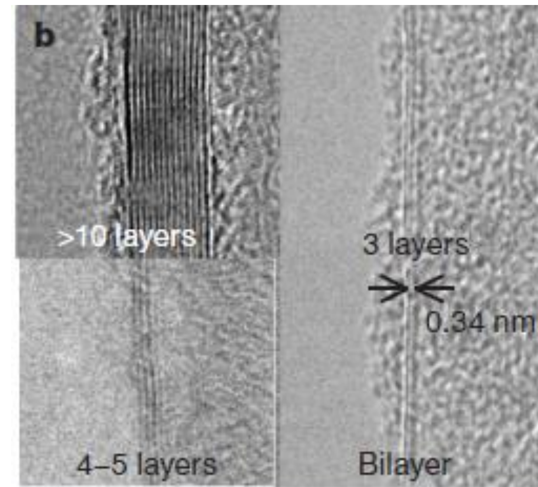
a) G and b) D* modes of a graphene layer, measured with the 633 nm excitation line, before (blue bullets) and after (red triangles) the heat treatment in argon atmosphere.

Water and impurity can cause the shift of 2D

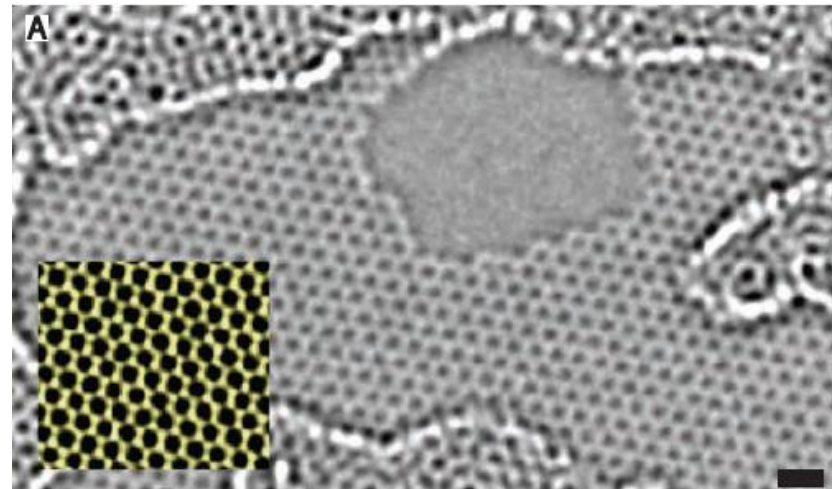
TEM of Graphene



Observe number of layer



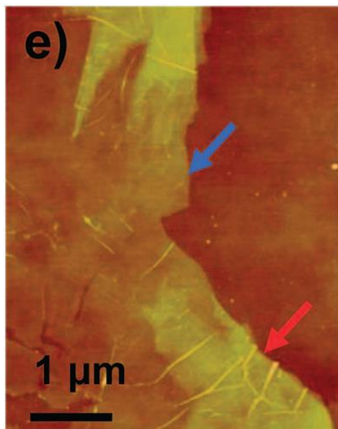
TEM images of graphene films of different thicknesses

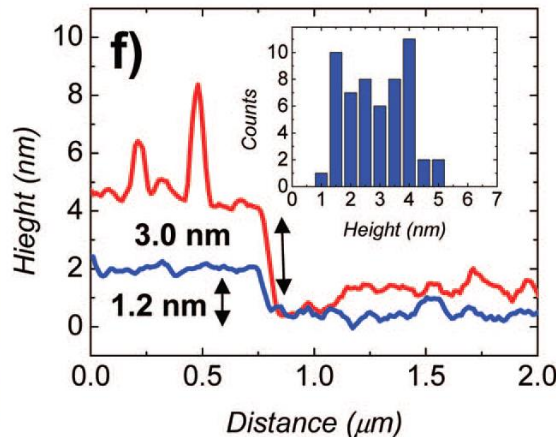


Directly observe graphene structure

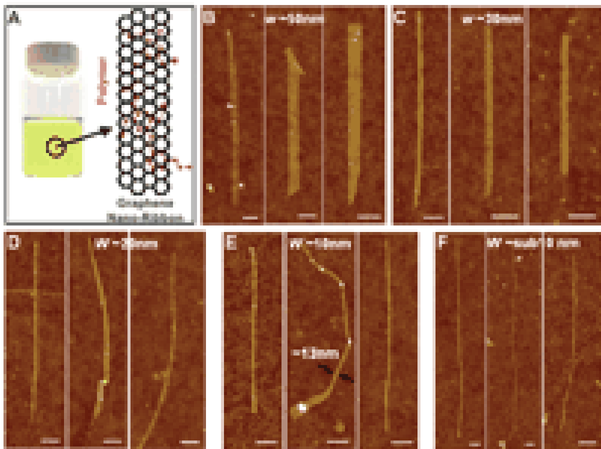
AFM and STM

AFM image

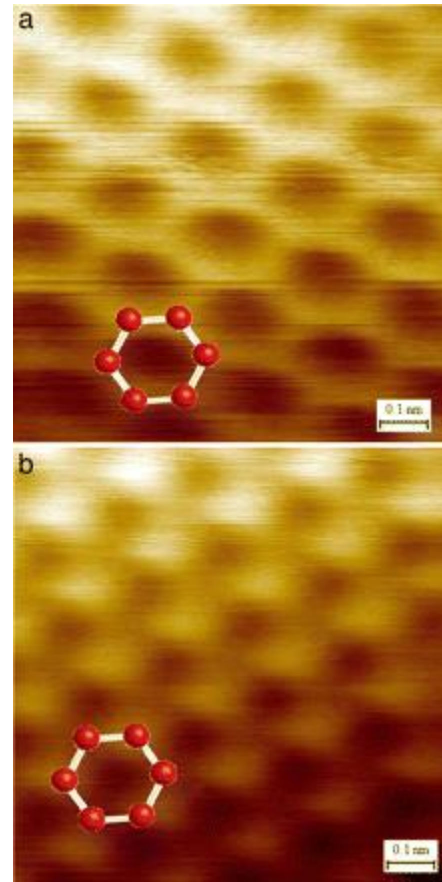




Measure height distribution



Measure narrow width



STM

Directly observe graphene lattice structu