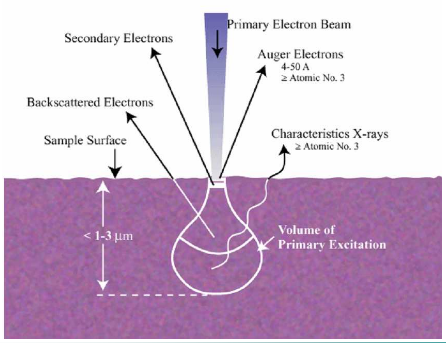
Lecture 7

Electron mean free path
Microscopy principles of SEM, TEM
Nanofabrication and Lithography

References:

1) L. Reimer, "Scanning Electron Microscopy - Physics of Image Formation and Microanalysis", 1985.
2) R.E. Lee, "Scanning electron microscopy and X-Ray microanalysis, 1993.
3) Woodruff & Delchar, Chapter 2 and pp. 449-460.
4) Attard and Barnes, pp,25-28, 47-62.
5) Kolasinski, pp.84-91, 107-108.
6) LEEM: http://www.research.ibm.com/leem/#item2

Electron beam interactions with the sample



7.1 Electron Scattering

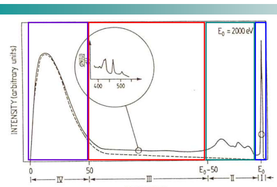
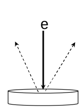


Fig. V.2. Qualitative large-scale overview of the energy distribution of electrons emitted from a surface which is irradiated by an electron beam of primary energy E_0.

Electron diffraction and microscopy:

Elastic backscattered e^-, ~ few % at 100eV

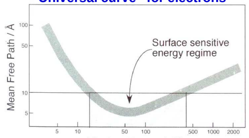


II: Interaction with plasmons

III: Inelastic electrons, Auger

IV: Secondary e^-s, <50eV

"Universal curve" for electrons

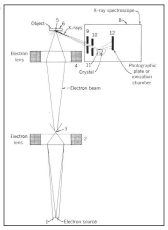


Short inelastic mean free path for electrons means that elastic scattering of electrons is **very surface sensitive**

History of the Electron Microscope

1937: grad students J. Hillier and A. Prebus at U of Toronto built an electron microscope that magnified 7000x

1940 Hillier hired by RCA to build an electron microscope to sell (and pay back his salary!) (Electron microscope, U.S. Patent No. 2,354,263; 1944)



From Hillier's patent

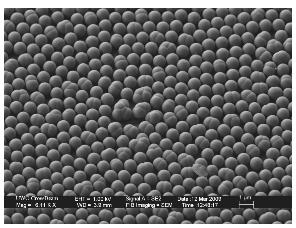
***Ernst Ruska* and *Max Knoll* built the first electron microscope in 1931**
(Nobel Prize to Ruska in 1986)

7.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM)

- topology, morphology, chemical information (BSE and EDX)

- 0.5-1000keV electron energy
- field of view 0.1 - 100 µm
- 5 nm resolution in plane
- Magnification 10x – 300,000x
- Typical operating pressure <1atms
- Non-destructive nature: though sometimes electron beam irradiation can cause sample damage

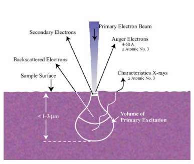


by Eric Barbagiovanni

- **Advantages**: surface, common technique
- **Disadvantages**: vacuum compatibility; coating non-conductive specimens, typical cost: US$50,000 to 300,000

Electron beam-solid interactions

Secondary electrons (SEs): are produced by the interactions between energetic e's and weakly bonded valence e's of the sample



Backscattered electrons (BSEs): are primary e's leaving the specimen after a few large angle elastic scattering events

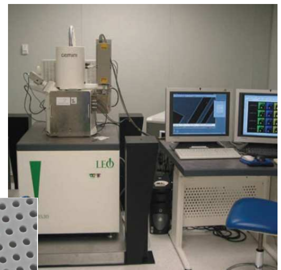
Auger electron: incident e^- kicks out an inner shell e^-, a vacant e^- state is formed; this inner shell vacant state is then filled by another e^- from a higher shell, and simultaneously the energy is transferred to another e^- that leaves the sample

Characteristic X-rays: emitted when a hole is created in the inner shell of an atom in the specimen due to inelastic e^- scattering, as it can recombine with an outer shell e^- (EDX)

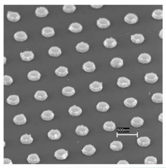
Cathodoluminescene (CL): light emission arising from the recombination of e-h pairs induced by excitation of e's in the valence band during inelastic scattering in a semiconducting sample

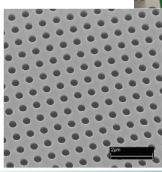
SEM/e-beam lithography in the Nanofab

The e-beam lithography system (right) is a LEO 1530 field emission scanning electron microscope (FE-SEM) fitted with a laser interferometer controlled stage (middle right).



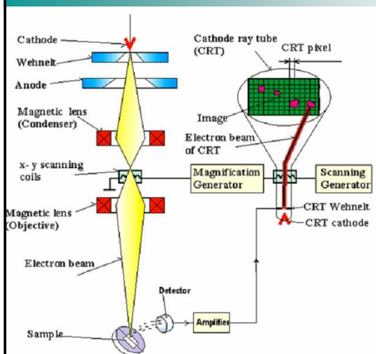
The micrograph (bottom right) shows a square array of 300nm holes on 700nm pitch written in PMMA on Si. Also shown is an array of Cr dots on Si patterned by e-beam lithography and liftoff (below).





http://www.uwo.ca/fab/

Schematic diagram of SEM



Filament (cathode): free e's by thermionic emission of W, LaB_6

Wehnelt Cylinder: focuses the e-beam and stabilizes beam current

Anode Plate: maintains the HV difference between the anode and the cathode, and accelerates the free electrons down the column

Condenser Lens: reduces the diameter of the electron beam to produce a smaller spot size

Scan Coils: electromagnetically raster the e-beam on the surface

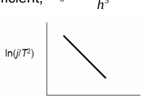
Final Objective Lens: focuses the e-beam on the surface; the smallest spot is about 5 nm (~ 1nm with a FI source)

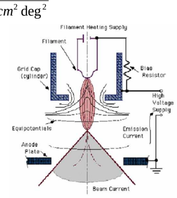
Detectors: within the scope chamber, but not part of the column are the detectors

Electron Sources: Thermionic Emission

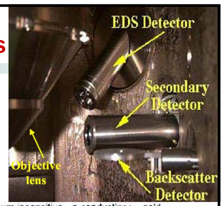
Thermionic emission occurs when sufficient heat is supplied to the emitter so that e's can overcome the work function, the energy barrier of the filament, E_w, and escape from it

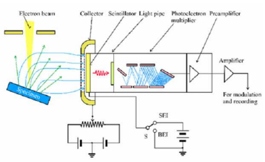
- **Richardson's Equation**: (derivation – aside)
  Current density, *j*: $j = A_o(1-\bar{r})T^2 \exp(-\frac{e\phi}{kT})$
  r = reflection coefficient; $A_o = \frac{4\pi mek^2}{h^3} = 120.4\frac{Amp}{cm^2 \deg^2}$
- **Richardson plot**:
  ln(j/T²) *vs* 1/T ⇒
  ⇒ straight line



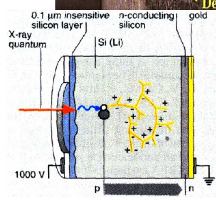


SEM Detectors





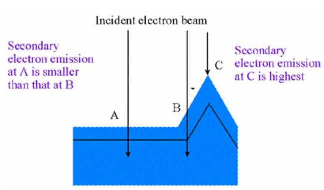
Everhart-Thornley (E-T) detector

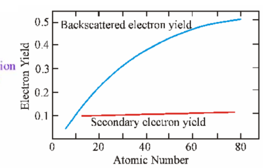


EDX spectrometer

Contrast of secondary electron micrograph

Contributions from (a) sample topography and (b) compositional contrast





Q: Why do the backscattered electron micrographs, rather than secondary electron micrographs reveal the compositional contrast?

7.3 Transmission Electron Microscope (TEM)

Multipurpose machine!

Elastic scattering:

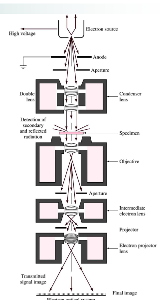
• atomic structure (lattice parameters, orientation) (~1pm)

• microstructure and defects (~1nm-1μm)

Inelastic scattering

• Chemistry EDX (~ 1nm) and EELS

- 100-3000keV electron energy
- resolution in plane 1nm (TEM) 0.6Å (HRTEM, current record)
- **Advantages**: atomic resolution and depth resolution
- **Disadvantages**: difficult sample preparation, need UHV



http://www.thebiotron.ca/modules-imaging.php

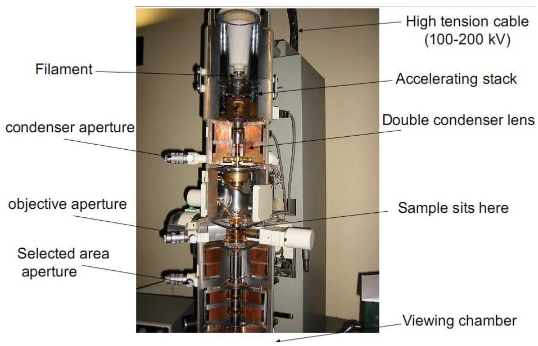
http://www.brockhouse.mcmaster.ca/facilities/tem.html

http://videolectures.net/kolokviji_gloter_tem/

http://www.ccmr.cornell.edu/igert/modular/docs/1_electron_microscopy.pdf

http://www.rodenburg.org/RODENBURG.pdf

Inside HRTEM



Sample preparation

Cross-section preparation (1-1.5 days)
- gluing face-to-face
- cutting a slice
- mechanical polishing down to a thickness of 30µm
- ion milling until perforation

FIB: a bit faster…

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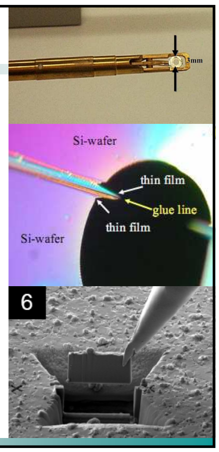
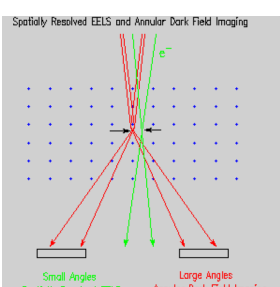


STEM- High Angle Annular Dark Field (HAADF)



Detect only scattering at high angle,

Primary sensitive to the atomic number and thickness

"vacuum": black

High Z elements: bright

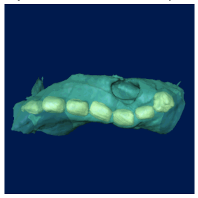
Low Z: grey…

http://www.research.ibm.com/atomic/batson/adfstem.htm

HAADF STEM Tomography

HAADF images show little or no diffraction effects, and their intensity is ~ Z^2.

This imaging technique proves ideal for tomographic reconstruction as it generates strong contrast that has a fully monotonic relationship with thickness.

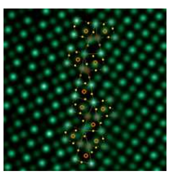


Magnetite crystals in bacteria strain MV-1, in this preparation the cell is preserved around the crystals.

The tilt series was acquired from +76 degrees to - 76 degrees; each crystal is ~60nm long.

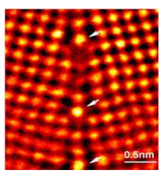
http://www-hrem.msm.cam.ac.uk/research/CETP/STEM_Tomo.html

Applications of HRTEM



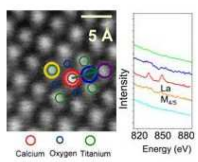
Direct Determination of Grain Boundary Atomic Structure In $SrTiO_3$

McGibbon MM et al., *Science* **266,** 102 (1994)



Impurity-Induced Structural Transformation of a Grain Boundary

Y. Yan et al, *Phys. Rev. Lett.* 81, 3675 (1998)



Single Atom Spectroscopy

M. Varela et al., *Physical Review Letters* **92**, 095502 (2004)

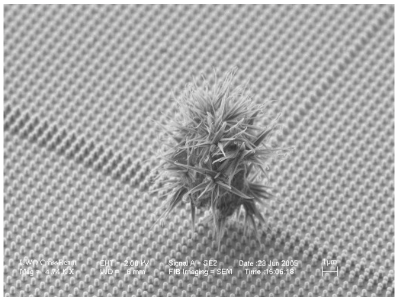
http://stem.ornl.gov/highlights.html

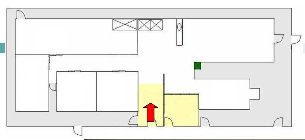
7.4 Nanofabrication and Lithogrpahy

Macro
- Machine Shop
- drilling, milling, cutting, welding, screws
- 3D objects assembled from pieces
- Start with CAD drawing

Micro
- Cleanroom
- lithography to define areas where we deposit, remove (etch) or modify (implant)
- 3D objects built layer by layer on a flat substrate
- Start with CAD drawing

Cleanroom





7.4.1 Thermodynamics and kinetics of thin film growth

What is a "thin film"?

How thin films are different from the bulk materials?

Thin films may be:

- Lower in density (compared to bulk analog)
- Under stress
- Different defect structures from bulk
- Ultra-thin films (<10-20nm): quasi two dimensional
- Strongly influenced by surface and interface effects

Steps in thin film growth

- Separation of particles from source (heating, high voltage)
- Transport
- Condensation on substrate

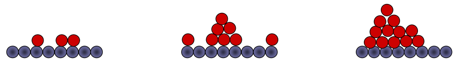
Detailed steps in film formation

1. Thermal accommodation
2. Binding (physisorption and chemisorption)
3. Surface diffusion (typically larger than bulk diffusion)
4. Nucleation
5. Island growth
6. Coalescence
7. Continued growth

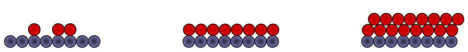
Nucleation and growth occurs on defects (or sites with higher bonding energy)

Three different growth modes

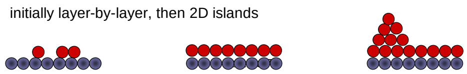
1. **<u>Island growth (Volmer – Weber)</u>**
   3D islands formation; film atoms more strongly bound to each other than to substrate and/ or slow diffusion



2. **<u>Layer-by-layer growth (Frank – van der Merwe)</u>**
   generally the highest crystalline quality; film atoms more strongly bound to substrate than to each other and/or fast diffusion

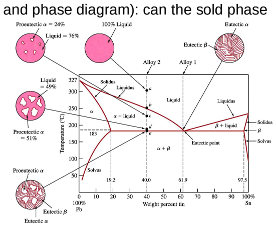


3. **Stranski – Krastanov (mixed growth)**
   initially layer-by-layer, then 2D islands



Thin film growth is not an equilibrium process!

1. Thermodynamics (Gibbs Free energy and phase diagram): can the sold phase be formed at the given temperature?



2. Kinetics (deposition rate and diffusion rate)

<u>Artificial superlattice is the best example of manipulating kinetics and thermodynamics</u>

7.4.2 Vacuum film deposition techniques

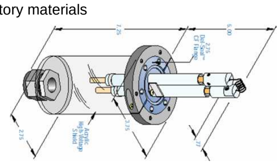
1. **Physical Vapour Deposition (PVD)**
   Evaporation: thermal and electron-beam assisted
   Sputtering: RF and DC Magnetron
   Pulsed Laser Deposition (PLD)
3. **Molecular Beam Epitaxy (MBE)**

2. **Chemical Vapour Deposition (CVD)**
   Plasma-Enhanced CVD (PE-CVD)
   Atomic Layer Deposition (ALD)

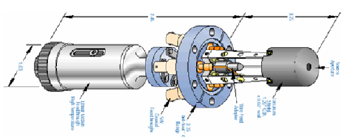
⇒ **Need good vacuum for thin film growth!**

Physical Vapour Deposition (PVD)

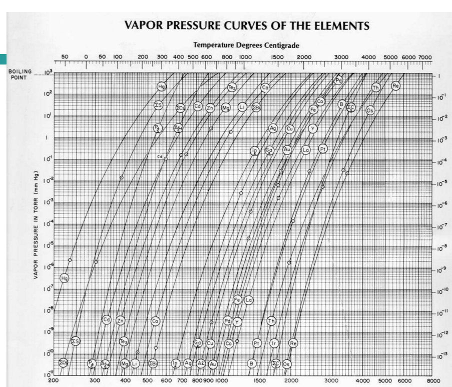
Thermal Evaporation for non-refractory materials



E-beam evaporation for refractory materials



http://www.mdc-vacuum.com

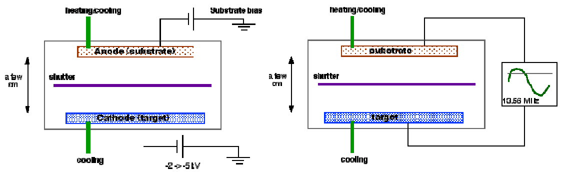


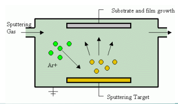
http://www.mcallister.com/vacuum.html – see a larger version attached in Appendix

Sputtering Deposition

- DC for conducting materials
- RF for insulating materials

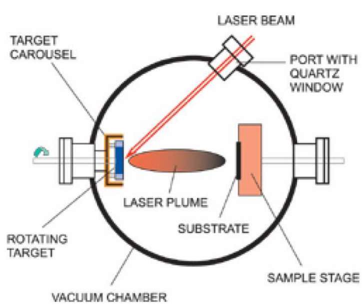
Magnetron sputtering is most popular due to high rate and low operation pressure





Pulsed Laser Deposition (PLD)

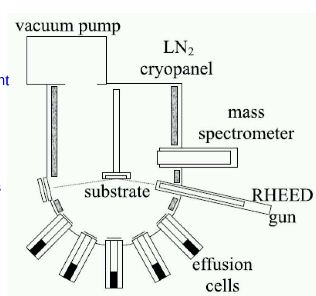
- Good for multielemental materials (P < 1 Torr)



Molecular Beam Epitaxy (MBE)

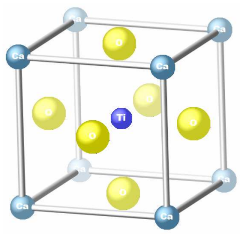
Molecular Beam Epitaxy
(p < 10^{-8}Torr)

1. Elemental Superlattices: Giant Magneto-Resistiance (GMR) Devices
2. Binary III-V Superlattices
3. Complex Oxide Superlattices



Complex oxides are not that complex:

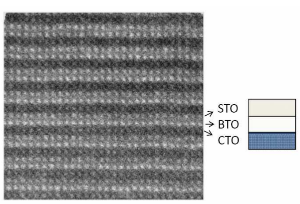
Most of them are based on the ABO3 cubic perovskite structure
Ex.:: SrTiO3, LaTiO3, LaMnO3, LaAlO3, …
⇒ Favorable to atomically smooth layered heterostructures



ABO3
A: M2+ (Ca, Sr, Ba, La)
B: M4+ (Ti, Zr, Mn)

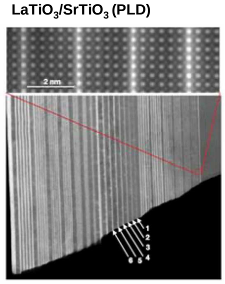
Superlattices grown by MBE

$SrTiO_3/BaTiO_3/CaTiO_3$



M. Warusawithana, J. Zuo, H. Chen and J. N. Eckstein

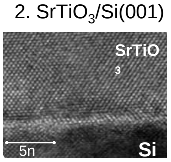
$LaTiO_3/SrTiO_3$ (PLD)



A. Ohtomo, H. Y. Hwang, *Nature* 419, 378 (2002)

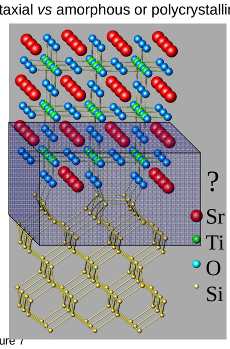
Epitaxial oxide material integrated with Si

1. Sc_2O_3/Si(111)
2. $SrTiO_3$/Si(001)



• Epitaxial structures may afford controllable interfaces (no dangling bonds…)
• Demonstration of interface stability and identification of potential stability problems under oxidizing/reducing conditions

Epitaxial *vs* amorphous or polycrystalline



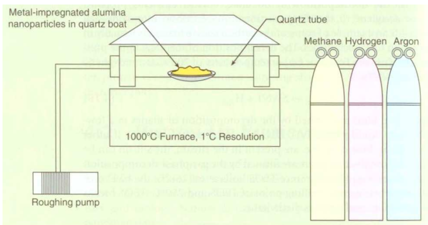
Chemical Vapour Deposition (CVD)

Precursors are needed!

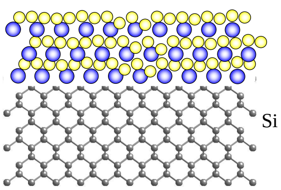
CH_4 (g) → SWNT + H_2 (g) ~ 700ºC, Fe, Ni catalysts

SiH_4(g) → Si + 2 H_2 (g)

$Si(OC_2H_5)_4$ (g) → SiO_2(s) + $(C_2H_5)_2O$ (g)



Atomic Layer Deposition



1. MCl_4 exposure
2. Purge
3. H_2O exposure
4. Purge ⇒ MO_2 ML

MCl_4(ads, surf) + 2 H_2O(g) → MO_2(s) + 4HCl(g)

$M(N(CH_3)(C_2H_5))_4$(ads, surf) + O_3(g) → MO_2(s) + …

•Surface saturation controlled process

•Excellent film quality and step coverage

Nanomaterials growth methods

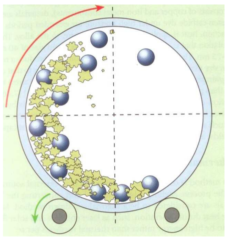
Two approaches

Top-down	Bottom-up
Patterning in bulk materials by combination of	Structure is assembled from well-defined chemically or physically synthesized building blocks
Lithography	Self-assembly
Etching	Selective growth
Deposition	
- can be applied for variety of materials	- require accurate control and tunable chemical composition, structure, size and morphology of building blocks
- limited by lithography resolution, selectivity of etching, etc.	- in principle limited only by atomic dimensions

Mechanical Methods (Mechanosynthesis)

Low cost fabrication: ball milling or shaker milling

Kinetic energy from a rotating or vibrating canister is imparted to hard spherical ball bearings (under controlled atmosphere)



(1) Compaction and rearrangement of particles

(2) First elastic and then severe plastic deformation of the sample material ⇒ formation of defects and dislocations

(3) Particle fracture and fragmentation with continuous size reduction ⇒ formation of nanograined material

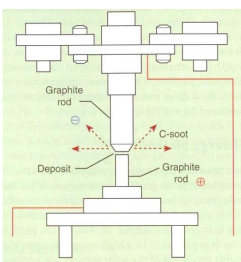
$$K_{IC} = Y\sigma_F\sqrt{\pi a} \qquad \sigma_F \sim \frac{1}{Y}\sqrt{\frac{K_{IC}}{a}} \sim \sqrt{\frac{\gamma E}{a}}$$

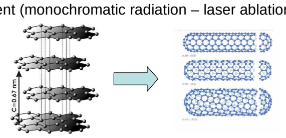
σ_F – stress level, when crack propagation leads to fracture; γ - surface energy of the particle; a - length of a crack

-material with defects with a wide distribution of size

High-Energy Methods: Discharge Plasma Method

Application of high energy electric current (monochromatic radiation – laser ablation)





Can be used for fullerenes and C nanotubes

Process depend on:

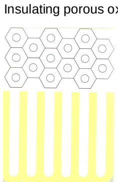
-Pressure of He, process temperature, applied current

final product requires extensive purification

Chemical Fabrication Methods

Anodizing (and electropolishing)

Insulating porous oxide layer is created on a conductive metal anode in electrolytic solution



Anodic reaction $2Al^0_{(s)} \rightarrow 2\ Al^{3+} + 6e$

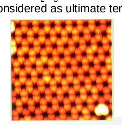
Oxide-electrolyte interface $2\ Al^{3+} + 3H_2O \rightarrow 2\ Al_2O_3 + 6H^+$

Cathodic reaction $6H^+ + 6e \rightarrow 3\ H_2$ (g)

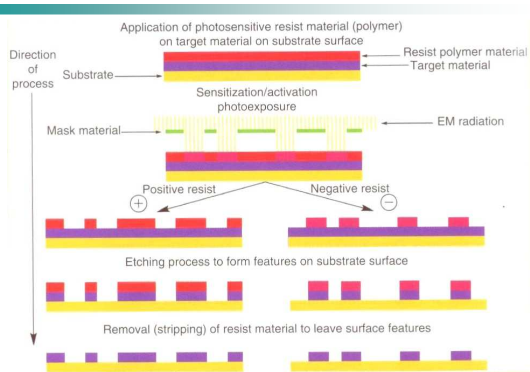
Overall oxide formation reaction:

$2Al^0_{(s)} + 3H_2O \rightarrow Al_2O_3 + 3\ H_2$

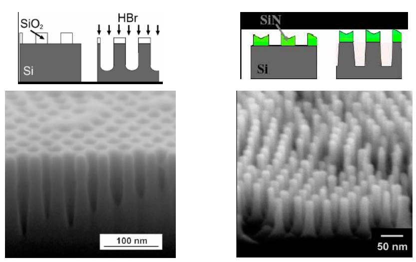
Porous Al_2O_3 membranes can be considered as ultimate template material



Lithographic Methods



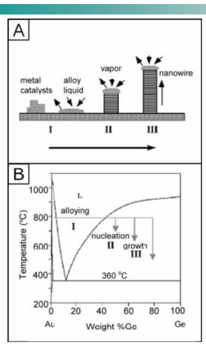
Top-bottom: High-Aspect Aspect-Ratio Si Structures



nanotextured Si surface

dense silicon pillar array

Bottom-up: vapor-liquid-solid growth

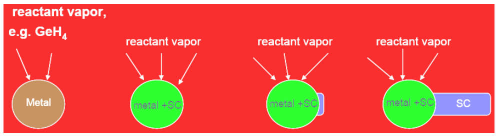


VLS growth of Ge NWsw/Au

- Metal particle catalyzed the decomposition of a gaseous species containing the semiconductor components, e.g. Ge, or Ga and As
- Metal catalyst particles absorb species, becoming saturated with them at eutectic point (relatively low temperature)
- When semiconductor reaches supersaturation, it precipitates out of the eutectic
- Metal prepared and deposited/grown on surface
- Metal droplet size determines eventual wire diameter

(from E. Garfunkel)

Cartoon of growth



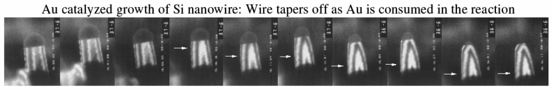
Metallic catalyst nanocluster

Eutectic (AuGe alloy) Temperature is controlled to keep it in the **liquid** state

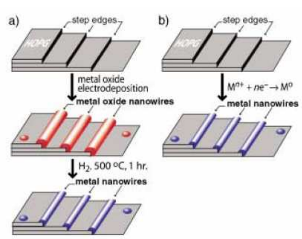
Nanowire nucleation begins when the liquid become saturated with Ge

Nanowire growth continues as long as Au-Ge alloy stays liquid and Ge concentration is high enough

Au catalyzed growth of Si nanowire: Wire tapers off as Au is consumed in the reaction

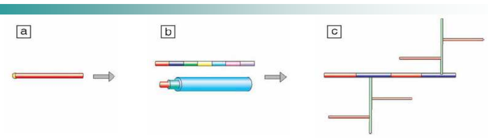


Electrochemical step decoration



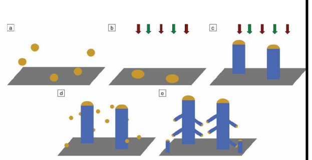
- minimization surface energy of the step
- metal oxide electrochemical deposition + reduction (H2)
- metal electrochemical deposition

Designed Synthesis of Hierarchical Structures



The evolution of nanowire structural and compositional complexity enabled today by controlled synthesis

(a) from homogeneous materials
(b) axial and radial heterostructures
(c) branched heterostructures



The colors indicate regions with distinct chemical composition and/or doping

Organization and Assembly of Nanowires

Using a patterned catalyst, NWs can be directly grown on a solid substrate in a designed configuration

NW materials produced under synthetic conditions optimized for their growth can be organized into arrays by several techniques

(1) electric - field – directed (highly anisotropic structures and large polarization)

(2) fluidic - flow – directed (passing a suspension of NWs through microfluidic channel structure)

(3) Langmuir–Blodgett (ordered monolayer is formed on water and transferred to a substrate)

(4) patterned chemical assembly or imprint

Imprint based patterning of metal nanoparticles