Nano Sensors

PhD/ MTech/ BTech
Course No.: EEL7450
L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL
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Lecture 25 dated 18th Mar 2025

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Methods for creating nanostructures

Important methods for the creation of nanomaterials and nanostructures are:

1. Top Down
    1. Mechanical grinding,
    2. Etching methods
        i. Without patterning
        ii. After patterning
            i. Optical lithography
            ii. Electron beam lithography
            iii. Nano imprint lithography (NIL)
            iv. Self-assembly and Anodized Aluminium Oxides
2. Bottom Up techniques
    1. Sol-gel process
    2. Gas Phase synthesis of nanomaterials
    3. Others

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Mechanical grinding

- The mechanisms responsible for formation of nanocrystalline structures by
  - mechanical attrition of single-phase powders,
  - mechanical alloying of dissimilar powders, and
  - mechanical crystallization of amorphous materials.
- The two important problems of
  - contamination and
  - powder consolidation will be briefly considered.
- Due to contamination problem, the method is not used for some materials.

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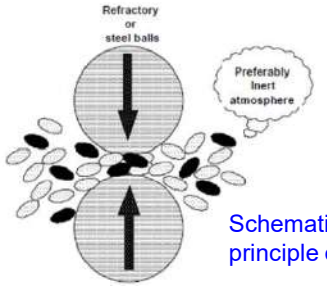
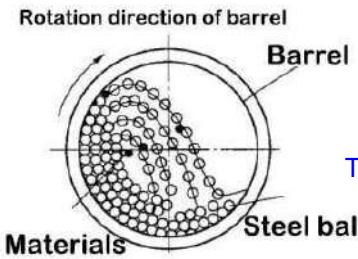
Mechanical grinding

- Mechanical milling is typically achieved using:
  - high energy shaker,
  - planetary ball, or
  - tumbler mills.
- The energy transferred to the powder from refractory or steel balls depends on
  - the rotational (vibrational) speed,
  - size and number of the balls,
  - ratio of the ball to powder mass,
  - the time of milling and
  - the milling atmosphere.
- Nanoparticles are produced by the shear action during grinding.



Schematic representation of the principle of mechanical milling



Tumbler mills

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Assignment: Write a note on Mechanical grinding, distinguishing various milling techniques with diagrams.

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Mechanical grinding

- Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process.
- For the production of fine particles, an adequate step to prevent oxidation is necessary.
- The process is restrictive for the production of non-oxide materials
- For others, it requires the milling to take place
  - in an inert atmosphere and
  - the powder particles be handled in an appropriate vacuum system or glove box.
- This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders.
- If the mechanical milling imparts sufficient energy to the constituent powders, a homogeneous alloy can be formed.

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Etching methods

Without patterning:

- single crystals are etched in an aqueous solution for producing nanomaterials,
- Example, the synthesis of porous silicon by electrochemical etching.

After Patterning (lithography):

i. Optical lithography
ii. Electron beam lithography
iii. Nano imprint lithography (NIL)

Lithography (from Greek - lithos: "stone" + grapho: "to write")

Lithography is a process used to selectively remove parts of a thin film.

It is an important process for industrial mass production of computer chips

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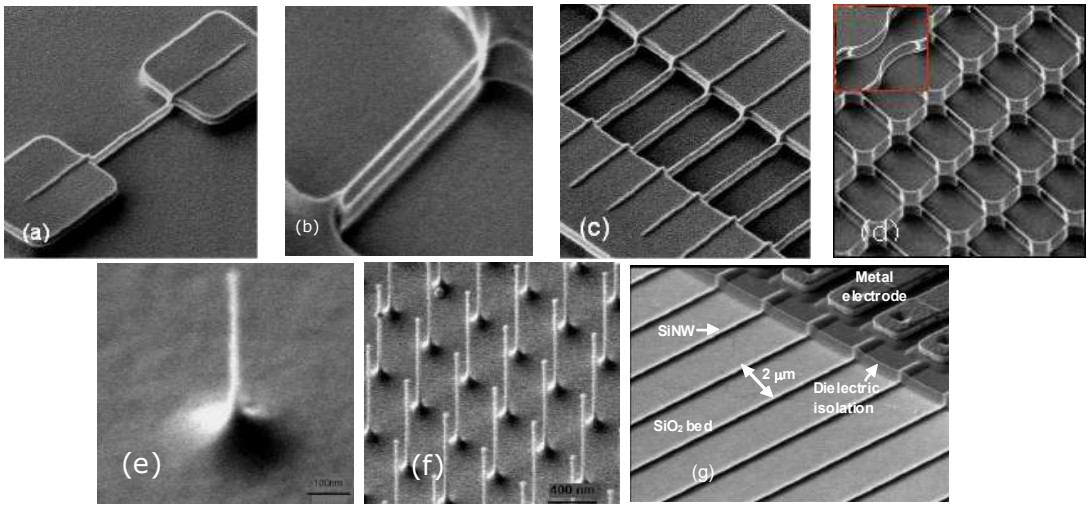
Nano-structures/ Nano-materials 1- D nanostructures



Silicon nanowire: (a) Single SiNW, (b) vertically stacked twin SiNWs (c) An array of SiNW (d) large area regular mesh of nanowires. The inset: curved SiNW (e) & (f) 1.0 μm tall isolated & dense-array of vertical SiNW of dia. ~ 20 nm (g) **SiNW array for bio-chemical sensors**; length-to-cross section ratio up to 40,000:1.

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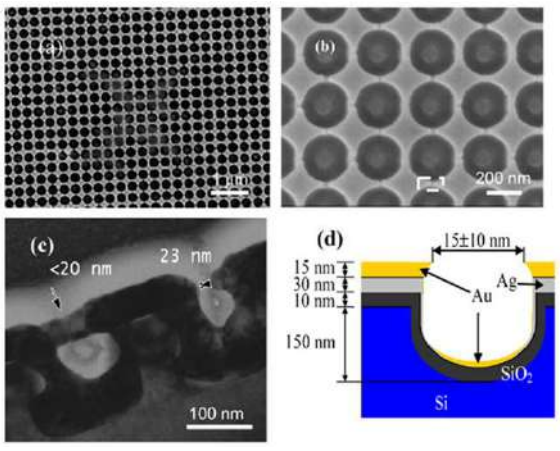
Nano-structure array for *SERS*

3D arrays of SERS substrate for ultrasensitive molecular detection

R.Z. Tan [a], A. Agarwal [a], N. Balasubramanian [a], D.L. Kwong [a], Y. Jiang [b], E. Widjaja [b], M. Garland [b]

Suitable for *trace level detection* of:
- **Biological warfare,**
- **Bio-markers,**
- **Explosives, etc.**



SERS substrates

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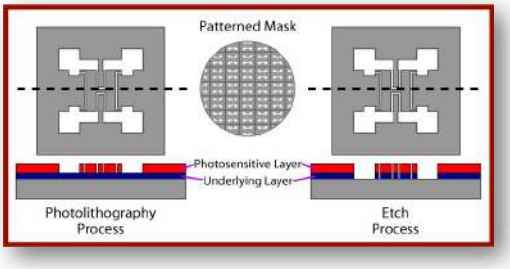
Photolithography

Different layers of a microsystem are realized as follows:

1. Photolithography transfers the pattern from a mask to a photosensitive layer
2. Then the pattern from the photosensitive layer is transferred into an underlying layer.
3. After the pattern transfer, the resist is stripped (removed).



Pattern Transfer to Underlying Layer

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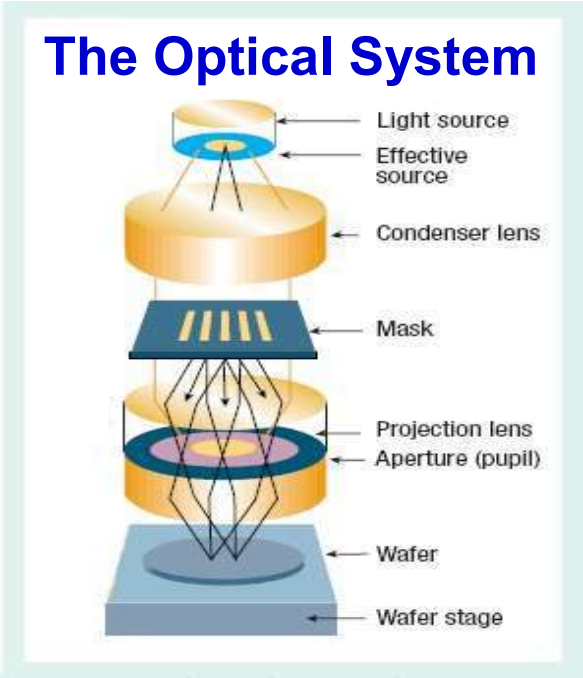
The Optical System



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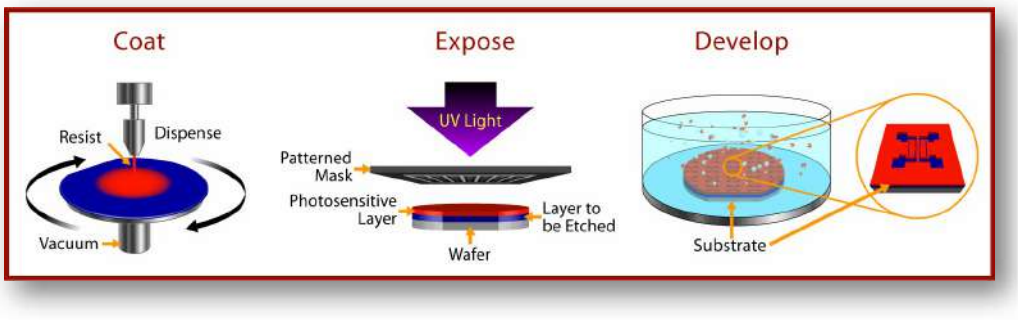
Three Steps of Photolithography (*broadly*)

1. PR Coating
2. UV Exposure
3. Develop



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1. Surface Conditioning

In most applications, surface conditioning is required preceding to the photoresist coating

- Surface cleaning to prepare the wafer to accept the photoresist
- Coating the wafer with a chemical that boosts adhesion of the photoresist to the wafer's surface (commonly used is Hexa-methyl-di-salizane or HMDS)

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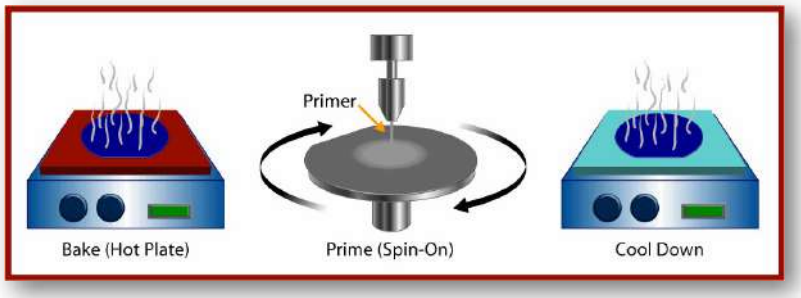
Surface Conditioning Steps



1. Wafer is baked to remove the water molecules on the wafer surface
2. HMDS is applied (prime) to create a hydrophobic surface
3. Wafer is cooled to room temperature

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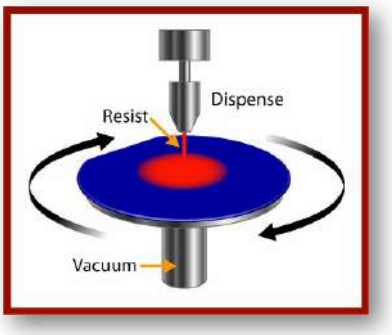
2. PR Spin Coating

- Wafer is placed on a vacuum chuck
- Vacuum holds the wafer on the chuck
- Resist is applied
- Chuck accelerates for desired resist thickness
- Chuck continues to spin to dry film



PR Spin Coating

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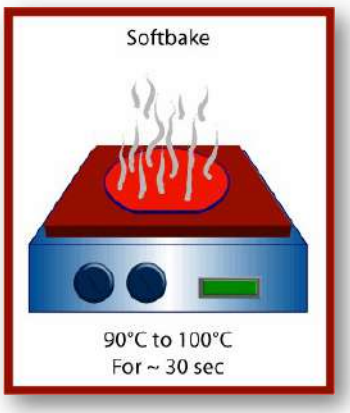
3. Soft bake

- After the photoresist is coated in the desired thickness, a softbake is used to remove the residual solvents of the photoresist
- After the softbake, the wafer is cooled to room temperature



Softbake after applying Resist

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4. Alignment

- Alignment is one of the most critical steps in the entire micro-systems fabrication process
- A misalignment of one micron or smaller can destroy the device and all the devices on the wafer
- Each layer must be aligned properly and within specifications to the previous layers & subsequent layers

Mask *Aligner*

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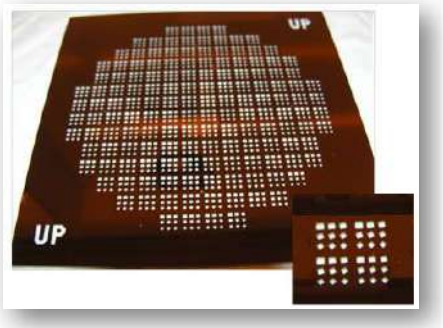
Mask vs. Reticle

- The patterned mask (or reticle) is a quartz or glass plate with the desired pattern (usually in chrome).
- Some equipment do not use a whole mask. Instead a smaller quartz plate is used with just a few die (inset). This plate is called a reticle.



Mask and Reticle (inset)

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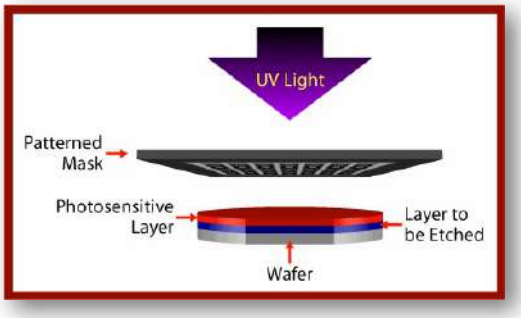
5. Expose



- The wafer is exposed by UV (ultraviolet) from a light source traveling through the mask to the resist
- A chemical reaction occurs in the resist due light exposure
- Only those areas not protected by the mask undergo a chemical reaction

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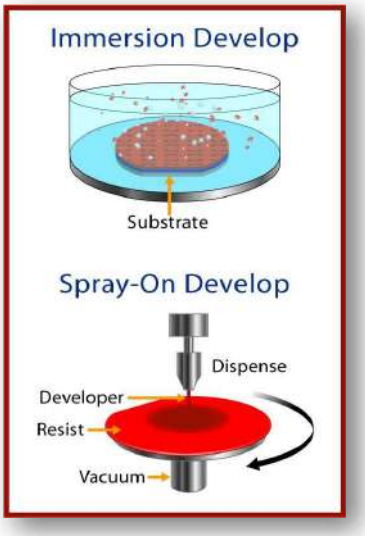
6. Development

- Portions of the photoresist are dissolves in the developer
- With positive resist, the **exposed** resist is **dissolves** while the unexposed resist remains on the wafer
- With negative resist, the unexposed resist is dissolves while the exposed resist remains.



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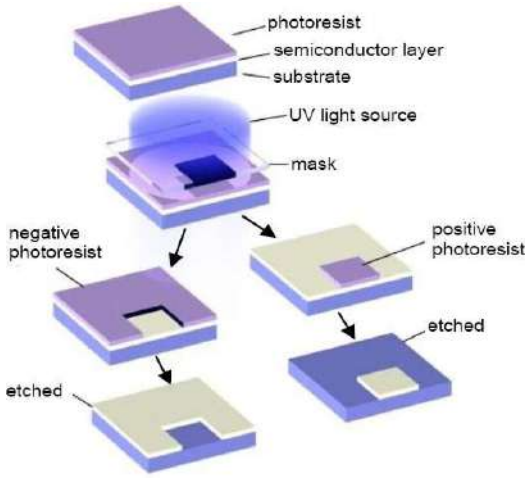
Photoresist (Resist)

Photoresist is a mixture of organic compounds in a solvent solution.

Two types of resist:

- **Positive resist** - **Exposed** regions become more **soluble**. A positive mask is left after development
- **Negative resist** - Exposed material harden. A negative mask is left after development



Photoresist- Positive vs. Negative

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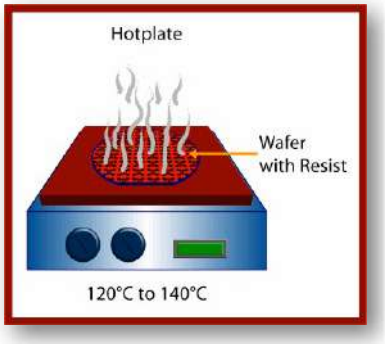
7. Hardbake

- Hardens the photoresist for the next process.
- The temperature of the hardbake is higher than that of the softbake after coat
- After the hardbake, the wafer is cooled to room temperature



Hardbake

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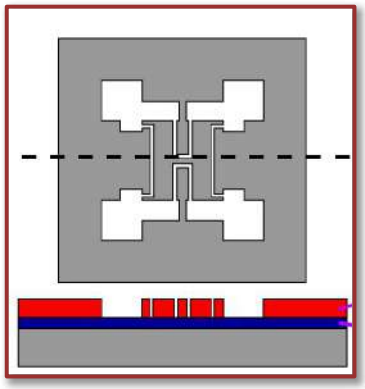
8. Inspect

Three critical parameters

- **Alignment:** the pattern must be positioned accurately to the previously layer
- **Line width or critical dimension (CD):** the pattern images are in focus and have the correct size
- **Defects:** things that could affect subsequent processes and eventually the operation of the devices



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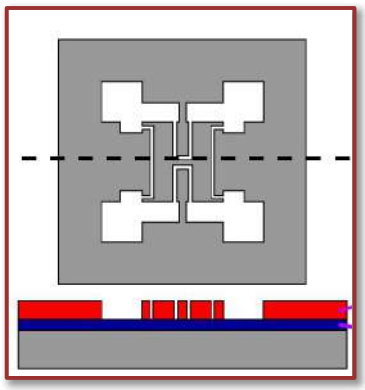

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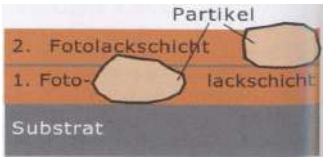
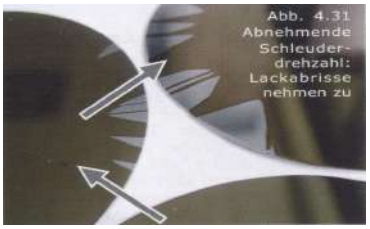
Defects

- Particles in the photoresist (dust, old photoresist)
- Bubbles
- Rough substrate
- Tear-off





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Questions/ Discussion

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Electron beam lithography (EBL)

1. Overview and resolution limit.
2. Electron source (thermionic and field emission).
3. Electron optics (electrostatic and magnetic lens).
4. Aberrations (spherical, chromatic, diffraction, astigmation).
5. EBL systems (raster/vector scan, round/ shaped beam)

Textbook: Nanofabrication: principles, capabilities and limits, by Zheng Cui

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E-beam lithography facts

- Developed in **1960s** along with scanning electron microscope (SEM).
- Breakthrough made in **1968** when a polymer called **PMMA** (poly methyl meth acrylate) was discovered to have high resolution.
- **Fast** growth in **1990s** when "**nano**" began to become "**hot**" and **computer** became more available for **automatic lithography** control.
- Since around **2000**, focused ion beam (FIB) patterning began to compete with EBL in some applications.
- Today EBL is still the most **popular nano-patterning techniques** for **academic research** and **prototyping**.

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E-beam lithography (EBL) overview

(direct writing with a focused e-beam)

- Electron beam is focused to **spot size <5nm** using electron optics.
- Very small wavelength: **resolution less limited** by **diffraction**.
- *Generate* pattern by direct writing: **no need of mask or mold**.
- Sequential pixel-by-pixel writing: **low throughput**, unsuitable for mass production.

For electron:
(V is electron kinetic energy in eV)

$$\lambda = \frac{1.226}{\sqrt{V}}(nm)$$

For EBL at 30kV acceleration voltage λ=0.007nm

For light:

$$\lambda = \frac{hc}{eV} = \frac{1.24}{V}(\mu m)$$

For an electron with kinetic energy of 1eV, the associated De Broglie wavelength is 1.23nm, about a thousand times smaller than a 1eV photon.

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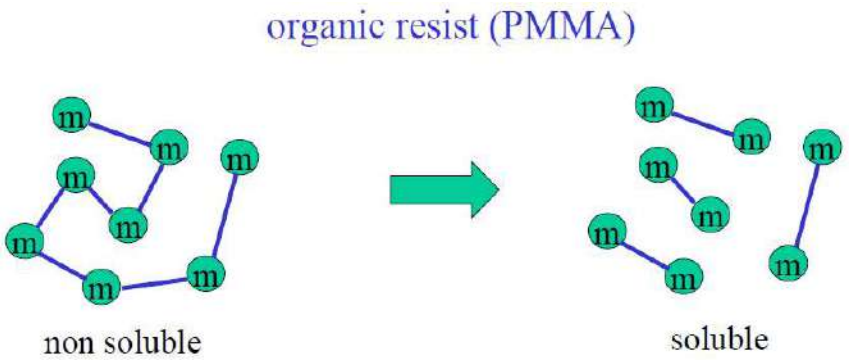
Exposure of resist



- Typical energy for breaking a bond: 10eV
- But typical energy of the e-beam: 10 - 100kV
  (problems of aberration **at low energy** that leads to **large beam spot size** and **low resolution**, **so use high energy for EBL**)
- Bond is broken by secondary (including Auger) electrons with low energy.

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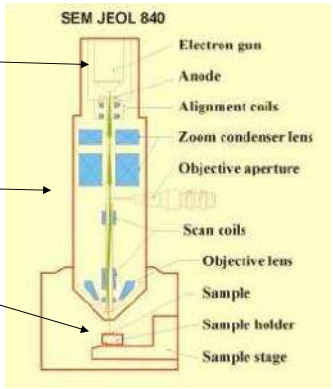
SEM/ EBL system components

- An **electron gun** or electron **source** that supplies the electrons.
- An electron **column** that **'shapes'** and **focuses** the electron beam.
- A mechanical **stage** that **positions** the **wafer** under the electron beam.
- A wafer handling system that automatically feeds wafers to the system and unloads them after processing. (optional)
- A computer system that controls the equipment.



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EBL systems: most research tools are based on SEM

SEM conversion
- Conventional SEM (≤30kV)
- Almost no SEM modification
- Add beam blanker
- Add hardware controller
- Low cost: <$100K

NPGS system

Dedicated EBL system
- Based on SEM system
- With perfect integration
- Interferometer stage
- Focus correction (laser sample height control)
- Cost $1-2M

Raith system

E-beam writer
- High energy column (100kV)
- Dedicated electron optics
- High reproducibility
- Automatic and continuous (over few days) writing
- High cost (>$5M)

Vistec system

Beam blanker: is a DC bias (~42V between two parallel plate electrodes) *perpendicular* to electron path, so that electrons are deflected away from the axis and thus "turned off"/ blocked/ blanked by the aperture below. The beam needs to be **blanked** so that it **won't expose the resist during its moving to next pattern** location.

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Electron beam lithography (EBL)

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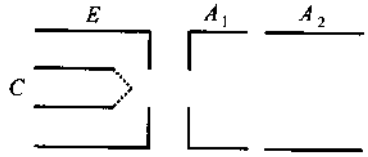
Electron guns/ source

Schematic structure of electron gun

Electrons can be emitted from a filament (emitter or cathode) by gaining additional energy from heat or electric field.



C: cathode for emitting electrons
E: extraction electrode
A_1, A_2: cathode lens electrode to focus the emitted electrons

Three types of electron guns:

- Thermionic emission gun (W, LaB_6, not-sharp tip).
- Field emission gun (cold, *very* sharp W tip, tunneling current).
- Schottky gun (field assisted thermionic emission, sharp tip).

- Whether it is field emission or not depends on the **electric field near the tip apex**, which determines whether tunneling is important or not.
- **Sharper tip** leads to higher electric field near tip apex, so **field emission** (by tunneling) plays a major role, it is thus called field emission gun (FEG).
- Even thermionic emission relies on the electric field from the extraction electrode, but here thermionic emission plays a major role.

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Electron gun: thermionic emission (tungsten hairpin filaments)

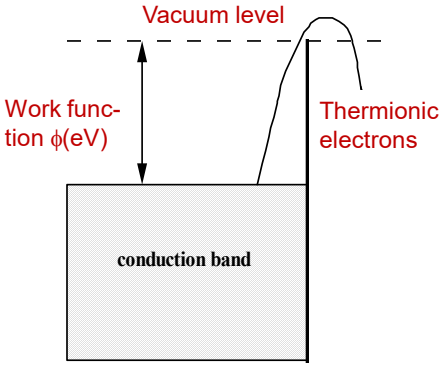
- The long time source of choice has been the W hairpin source
- Working at high temperature, some electrons have thermal kinetic energy high enough to overcome the energy barrier (work function)

But kT still << work function ~4eV). At 2000°C, $kT=1.38\times10^{-23}\times2273/1.6\times10^{-19}=0.20eV$.

- Escaped electron is then extracted by the electric field generated by the nearby electrode.
- Current density J_c depends on the temperature and cathode work function ϕ.
- Cheap to make and use ($12.58 ea) and only a modest vacuum is required. Last tens of hours.

For a good introduction, go to:
http://en.wikipedia.org/wiki/Thermionic_emission

W filament



Schematic model of thermionic emission

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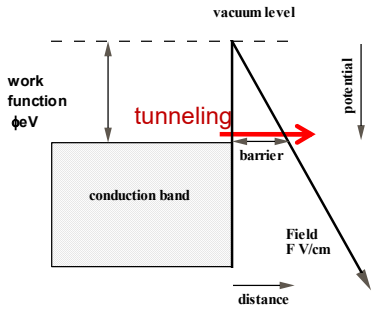
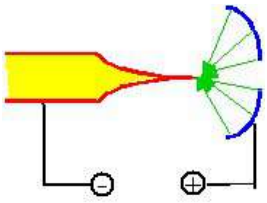
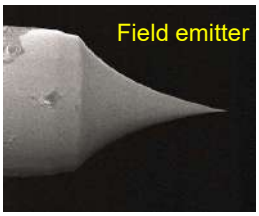
Field emission guns (FEGs)







Current density (Fowler-Nordheim equation):

$J = A\cdot F^{2}\cdot\varphi^{-1}\exp(-B\varphi^{1.5}/F)$ here $A=1.5\times10^{-6}$; $B=4.5\times10^{7}$; $F>>10^{8}$(V/m)

- Field emission (i.e. tunneling) becomes dominant for electric field $F>>10^{8}$V/m.
- Need very high vacuum to prevent arc-over at tip apex.
- Strong nonlinear current-voltage characteristic.
- Very short switching time (t<ns), since no need to heat up.
- Small beam spot size, since field is high enough for tunneling only near tip apex.

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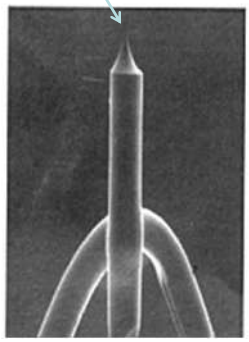
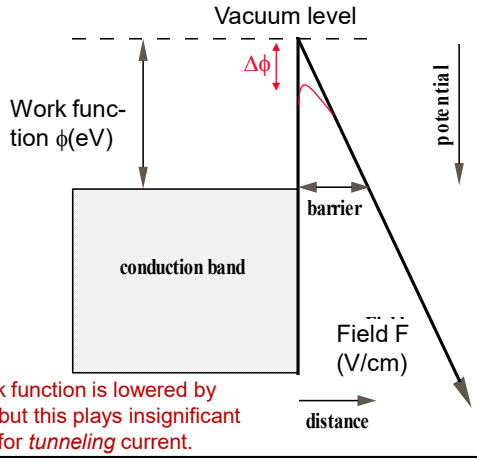
Cold field emission guns (FEG)

- Electrons "tunnel out" from a tungsten wire because of the high field (~10^8V/cm) obtained by using a sharp tip (100nm) and a high voltage (3-4kV).
- The emission current is temperature independent (pure tunneling current, operate at room temperature, so the name "cold").
- Needs ultra-high vacuum (UHV), but gives long life and high performance.





Work function is lowered by Δϕ, but this plays insignificant role for *tunneling* current.

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Cold field emission gun (FEG) behavior

- The tip must be **very clean** to perform properly as a field emitter.
- Even at 10^{-6}Torr, a monolayer of gas is deposited in just 1 sec.
- So tip needs higher vacuum, **~10^{-10}Torr** vacuum.
- At this vacuum, the tip is usually covered with a mono-layer of gas in 5-10 minutes.
- Cleaning is performed by "flashing" - heating the tip for a few seconds to desorbs gas.
- The emission then stabilizes for a period of 2-5 hours.
- On the stable region (hour 4 to hour 6), total noise + drift is a few percent over a few minutes, still not stable. (Right after flashing, current may drop ~50% within a hour)
- Flash is typically done automatically every morning, and SEM is good for 8-10 hours.
- For e-beam lithography that need more stable current, good only during hour 4 to hour 8.
- Because of the **current instability**, cold FEG is not good choice for e-beam lithography, though it is the best for SEM imaging applications.
- Cold FEG is more expensive than Schottky emission guns, but last longer, up to 5 years.

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Schottky emitters: field assisted thermionic source

- Work function depends on temperature T and electric field F by:

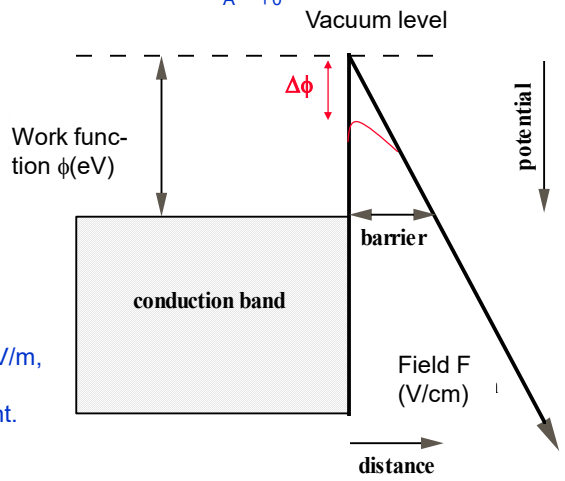
$$\phi = \phi_0 - e\sqrt{\frac{eF}{4\pi\varepsilon_0}};\ \sqrt{\frac{e}{4\pi\varepsilon_0}} = 3.8\times10^{-5}(V\cdot m)^{\frac{1}{2}}$$

- Cathode behaves like a thermionic emitter with $E_A = \phi_0 - \Delta\phi$.

$$j = A\cdot T^2\cdot\exp\left(-\frac{E_A}{kT}\right)$$

For F=1×10^{8}V/m, Δϕ=0.38eV.
Take T=1750K, then kT=0.15eV,
current density is increased by:
$j/j_0 = e^{0.38/0.15} = 13$.

For F significantly higher than 1×10^{8}V/m, the above equation is no longer valid since tunneling is becoming important.



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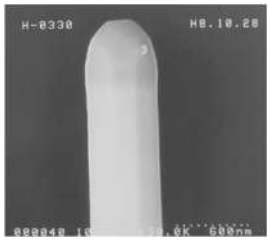
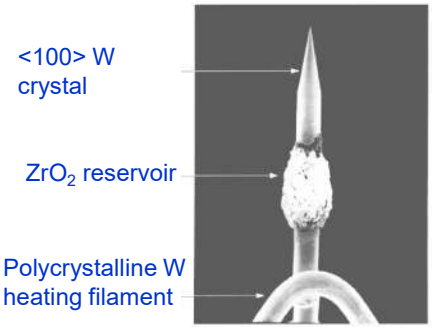
Schottky emitters: field assisted thermionic source

- It is usually misleadingly called thermal or Schottky field emission guns.
- But it is not a truly field emission gun, because the tip is blunt and if the heat is turned off there is no emission (tunneling) current.
- A Schottky source is actually a field assisted (to lower ϕ) thermionic source.



Hitachi Schottky Emitter Tip (not sharp)

- Schottky emitters can produce larger amounts of current compared to cold FEG systems, so more useful for e-beam lithography.
- Because they are always on (hot, 1750K), organic contamination is not an issue (burned away immediately), hence they are very stable (few % per week change in current)
- They eventually fail when the Zirconia reservoir is depleted, after 1-2 years.
- Zirconia is used to further lower the ϕ (ZrO_2 has a low work function).



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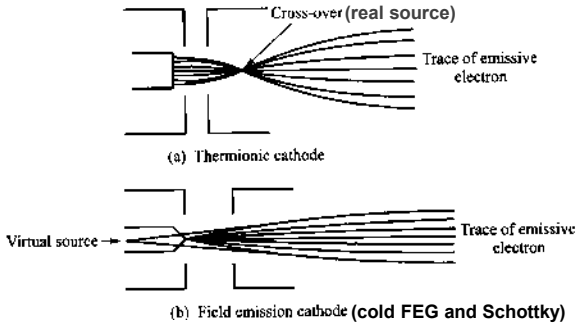
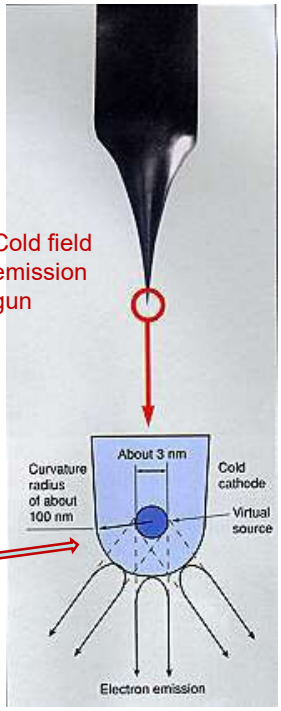
Source size

The cross-over is an *effective real or virtual* source for the downstream electron optical system.





- The source size is the *apparent* width of the disc from which the electrons appear to come.
- The tip physical size does NOT determine the source size.
- Small is good for high resolution SEM, because less demagnification is needed to attain a given probe size.
- But too small is not necessary, because anyway demagnification is needed to minimize effects of vibration and stray fields.

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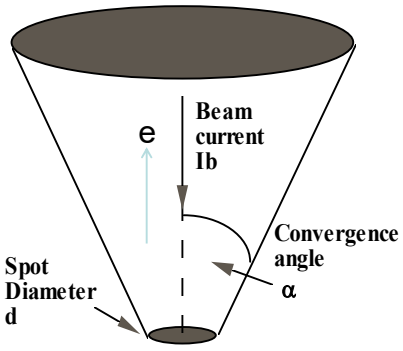
Source brightness β

$$\beta = \frac{4I_b}{\pi^2 \alpha^2 d^2}$$



Measuring β at the specimen

- Brightness is defined as current per unit area per solid angle, with unit amp/cm^2/steradian.
- Brightness is the most useful measure of gun performance.
- Brightness depends on energy, so one must compare different guns at the same beam energy (acceleration voltage).
- High brightness is not the same as high current.

E.g. thermionic emission can have very high beam current, but low brightness (due to large d). Most current will then be blocked by a small aperture (to limit α) in order to have an acceptable small beam spot onto the specimen for high resolution imaging.

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Energy Spread

- Electrons leave guns with an energy spread that depends on the cathode gun type.
- Lens focus varies with energy (chromatic aberration, see later slides), so a high energy spread hurts high resolution images, as not all electrons are focused on the sample surface since they have different energy.
- The energy spread of a W thermionic emitter is about 1.5-2.5eV.
- For field emission and Schottky guns, the energy spread is about 0.3-0.7eV.

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Comparison of electron emission sources

Key parameters of electron sources:
virtual source size, brightness, energy spread of emitted electron

Emitter type	Thermionic	Thermionic	Cold FE	Schottky FE
Cathode materials	W	LaB_6	W	ZrO/W
Operating temperature (K)	2800	1900	300	1800
Cathode radius (μm)	60	10	<0.1	<1
Virtual source radius (nm)	15,000	5000	2.5	15
Emission current density (A cm $^{-2}$)	3	30	17,000	5300
Total emission current (μA)	200	80	5	200
Brightness	10^4	10^5	2×10^7	10^7
Maximum probe current (nA)	1000	1000	0.2*	10
Energy spread at cathode (eV)	0.59	0.40	0.26	0.31
Energy spread at gun exit (eV)	1.5–2.5	1.3–2.5	0.3–0.7	0.35–0.7
Beam noise (%)	1	1	5–10	1
Emission current drift (% hr $^{-1}$)	0.1	0.2	5	<0.5
Vacuum requirement (Torr)	$\leq10^{-5}$	$\leq10^{-6}$	$\leq10^{-10}$	$\leq10^{-8}$
Cathode life (h)	200	1000	2000	2000
Cathode regeneration(flashing)	Not required	Not required	Every 6–8 h	Not required
Sensitivity to external influence	Minimal	Minimal	High	Low

*Hitachi cold FEG SEM can go to 2nA.

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Questions

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