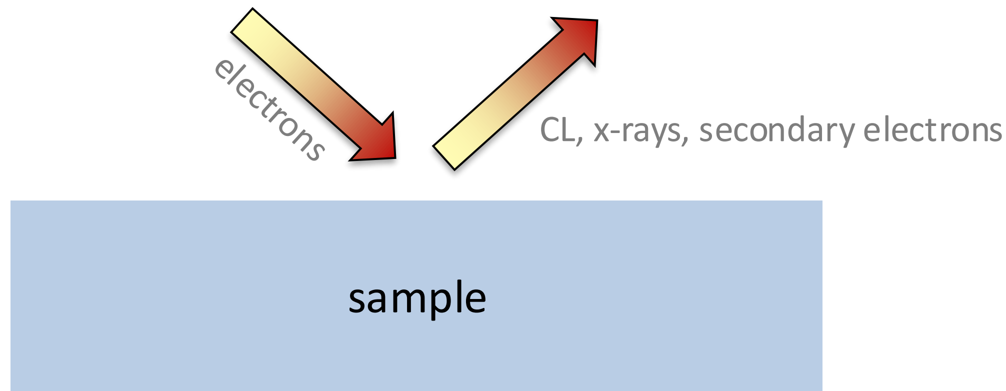
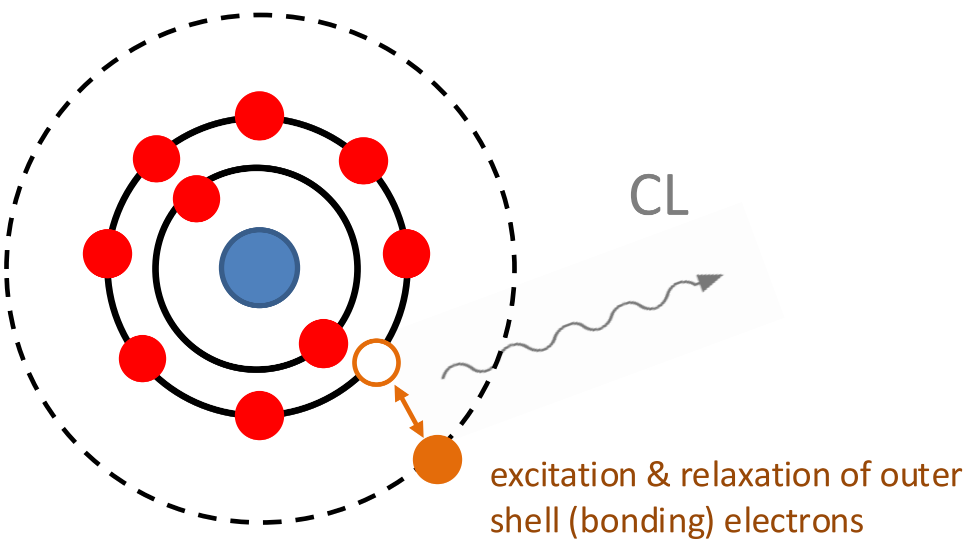
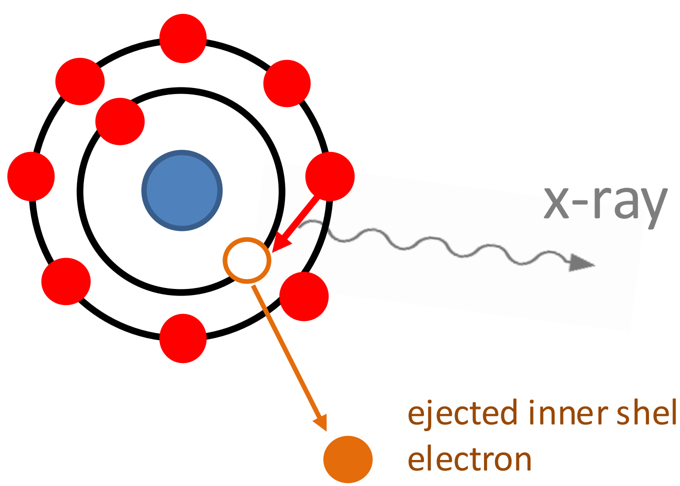
# 68320 Nanofabrication and Nanocharacterization Techniques

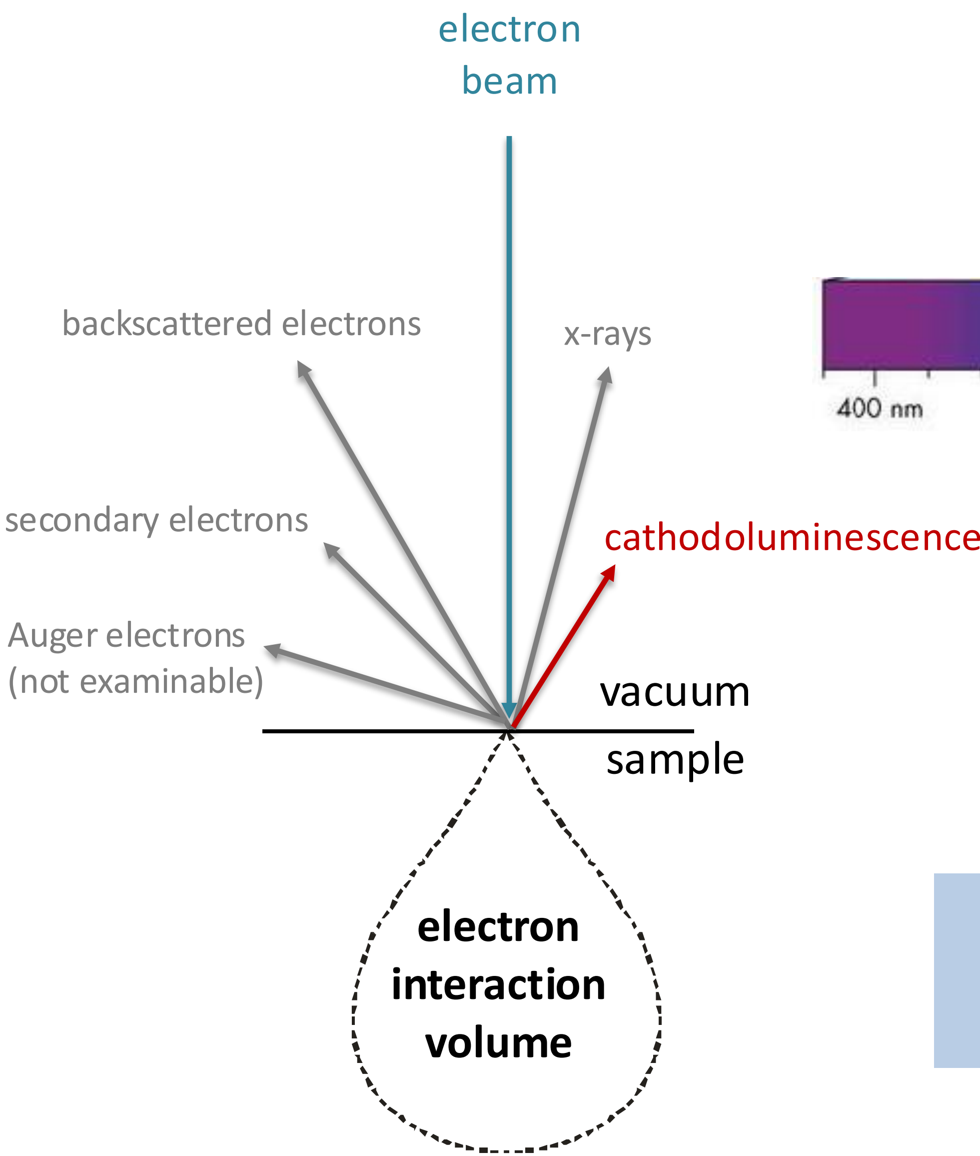
## Lecture 4: Emission of cathodoluminescence, x-rays & electrons

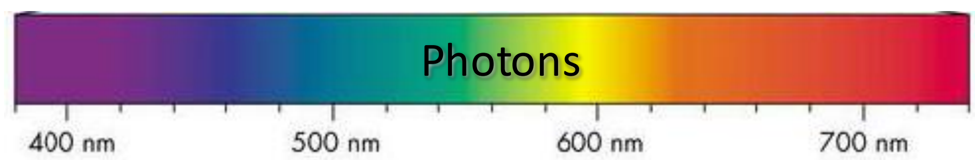


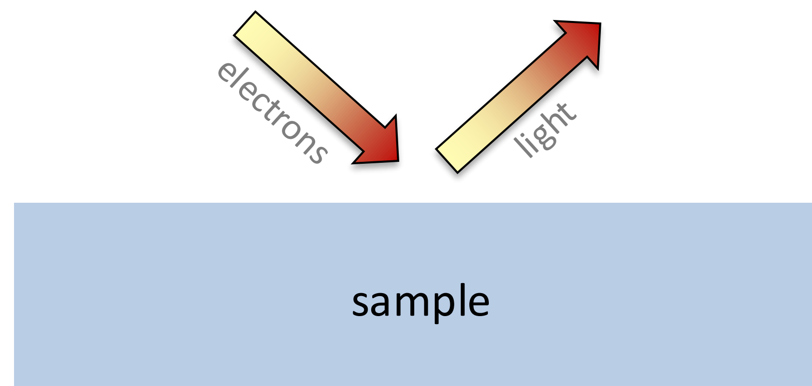



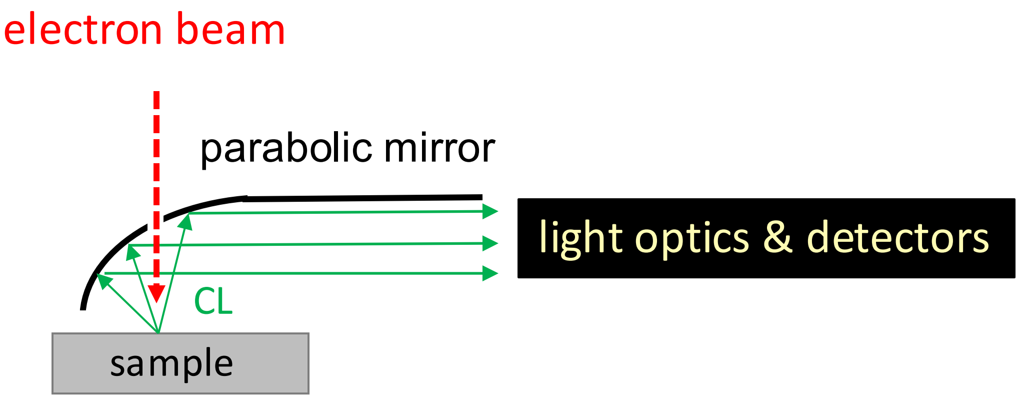
# Cathodoluminescence (CL) analysis in a scanning electron microscope



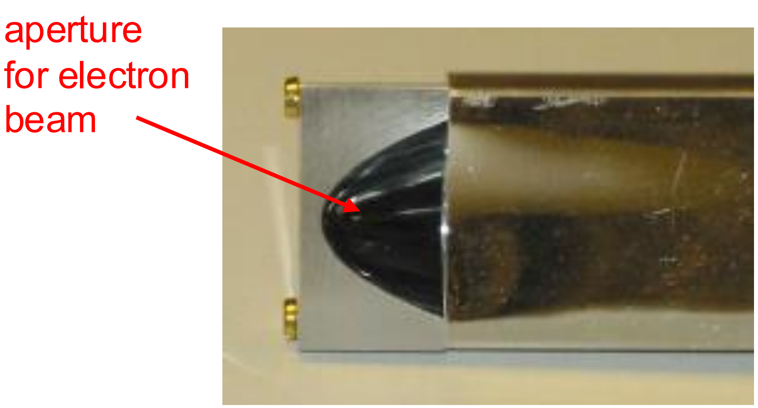



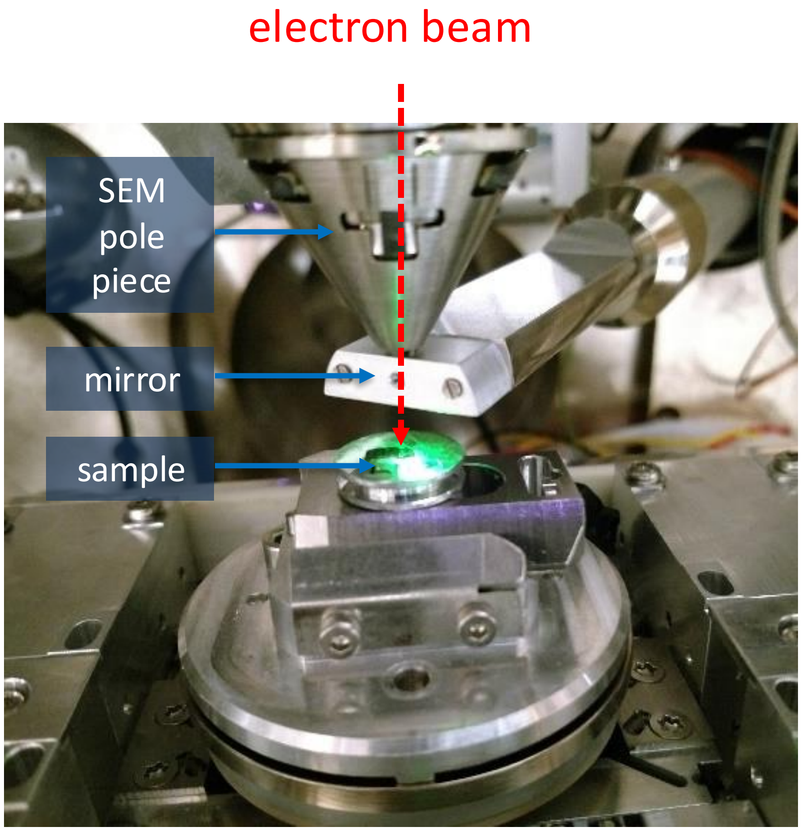



# CL: Most common experimental setup



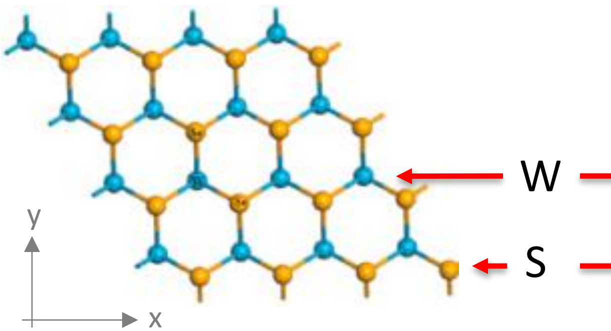

parabolic mirror (bottom view)

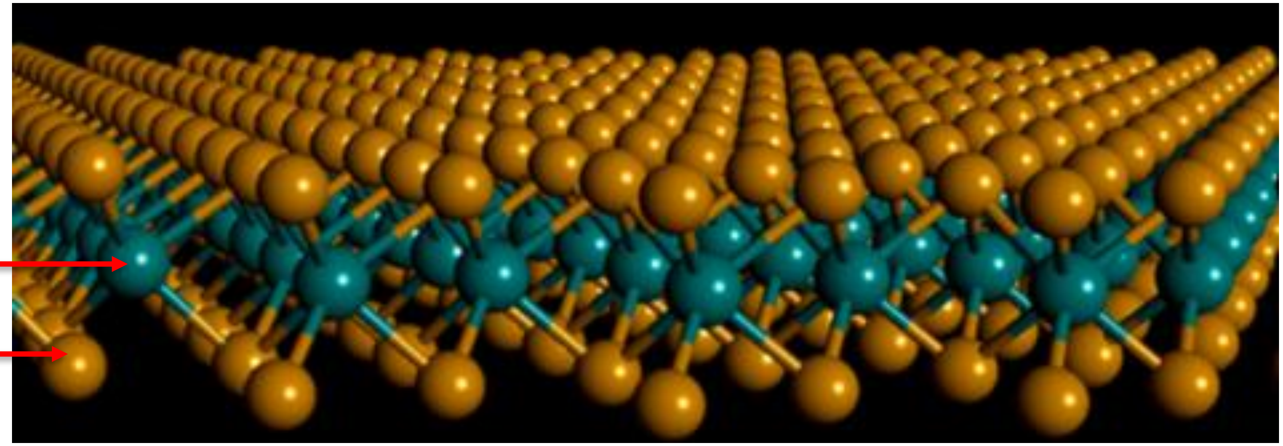


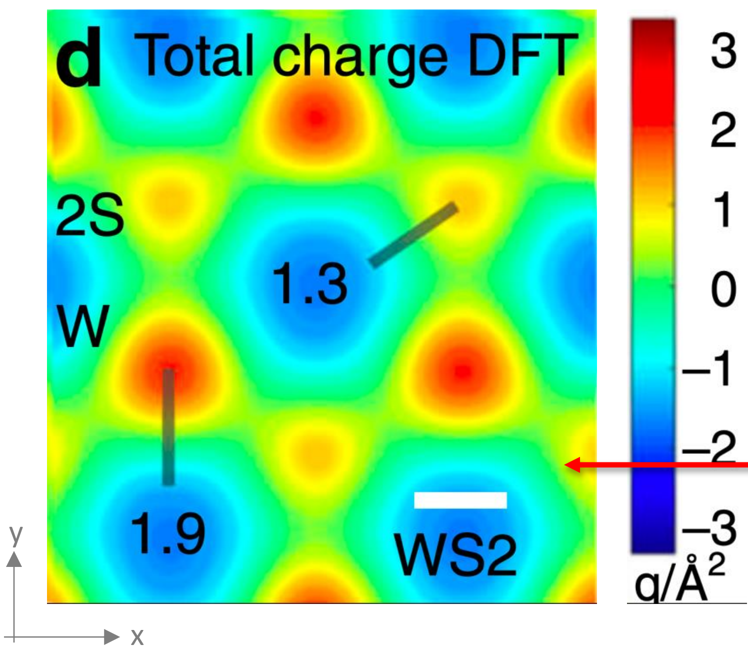



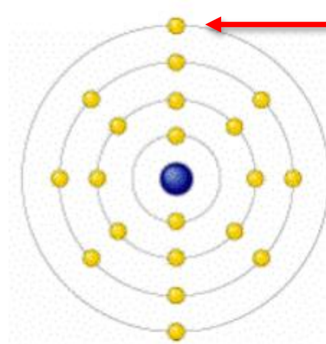
# CL generation: Bond breaking

2D semiconductor $WS_2$





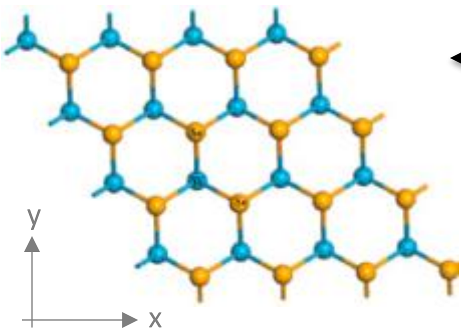



“Outer shell electrons” (a.k.a. “valence electrons”) participate in chemical bonds.

CL involves excitation/ionization of valence electrons.

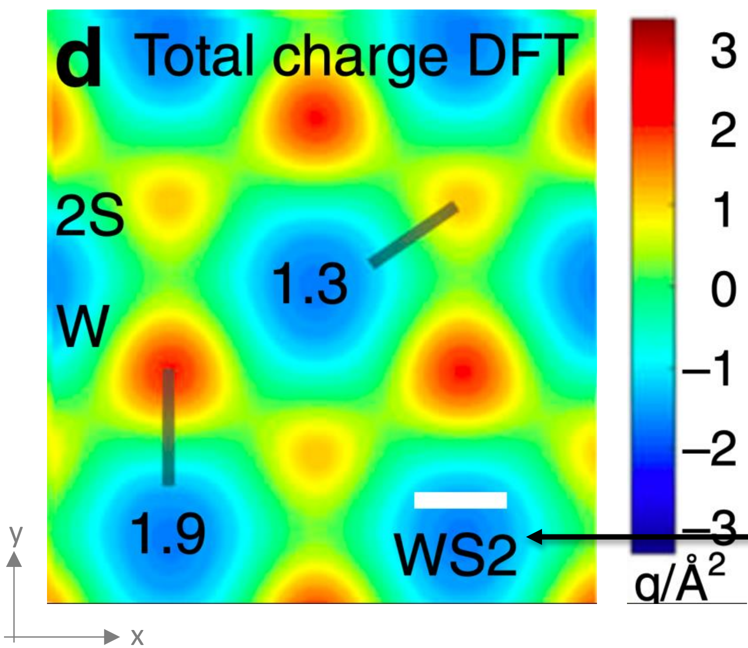
Valence electrons are “spread out” between the atoms, as illustrated by this “charge density plot” calculated for the 2D material $WS_2$.

# Charge density & energy bands




In a crystal, atoms are arranged in a regular, repeating pattern, creating a **periodic potential** that affects the wavefunction of the electrons.

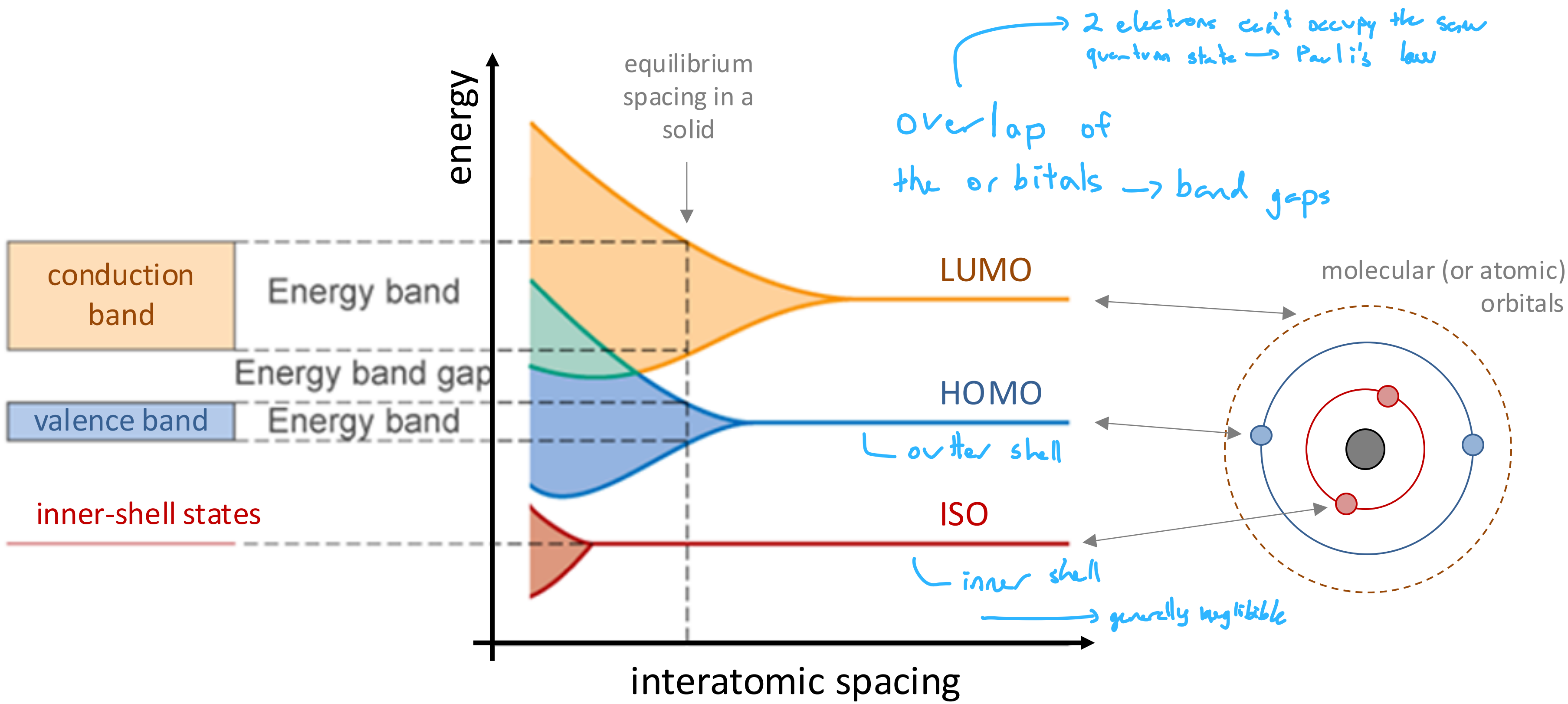
**Bloch's theorem:** the wavefunction of an electron in a periodic potential can be written as the product of a **plane wave** [NOTE: electrons in the valence band and inner shell states are 'tightly bound to the nuclei' and best thought of as standing waves; a **standing wave** results from the interference of two waves with the same frequency and amplitude traveling in opposite directions] and a function that has the same periodicity as the crystal lattice.




The allowed energy levels of electrons in a crystal form **energy bands**. Each energy band corresponds to a set of Bloch states, where each Bloch state is associated with a specific energy level within the band.

The **charge density** reflects the probability distribution of electrons in the crystal and is directly computed from the Bloch states. Since the crystal potential is periodic, the charge density will also inherit this periodicity.

# From atomic orbitals to energy bands



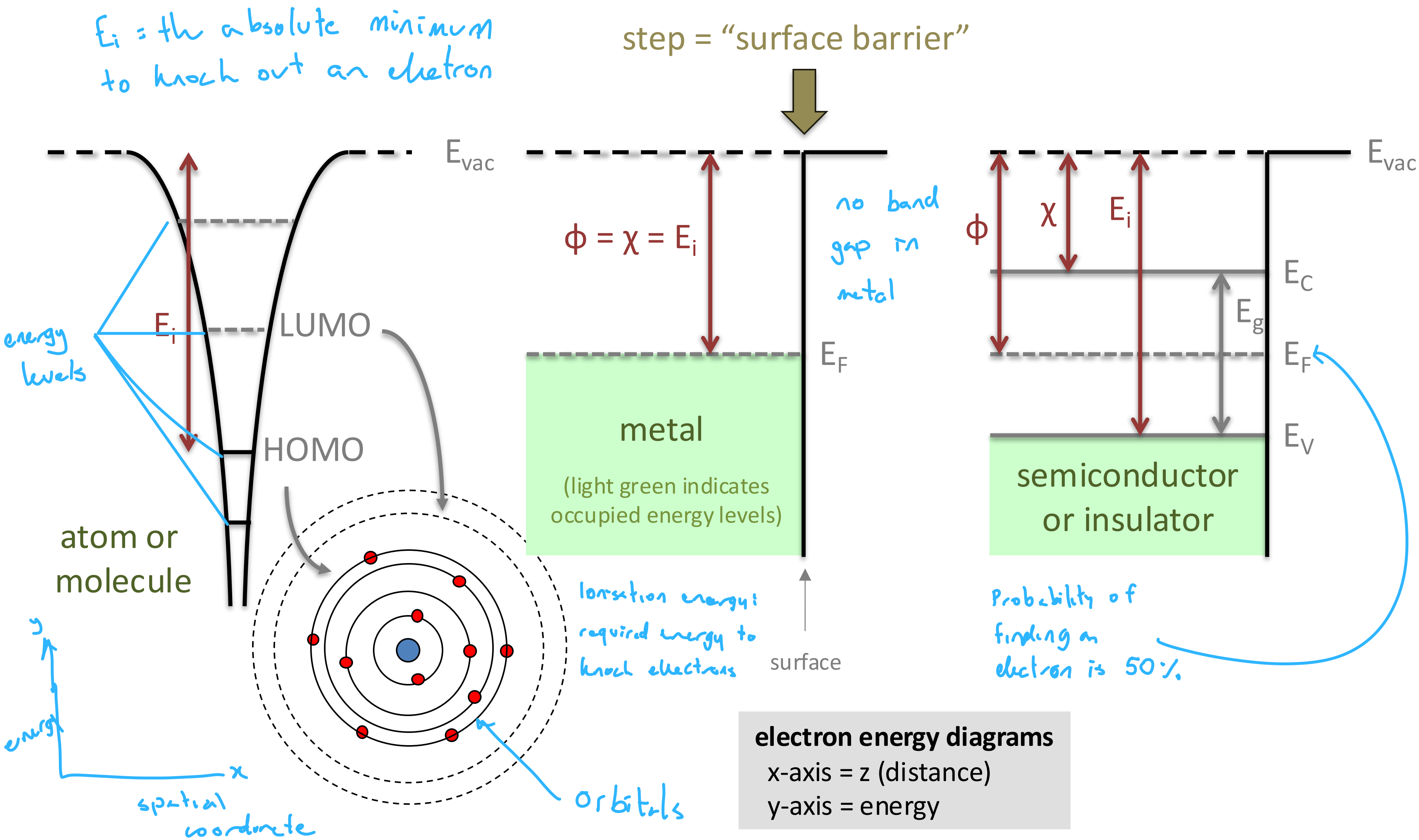

The allowed energy levels in a crystal form **bands** which arise from solutions to the Schrödinger equation with **Bloch states** as the **basis**.

**Pauli exclusion principle** plays a role: “no two fermions (such as electrons) can occupy the same quantum state simultaneously”.

LUMO: lowest unoccupied molecular orbital
HOMO: highest occupied molecular orbital
ISO: inner-shell atomic orbital

band gap → dielectric (semiconductors and insulators)
no band gap → metal

# Work function & related quantities




**electron energy diagrams**
x-axis = z (distance)
y-axis = energy

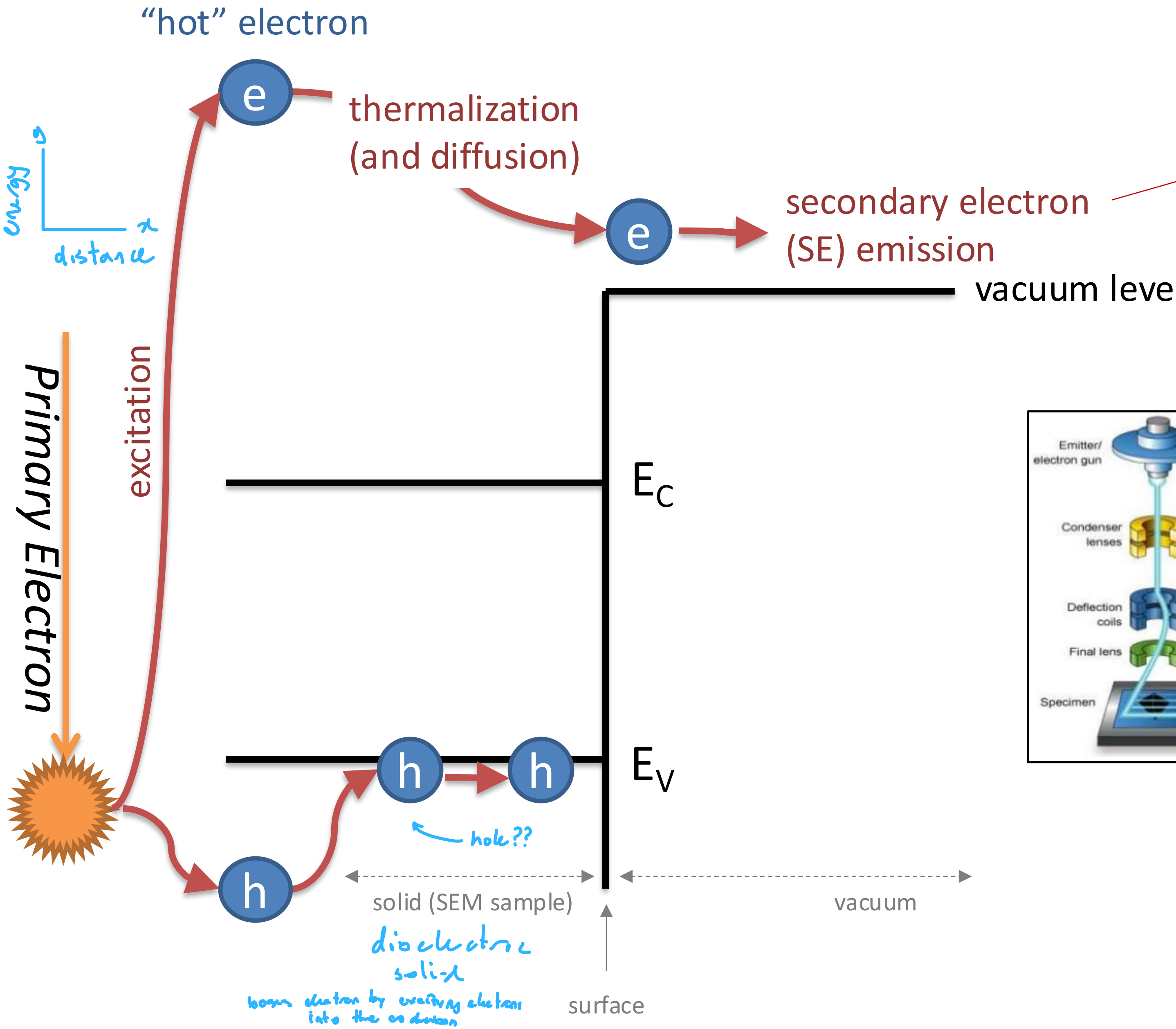
LUMO = lowest unoccupied molecular orbital
HOMO = highest occupied molecular orbital

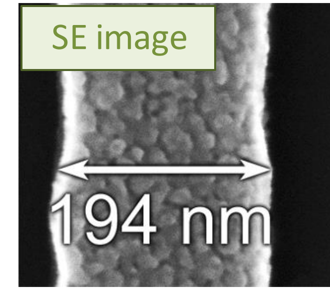
$\phi$ = work function
$\chi$ = electron affinity
$E_i$ = ionization energy

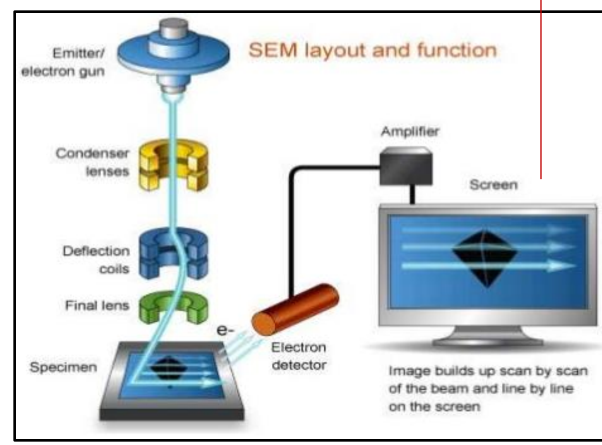
$E_{vac}$ = vacuum level
$E_C$ = bottom of conduction band (CB)
$E_V$ = top of valence band (VB)
$E_F$ = Fermi energy

# SEM: Electron excitation & emission

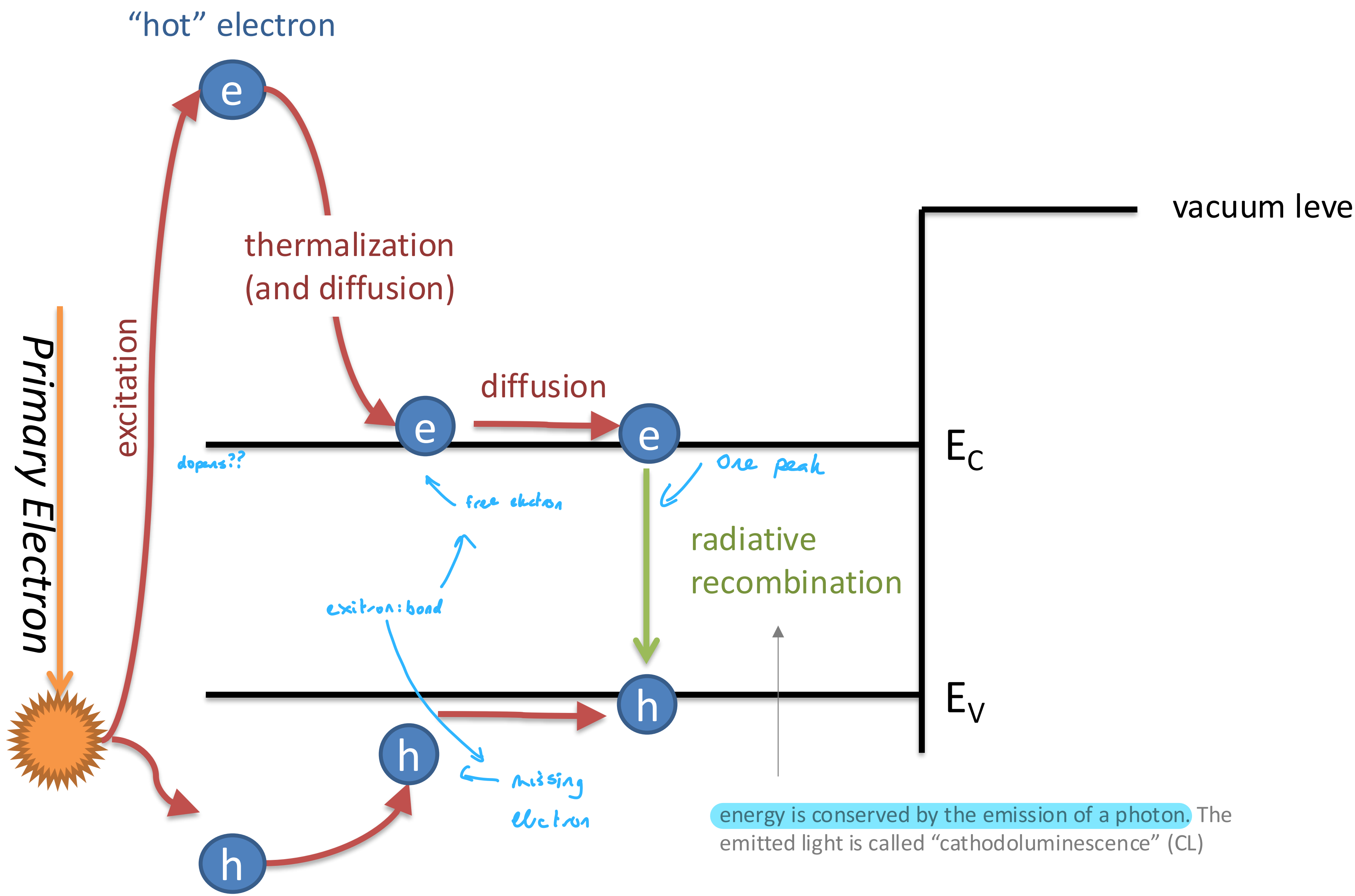
IMPORTANT TO KNOW



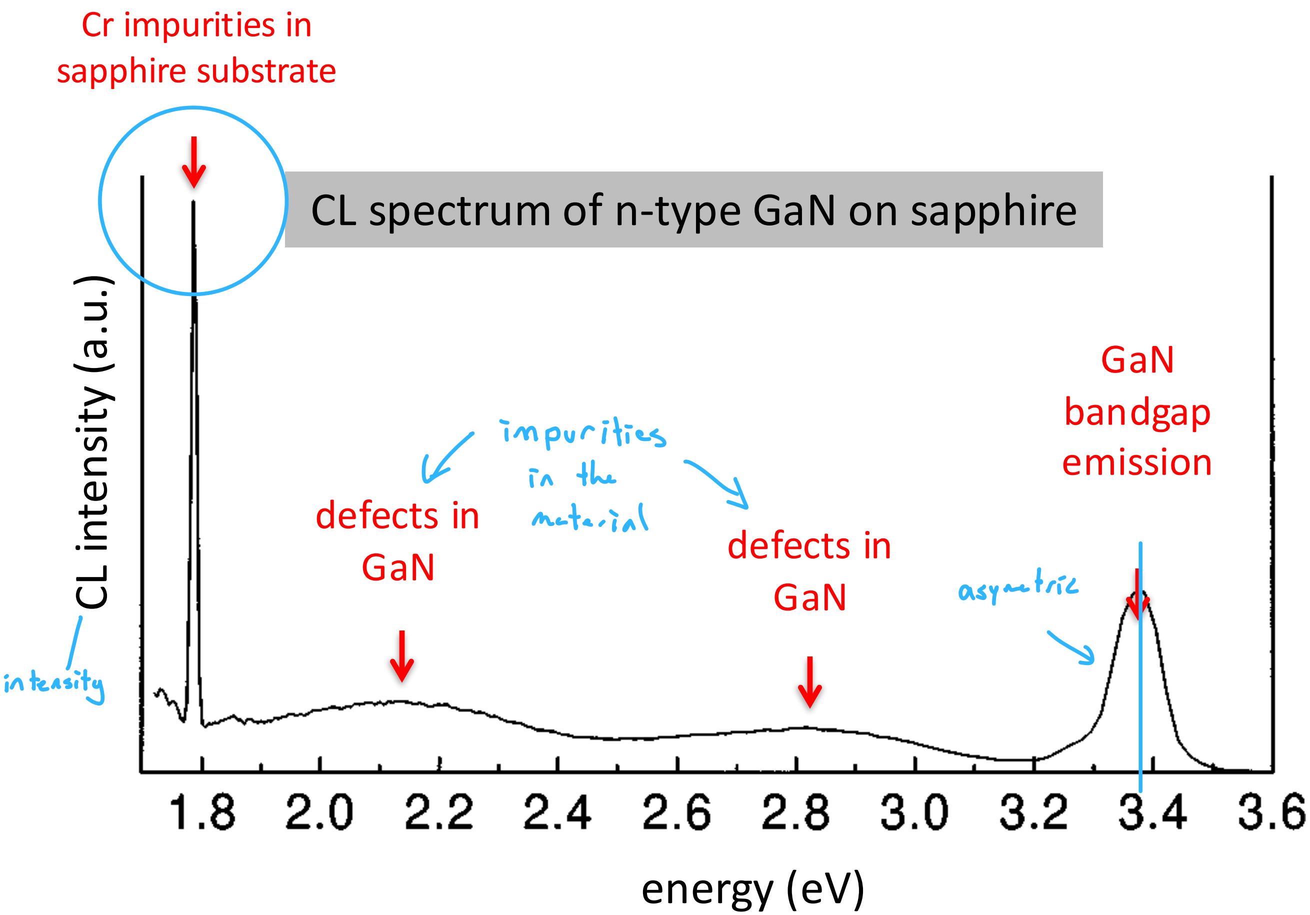



# CL generation



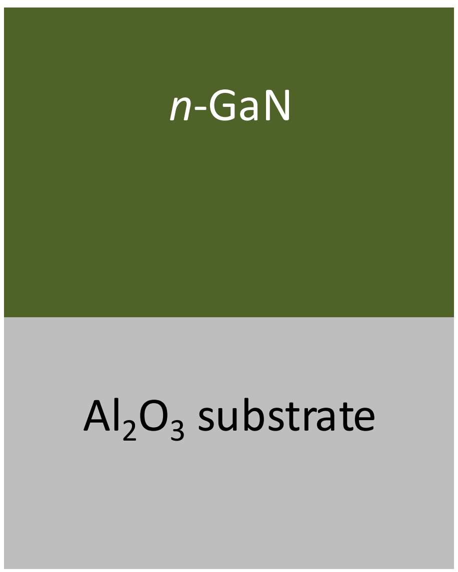

energy is conserved by the emission of a photon. The emitted light is called "cathodoluminescence" (CL)

# CL spectra

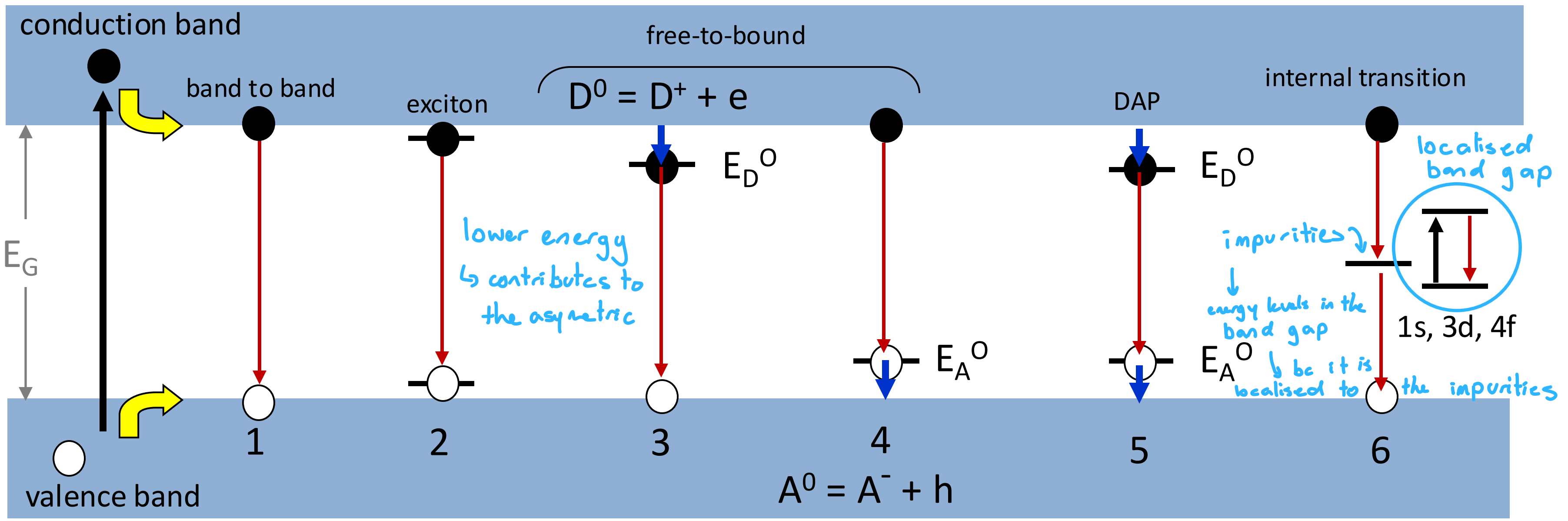



material in Portfolio 1

Sample schematic



# Radiative recombination mechanisms




**1 band to band** $\mathbf{E_{CL} = E_G}$

2 free and bound exciton $E_{CL} = E_G - E_{EX}$

3 free hole to donor-bound electron $E_{CL} = E_G - E_D$

4 free electron to acceptor-bound hole $E_{CL} = E_G - E_A$

5 donor - acceptor pair $E_{CL} = E_G - E_D - E_A + q^2/(4\pi\varepsilon_o\varepsilon r)$

**6 internal transitions at point defects: e.g., vacancies, interstitial, impurities…**

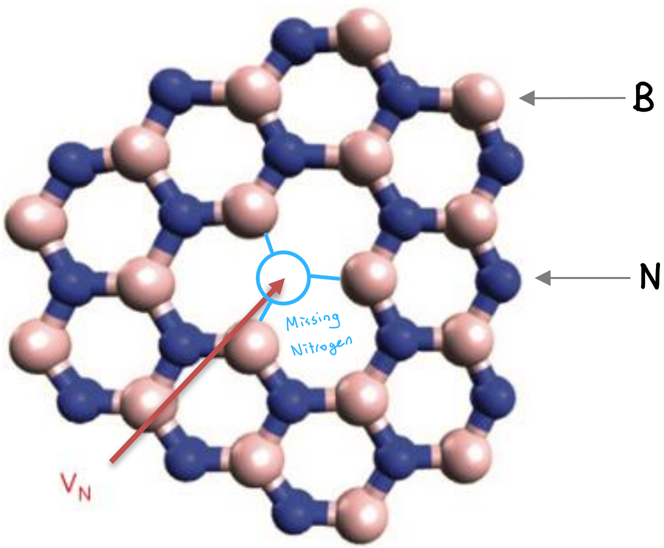
# 'Point defect' – an example

From a paper on research done at UTS, in the MAU (i.e., a PhD project)

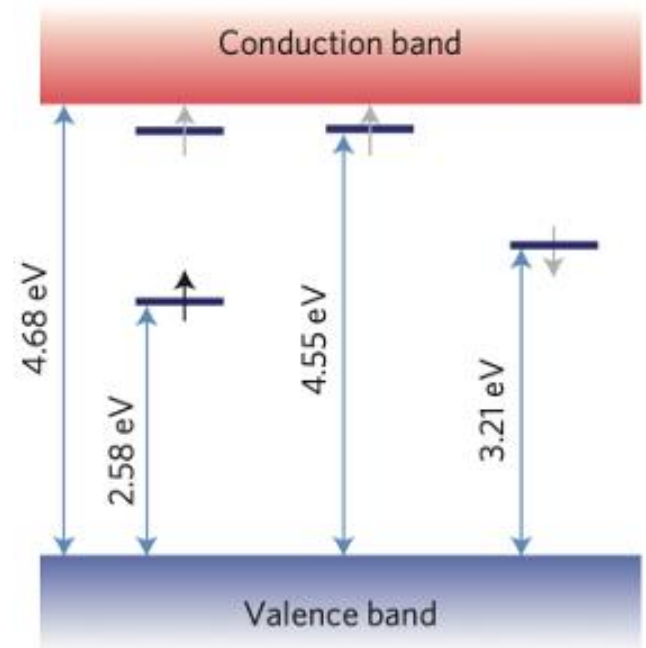
Types: 1. foreign atom

2. missing atom

$V_N$ defect in the hBN lattice




$V_N$ defect states in the band gap of hBN




**Material:** hexagonal boron nitride (hBN) – a 2D material analogous to graphene
**Defect:** missing nitrogen atom (nitrogen 'vacancy' $V_N$)

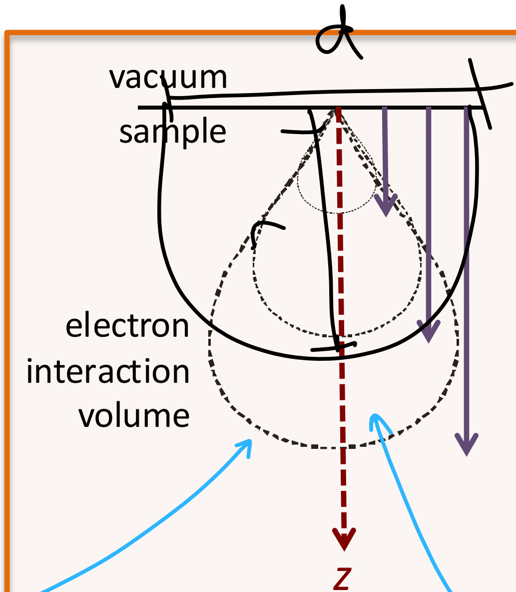
# CL spatial resolution

modulate the spectra

- limited by 3 factors: size of the interaction volume, carrier diffusion and **self-absorption**
- **not** limited by the wavelength of the emitted light

Portfolio 1
- Qs have to do with where all the light comes from

REVISION




$$R_e(\mu m) = \frac{27.6 A E_o^{5/3}}{Z^{8/9}\, r}$$

$R_e$ = maximum electron range, (shown here for 3 beam energies $E_o$)

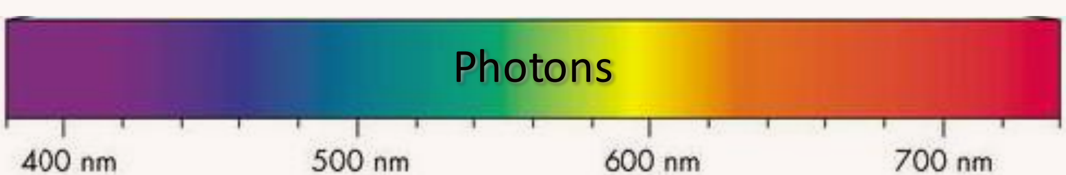
Resolution of CL is determined by:
- the interaction size
  - limiting factor is the beam diameter
  - wavelength of the emitted energy DOES NOT affect the resolution at all

the interaction volume determines the resolution + diffusion
↳ it is the limitation

represents the spatial domain

where the light is coming from as a function of depth
↓
how much light is produced as a function of depth

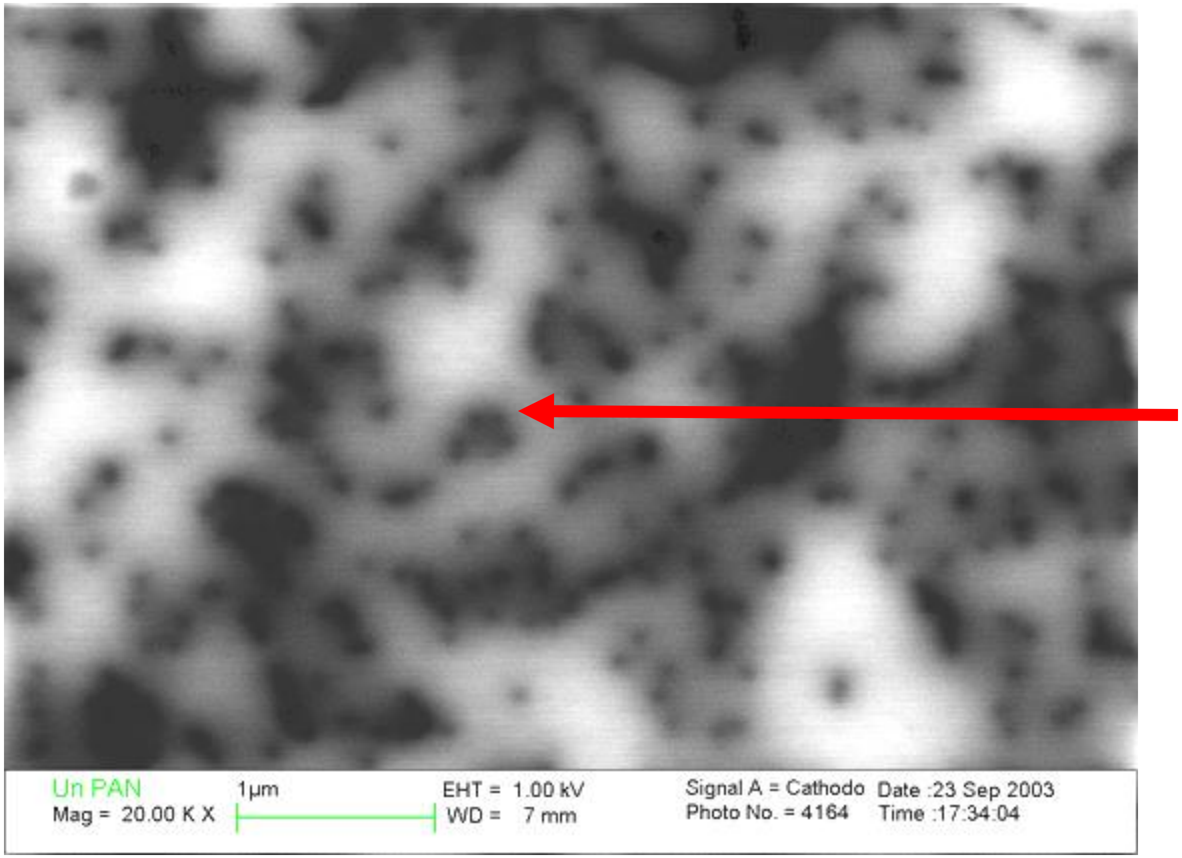
diffraction resolution limit in optical microscopy ≈ $\lambda/2$



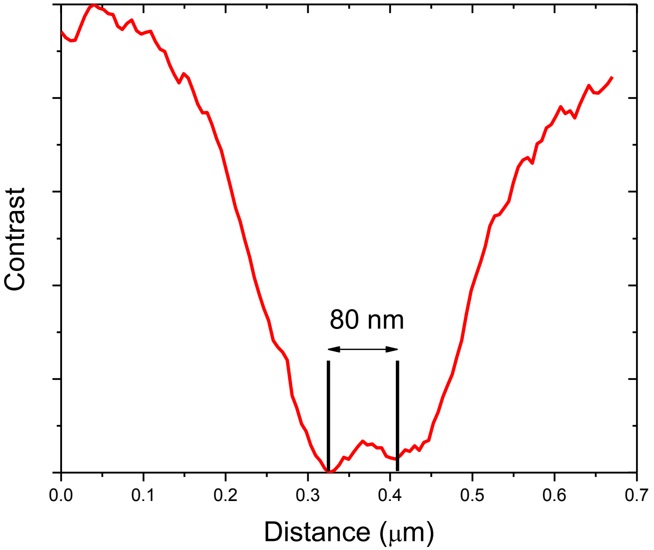
# CL spatial resolution

not limited by the wavelength of the emitted light (which is ~ 300 nm)

CL image of GaN (electron beam energy = 1 keV)



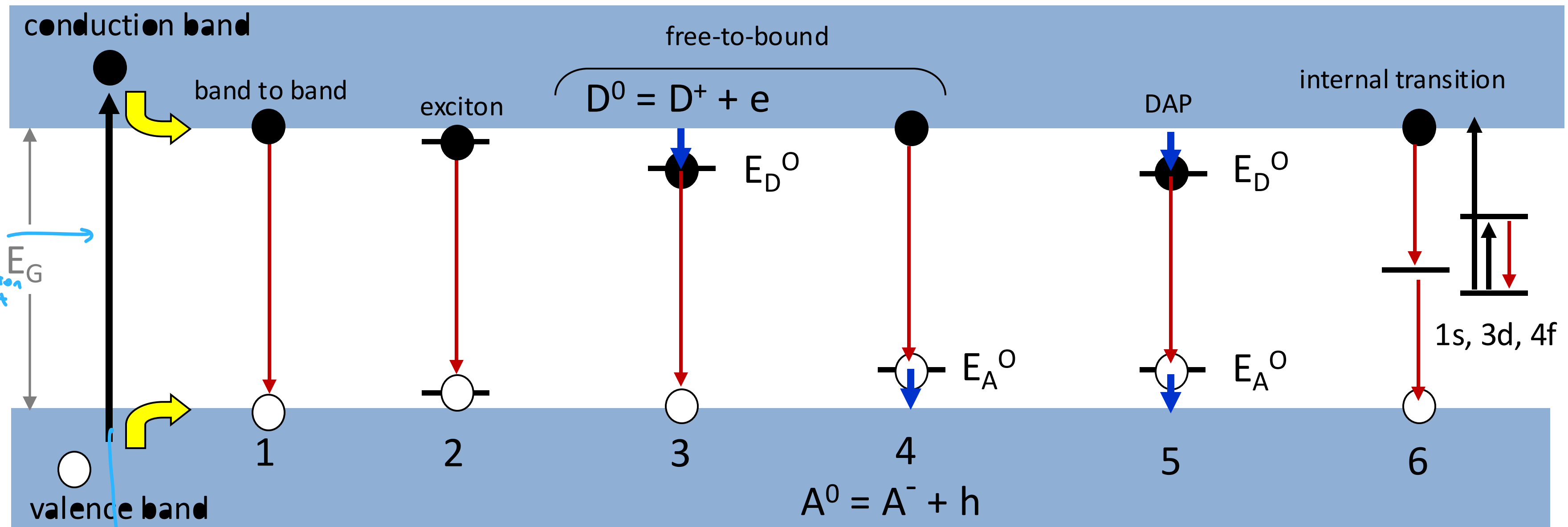

Threading dislocations separated by ~ 80nm



# Absorption of CL by the sample

1. generation of light
2. absorption of light on the way out of material
3.

pertains to the absorption of light




most efficient absorbed by material

The black arrows represent electron excitation pathways. In CL, the electrons in the sample are excited by the electron beam (i.e., by the so-called "primary electrons").

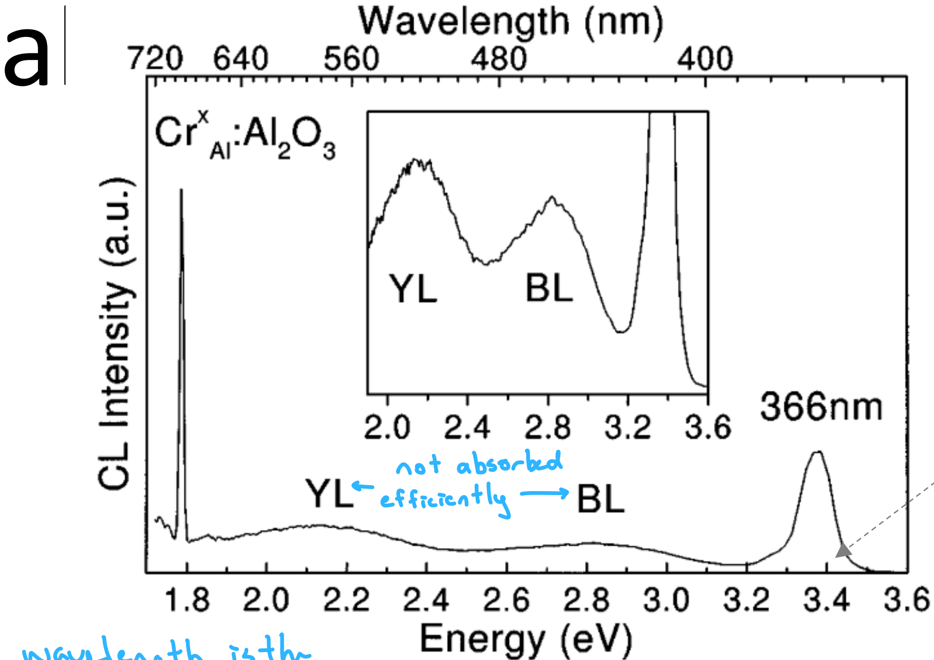
Electrons in the sample can also be excited by photons, including CL photons. This results in absorption of the photons (i.e., some of the CL photons are absorbed by the sample and therefore do not reach a detector).

**1 band to band** ← Very efficient CL absorption pathway, because there is a high density of energy states in the conduction band and in the valence bands. However, the photon energy must be $\gtrsim E_G$.

**6 internal transitions at point defects** ← The efficiencies of these pathways depend on the defect concentrations ("densities"), and on the photon energy. In high quality semiconductors (i.e., "optoelectronic grade"), these pathways are extremely inefficient, and the resulting absorption is negligible

Mabel Angelina Marilyn Madera Acosta (Elizabeth)

# CL spatial resolution: Role of absorbtion



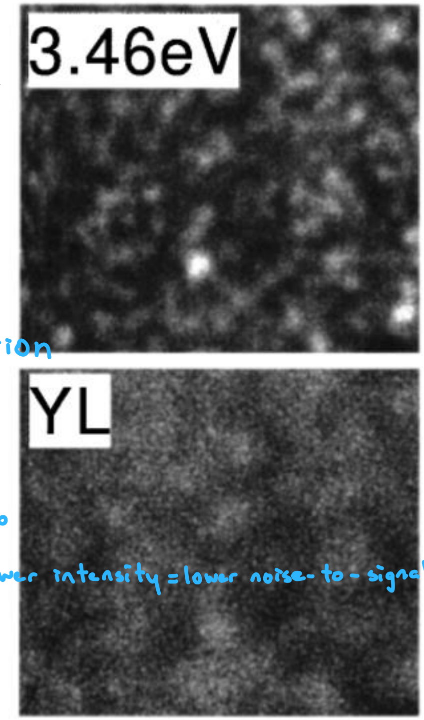

not absorbed efficiently

band gap energy

↳ absorbed efficiently
-highest resolution

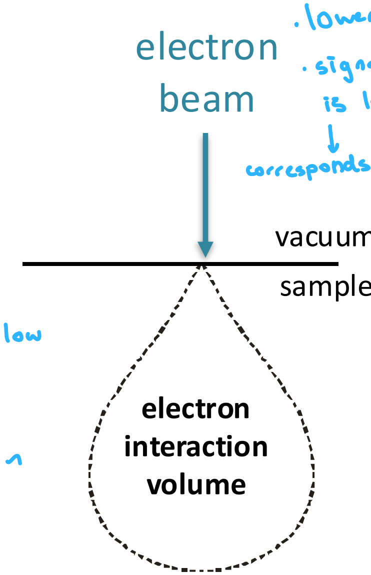
wavelength is the reciprical to energy

3.46 eV bandgap emission is absorbed by the sample, hence image resolution is high




. lower resolution
. signal-to-noise ratio is lower → lower intensity = lower noise-to-signal ratio
↓ corresponds to less signal

All CL emissions are generated throughout the interaction volume. However, the 3.46 eV bandgap emission is absorbed by the sample, and only CL generated near the surface is emitted




low beam energy: light generation on surface low

new peak = another peak goes down

↑ beam energy: smaller the band gap emission

Read paper!

YL defect emission is not absorbed by the sample, hence image resolution is lower (analogous to backscattered electron image resolution)

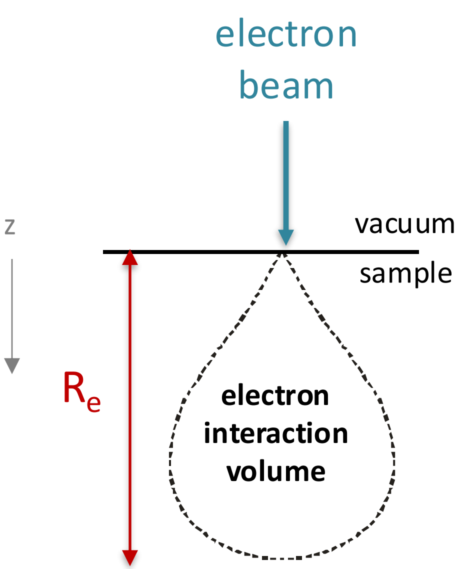
↳ collect the light for longer to get better noise-to-signal ratio

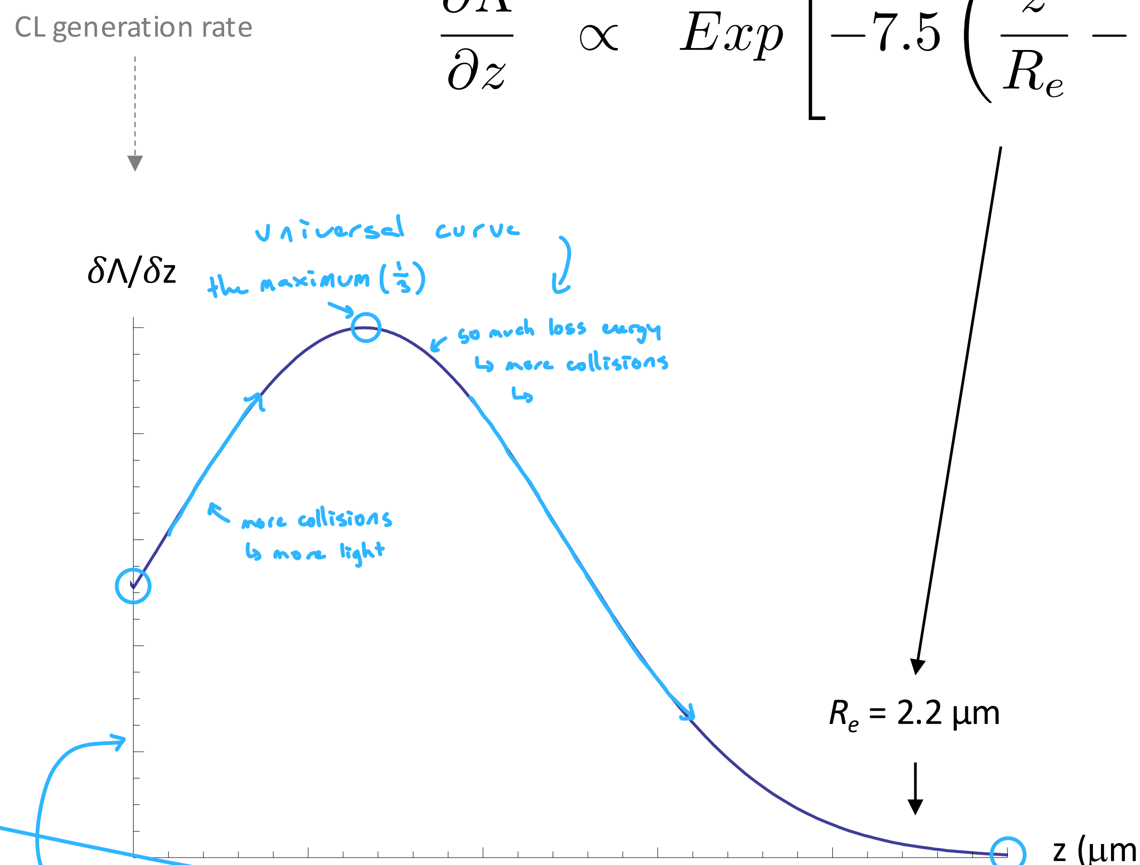
for details, see the paper
"14. CL Depth profiling.pdf" (available in Canvas/Modules/LITERATURE)

# Normalized CL generation (i.e., excitation) vs depth

- $z$ = depth below the sample surface (nm)
- $R_e$ = max electron range (nm)

$$\frac{\partial \Lambda}{\partial z} \propto Exp\left[-7.5\left(\frac{z}{R_e}-0.3\right)^2\right]$$




atomic weight [g/mol]

$$R_e(nm)=\frac{27.6AE_o^{5/3}}{Z^{8/9}\rho}$$

energy of beam [keV]

atomic number

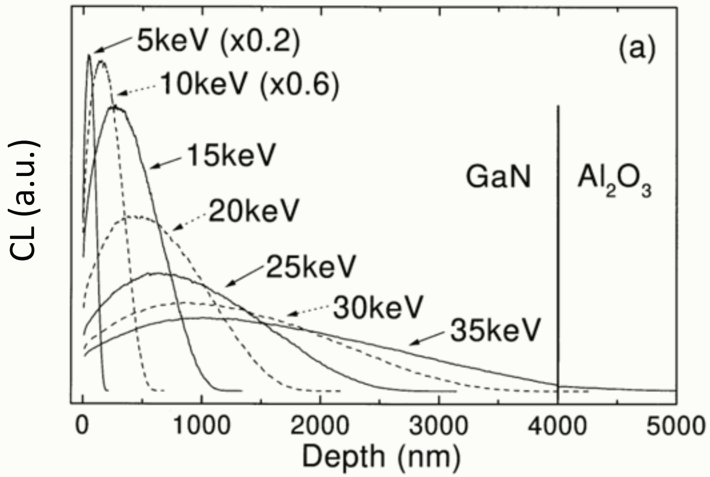
density g/cm³

↳ don't just add!
·Google it!
↳ Tut 4 portfolio 2

This plot was calculated for the material GaN, and $E_0$ = 20 keV

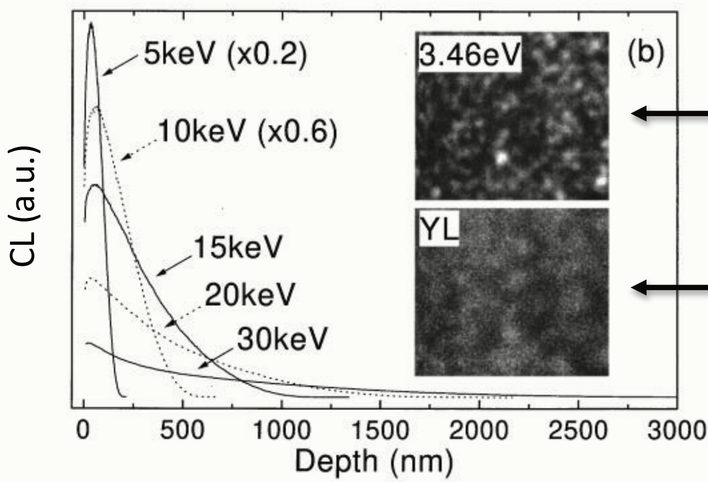
# CL spatial resolution: Self-absorption

- CL generation rates vs depth
- Also representative of CL emission rate for light that is not absorbed by the sample



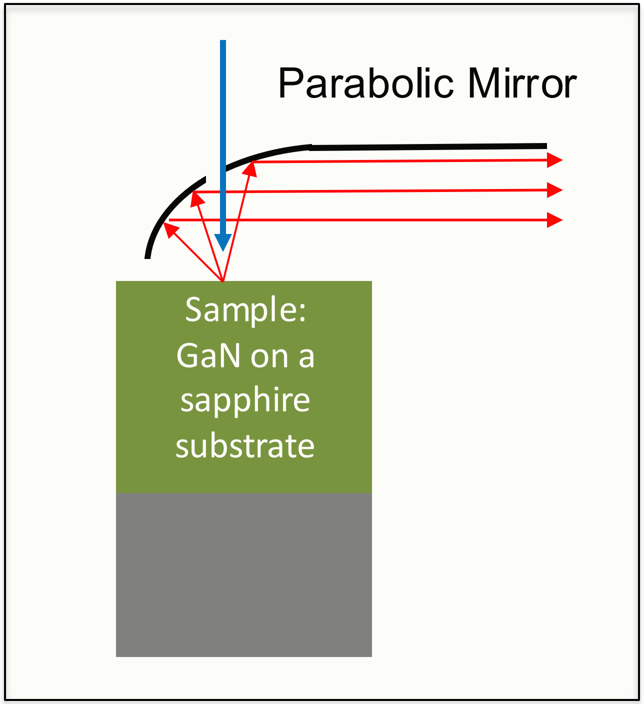

Beam Energy

- CL emission rate for light that is absorbed by the sample




Band gap emission

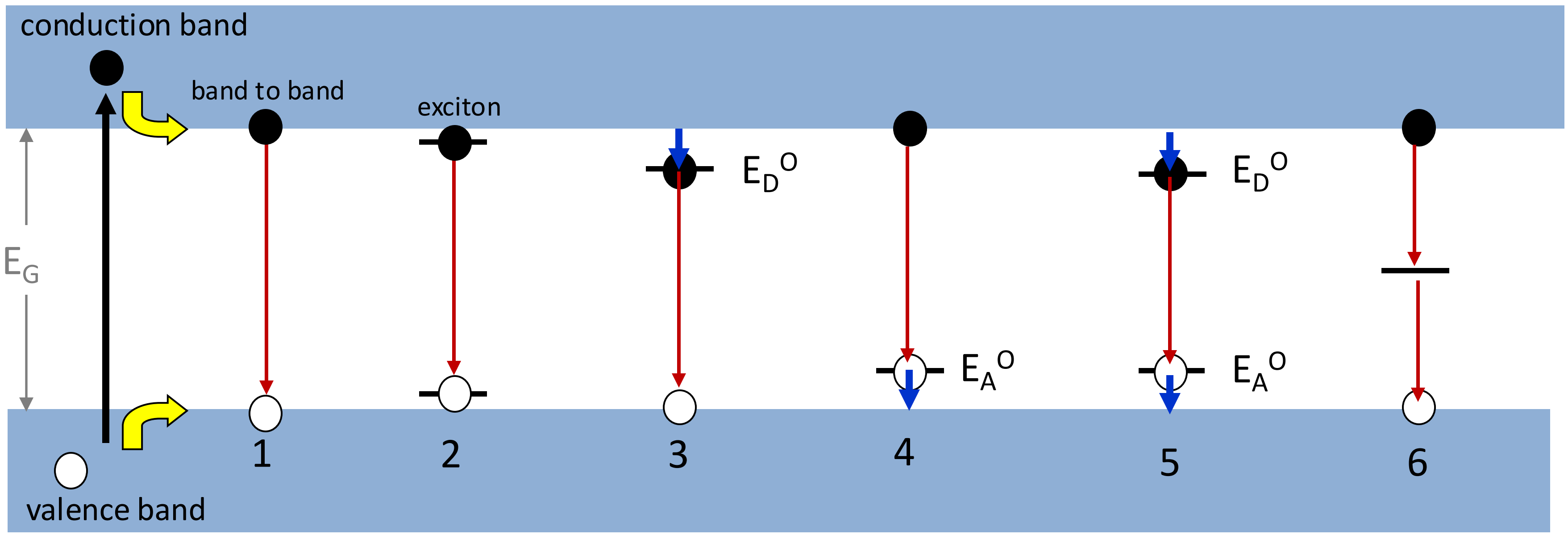
Experimental setup



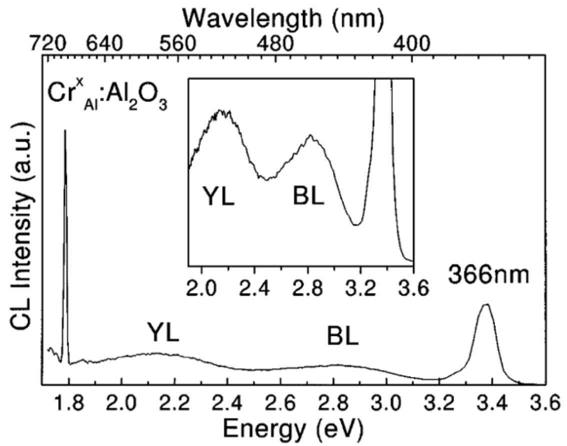

CL image 1: photon energy ~ 3.46 eV (bandgap emission), which is absorbed by GaN

CL image 2: photon energy ~ 2.2 eV ("yellow luminescence", YL), which is not absorbed by GaN; image resolution is lower (compared to image 1)

# Recombination competition




After excitation into the conduction band, the electron can recombine through any one of the available pathways – the recombination is therefore 'competitive'.




Hence, if, for example, the concentration of a defect responsible for the 'BL' emission increases, the corresponding peak intensity will increase at the expense of the other emissions (i.e., the other will decrease)

# Recombination rates are additive

carrier density {number of electrons in the conduction band per nm$^3$} [units: nm$^{-3}$]

total recombination rate per unit volume [units: nm$^{-3}$s$^{-1}$]

$$\Pi = n \sum_i k_i$$

recombination rate through pathway i [s$^{-1}$]

$$k_i = \frac{1}{\tau_i} = v \sigma_i N_i$$

life of the electron

recombination time [s]

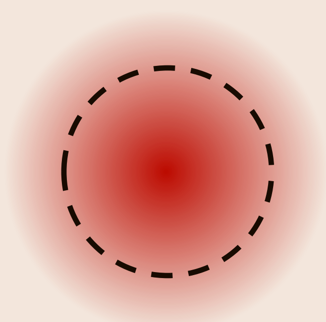
recombination center density [centers/nm$^3$]

carrier thermal velocity (nm/s)

carrier capture cross-section (nm$^2$)

has a certain energy per a velocity

## cross-section



**Red:** a spherical particle (field that's most intense in the center and decays with distance from the center) as "seen" by an incoming electron

**Black:** cross-sectional area (in units of m$^2$) of an abrupt, uniform sphere that represents the particle.

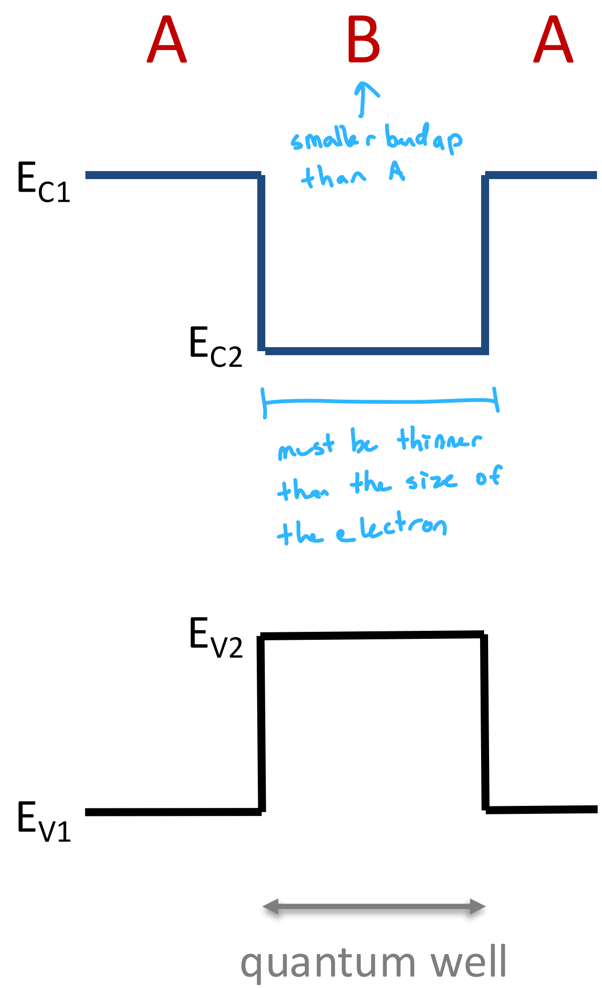
# Quantum well

can be stacked
↳ for efficiency

Material A & B are semiconductors

- Semiconductor B embedded in A
- Bandgap of B is smaller than bandgap of A
- Layer B is very thin (smaller than the wavelength of free electrons in the material

sandwitch the material



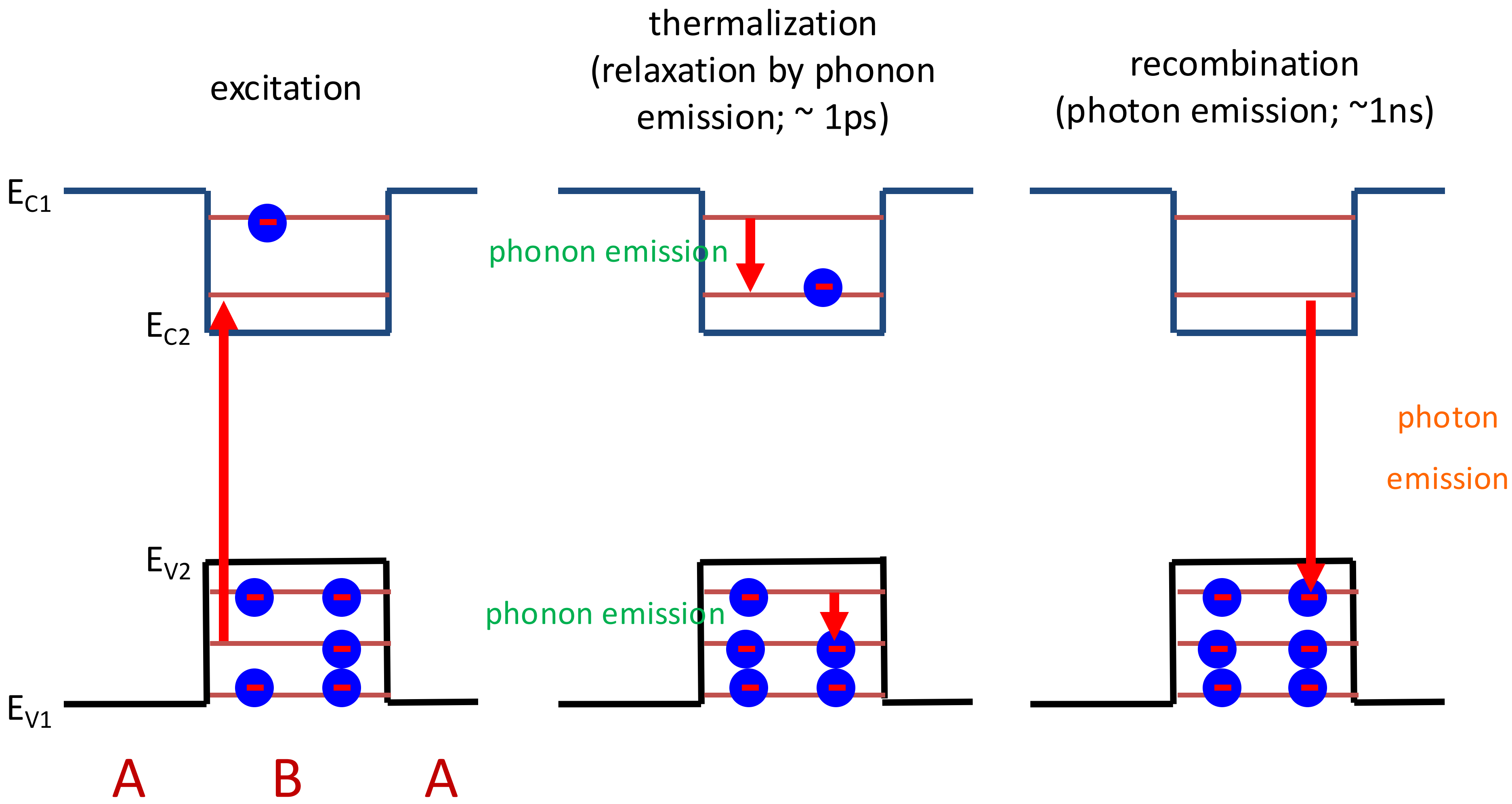

smaller bandgap than A

must be thinner than the size of the electron

- Quantum well traps the excited electrons of A and traps in B. Forces recombination

Please help me
My brain is dead

# Light generation in a quantum well




Electrons can also be excited in material A, diffuse into the quantum well (material B), and recombine in the quantum well

# Recombination rates are additive

carrier density {number of electrons in the conduction band per nm$^3$} [units: nm$^{-3}$]

total recombination rate per unit volume [units: nm$^{-3}$s$^{-1}$]

$$\Pi = n \sum_i k_i$$

recombination rate through pathway i [s$^{-1}$]

$$\begin{aligned} k_i &= \frac{1}{\tau_i} \\ &= v\sigma_i N_i \end{aligned}$$

recombination time [s]

recombination center density [centers/m$^3$]

carrier thermal velocity (m/s)

carrier capture cross-section (m$^2$)

Portfolio 1 : Assume it is experimental data

# Quantum well & surface states

for a fansy Portfolio 1

pi ??

$$\Pi = (k_{RR} + k_s + k_{QW})n$$

radiative recombination rate outside the QW

↓ in semiconductor A

non-radiative recombination at the surface

↓ in semiconductor B

radiative recombination rate in the QW

↓ At the sample surface ↓ lots of defects in reality ↓ extremely reactive ↓ electrons will either reflect or interact (read more into this)

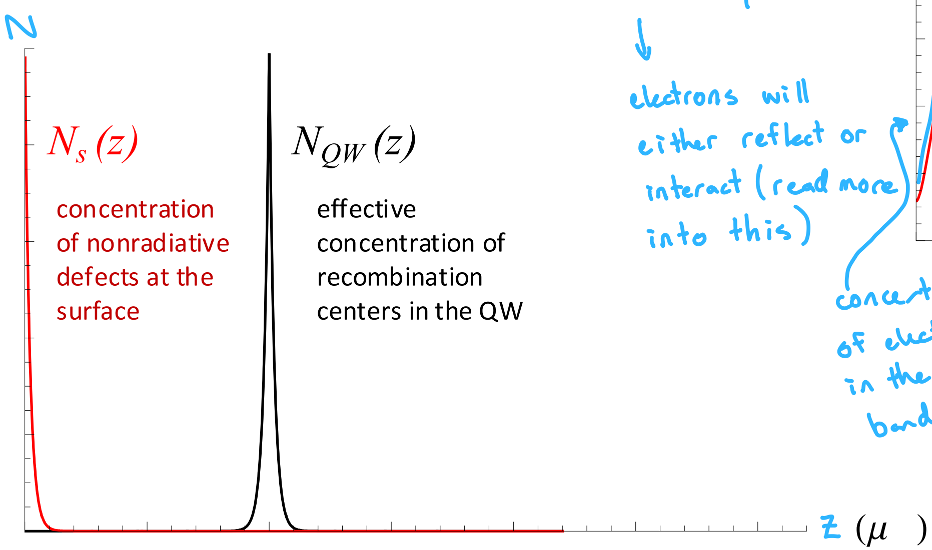
I'm so stressed

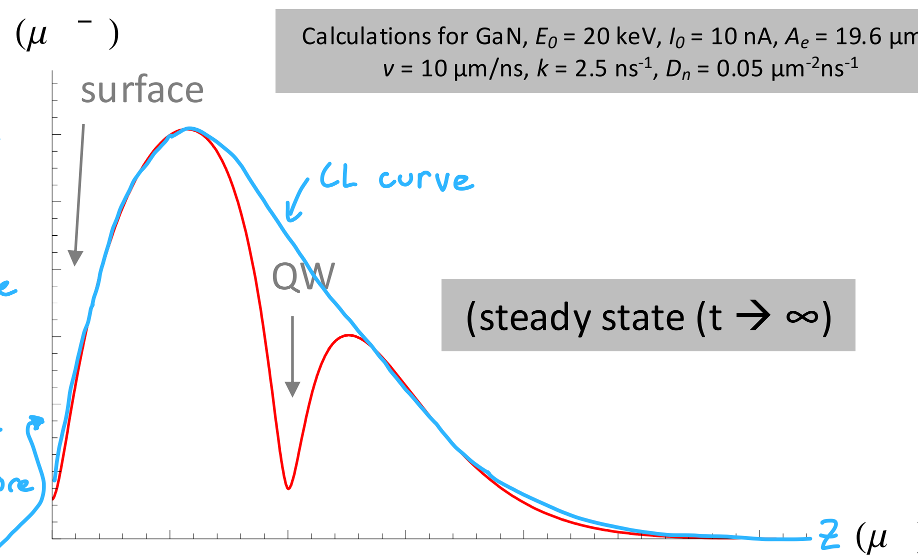
$$k_s = v\sigma_s N_s$$

$$k_{QW} = v\sigma_{QW} N_{QW}$$

Calculations for GaN, $E_0$ = 20 keV, $I_0$ = 10 nA, $A_e$ = 19.6 µm$^2$, $v$ = 10 µm/ns, $k$ = 2.5 ns$^{-1}$, $D_n$ = 0.05 µm$^{-2}$ns$^{-1}$

(steady state (t → ∞)

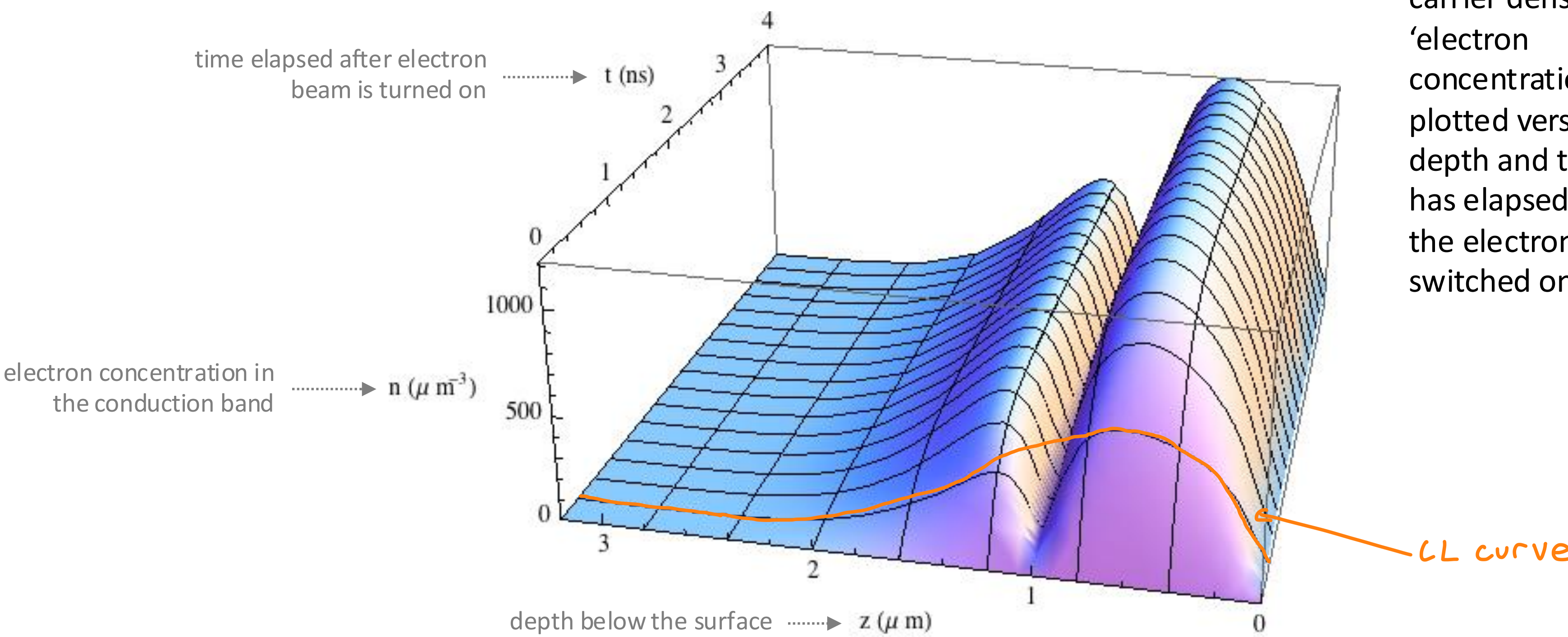


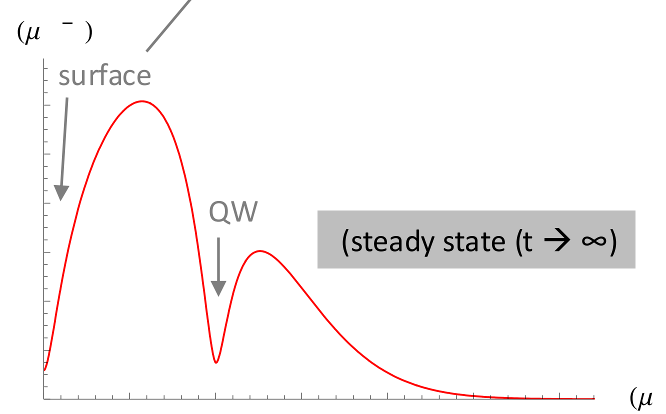

concentration of electrons in the conduction band

← depth below the surface

# Quantum well & surface states




carrier density (i.e., 'electron concentration') plotted versus depth and time that has elapsed after the electron beam is switched on



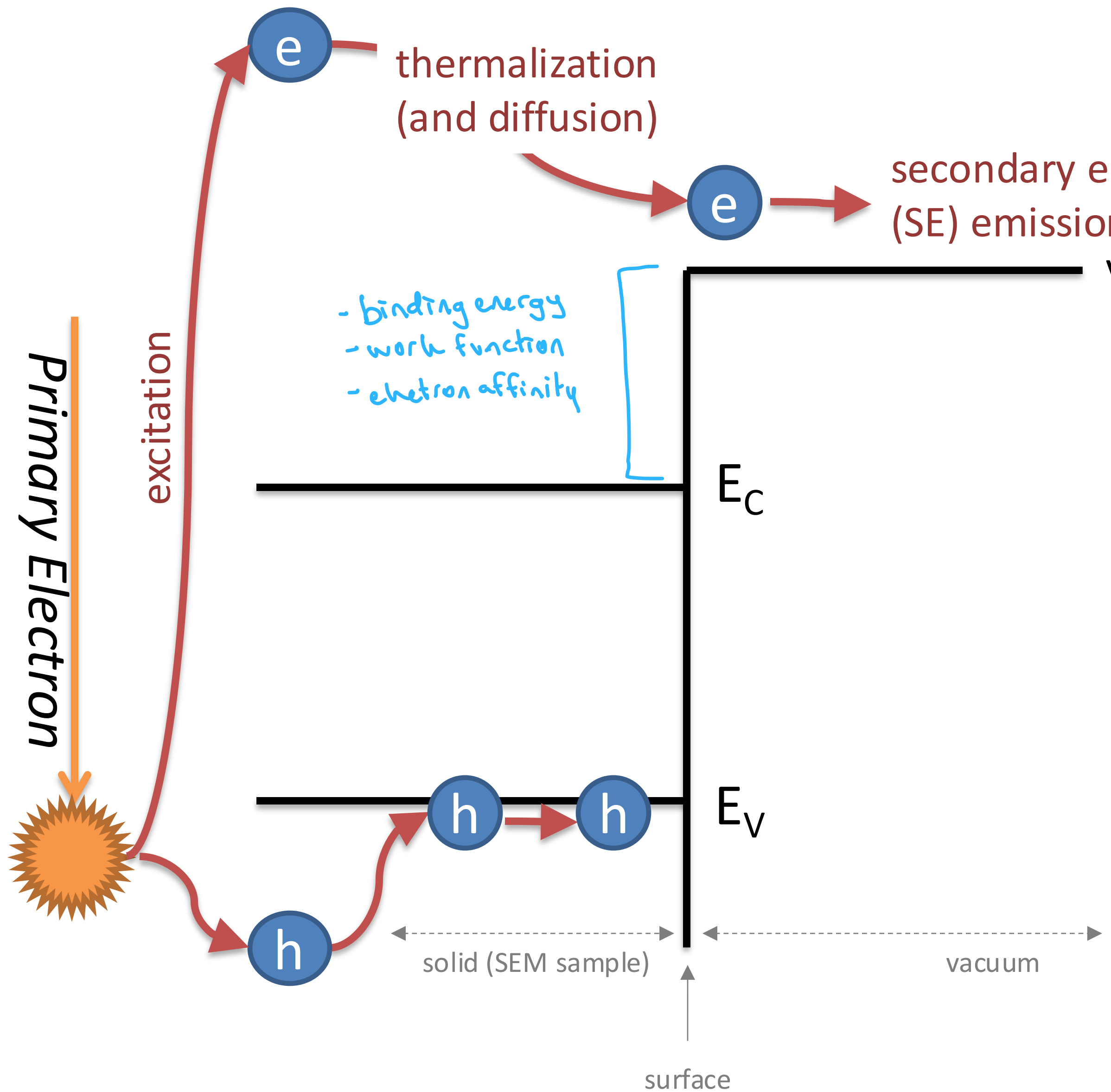
# Electron emission:

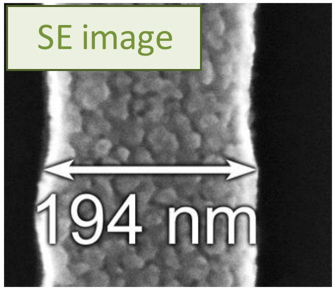
## Secondary Electron (SE) imaging in Scanning Electron Microscopy (SEM)

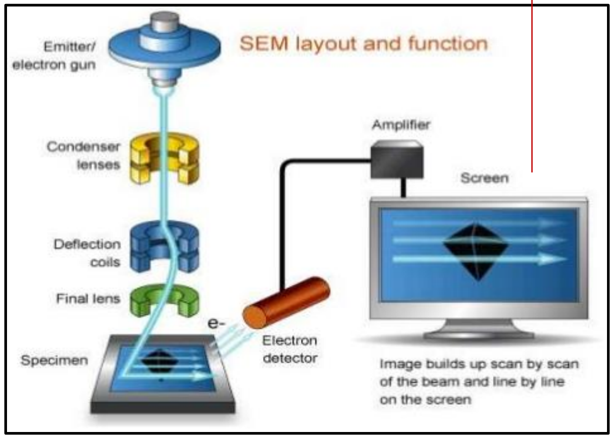
# SEM: Electron excitation & emission

RE-CAP

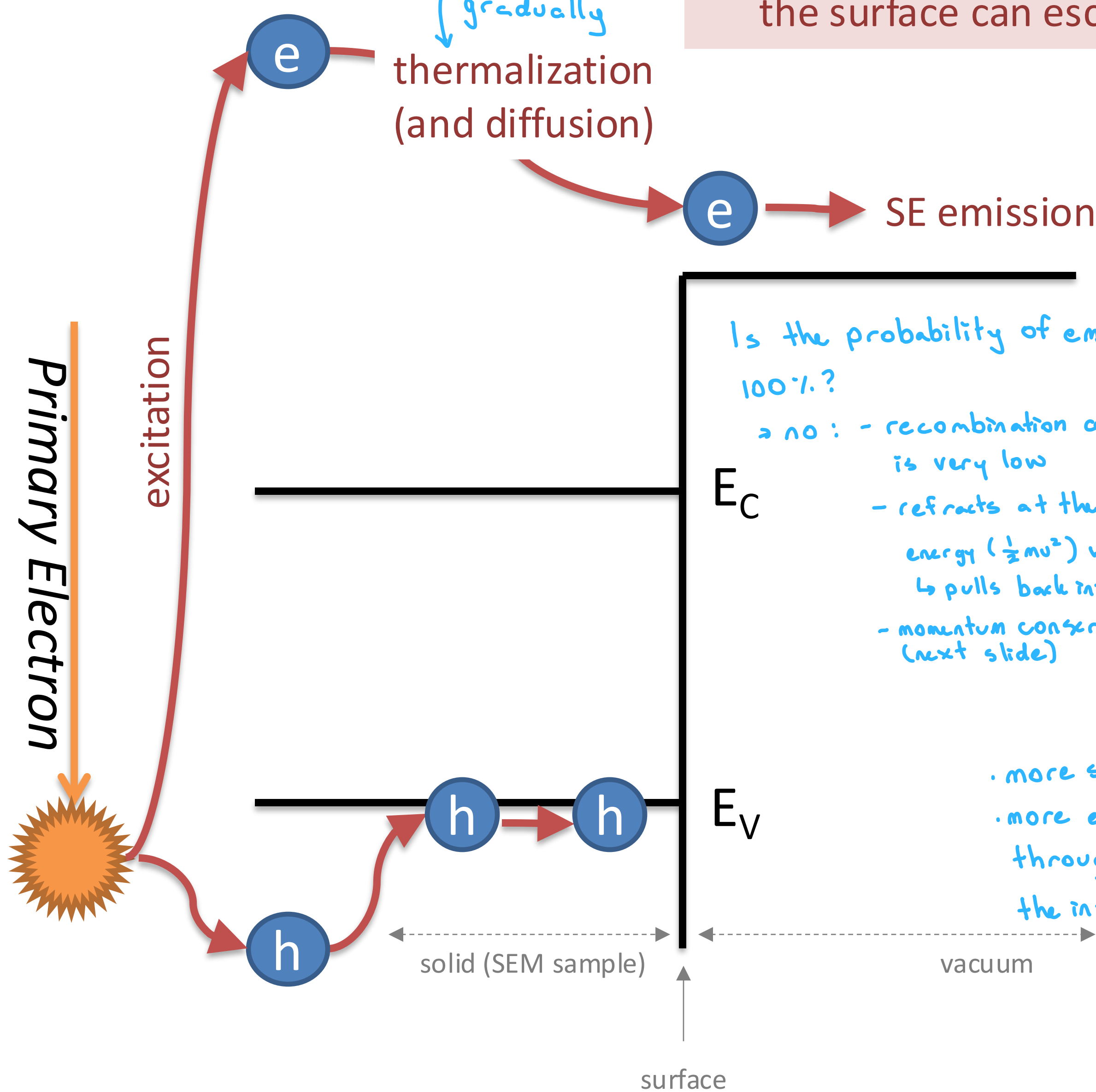
↳ forget quantum well



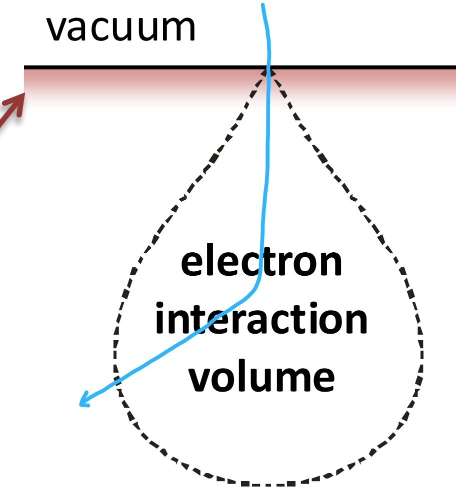



# SEM: SE emission




only electrons generated near the surface can escape...




Is the probability of emission 100%?

→ no: - recombination can happen but is very low

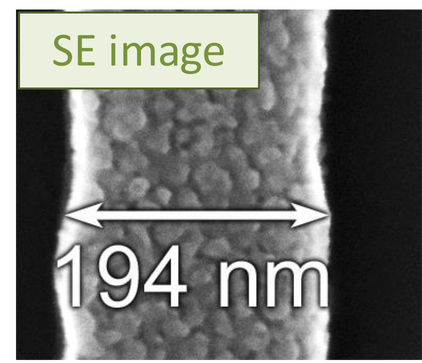
- refracts at the surface; loses energy ($\frac{1}{2}mv^2$) which changes momentum
  ↳ pulls back into the material
- momentum conservation (next slide)

hence the image resolution is high & edge highlighting is prominent in SE images

**edge highlighting**

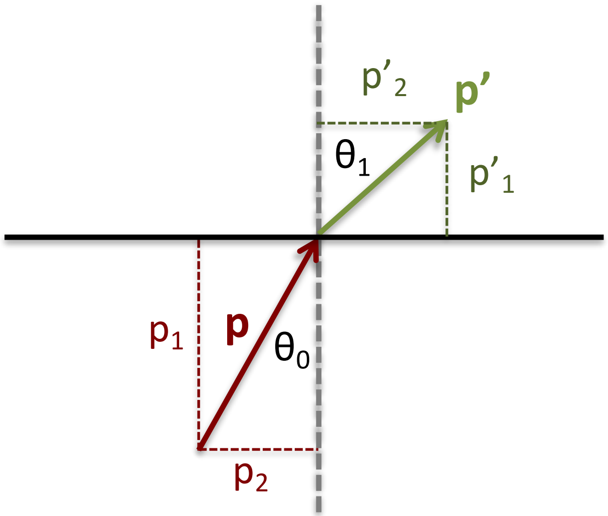
. more surface area

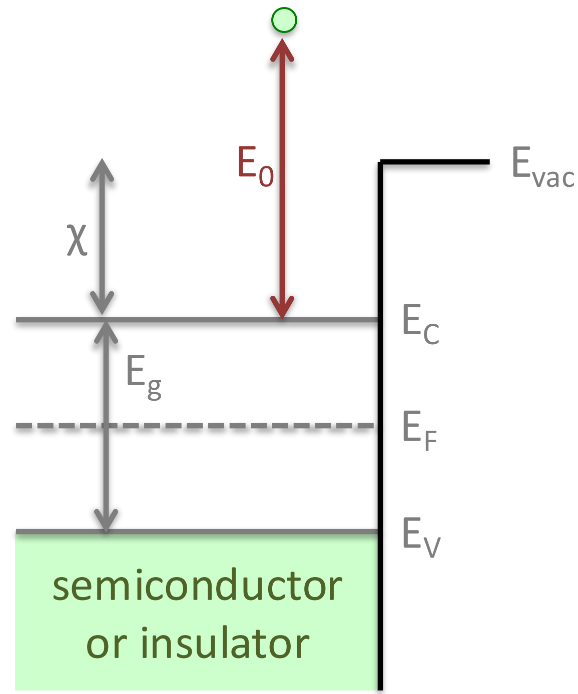
. more electrons escape through the side of the interaction volume




metal on glass

# Electron reflection, emission & refraction



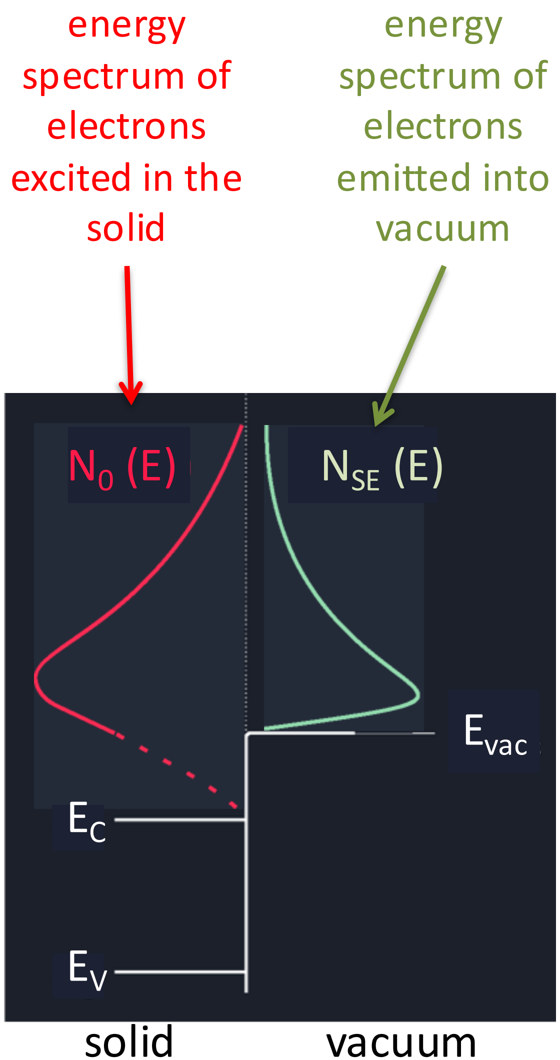



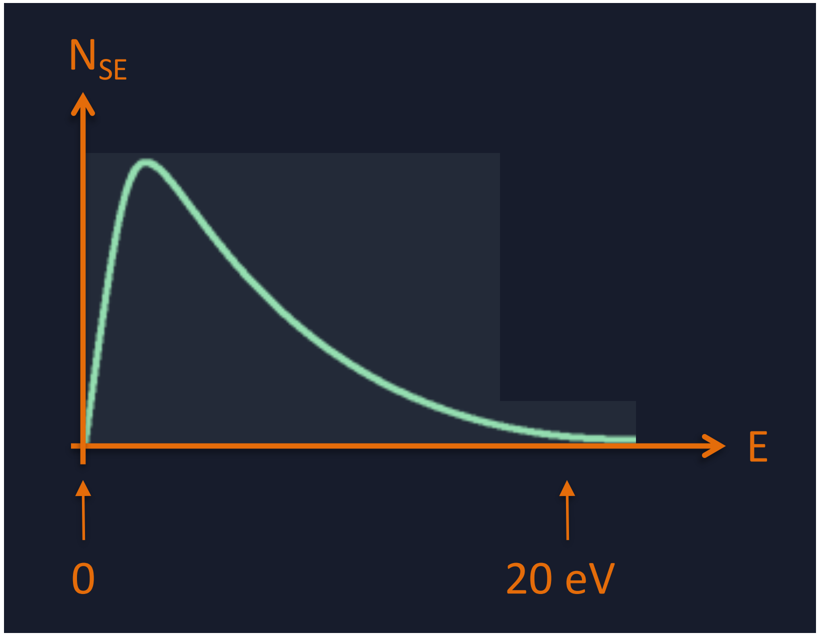

electron kinetic energy, $E_K = 0.5\ mv^2$
electron momentum, $\mathbf{p} = m\mathbf{v}$
momentum normal to surface, $p_1 = p \cos(\theta_0)$
momentum parallel to surface $= p_2 = p \sin(\theta_0)$

on crossing the surface:

- $p_2$ is conserved: $p \sin(\theta_0) = p' \sin(\theta_1)$
- electron loses $\chi$ from $E_K$

# SE energy spectrum




Emitted secondary electrons have low energies

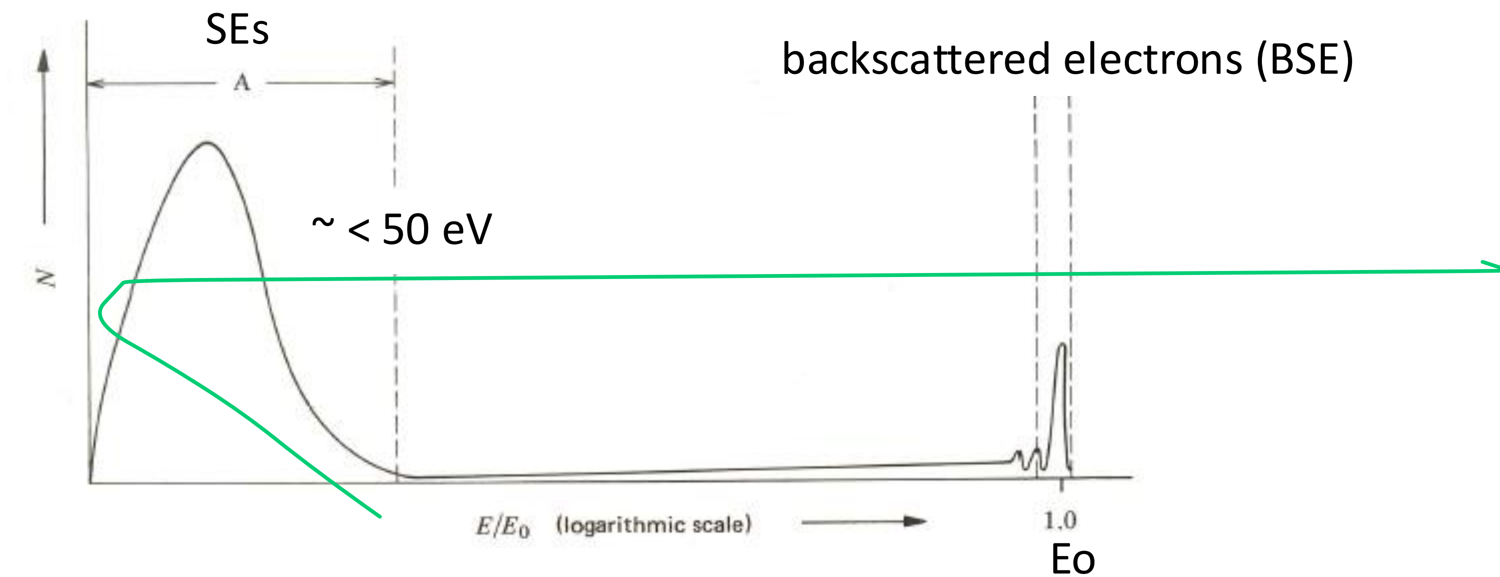
2 overlaid diagrams showing:
- Electron energy (y-axis) vs distance
- Electron spectra (x-axis) vs energy

1 diagram showing:
- Electron spectra (y-axis) vs energy

# Secondary Electrons

Revision slide

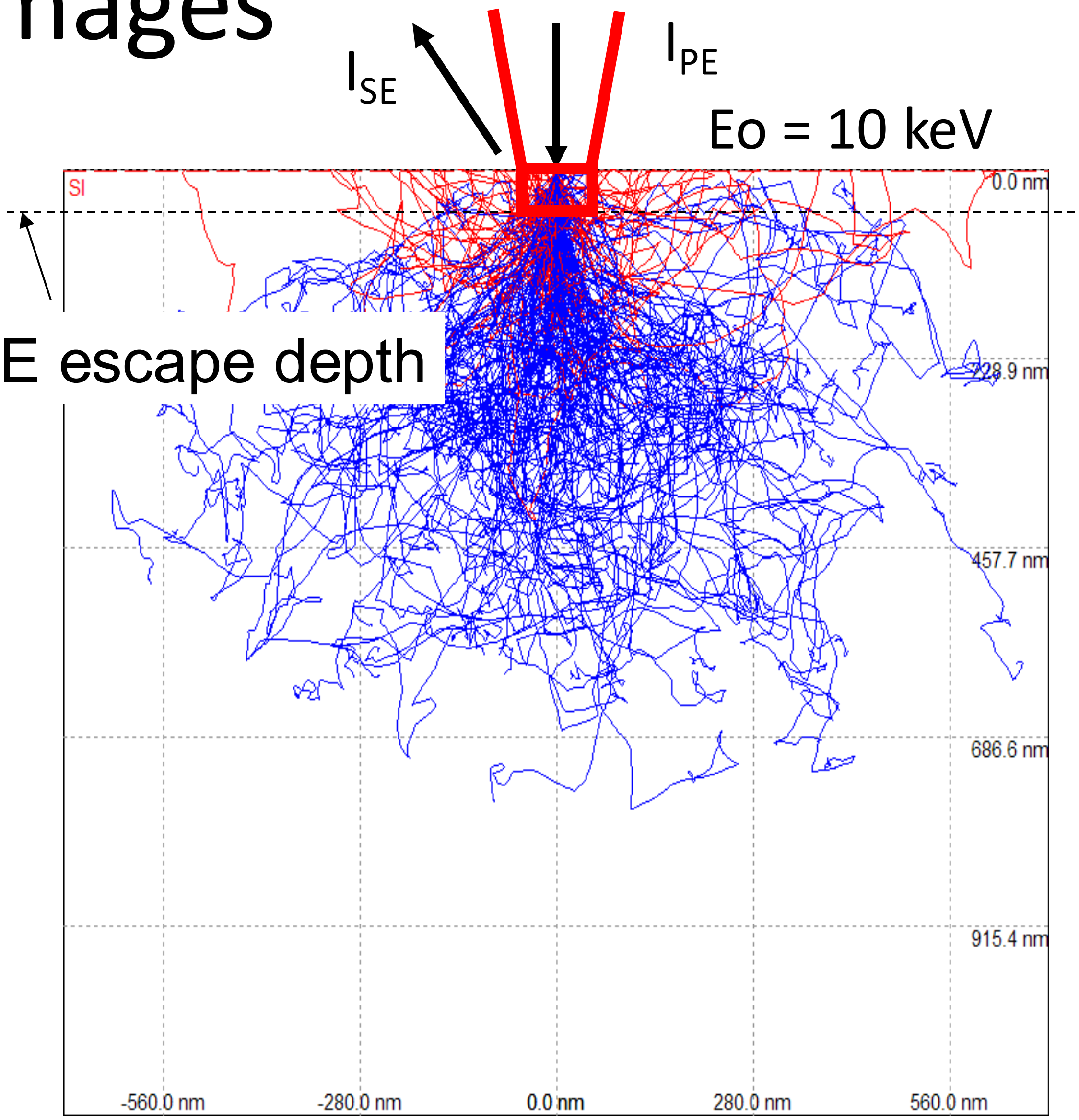
- SE **generated** by breaking chemical bonds **along <u>the entire path length</u> of the primary electron** in the sample which dissipates primary beam energy by inelastic scattering
- Creates an electron hole pair with an **electron in the conduction band and a hole in the valence band** which thermalise to the band edges
- Only **SEs within 10 – 100 nm of the surface have sufficient energy to escape** the surface for detection




Emissive Electron Energy Distribution

# Simulations of spatial Resolution in SE Images

Read papers

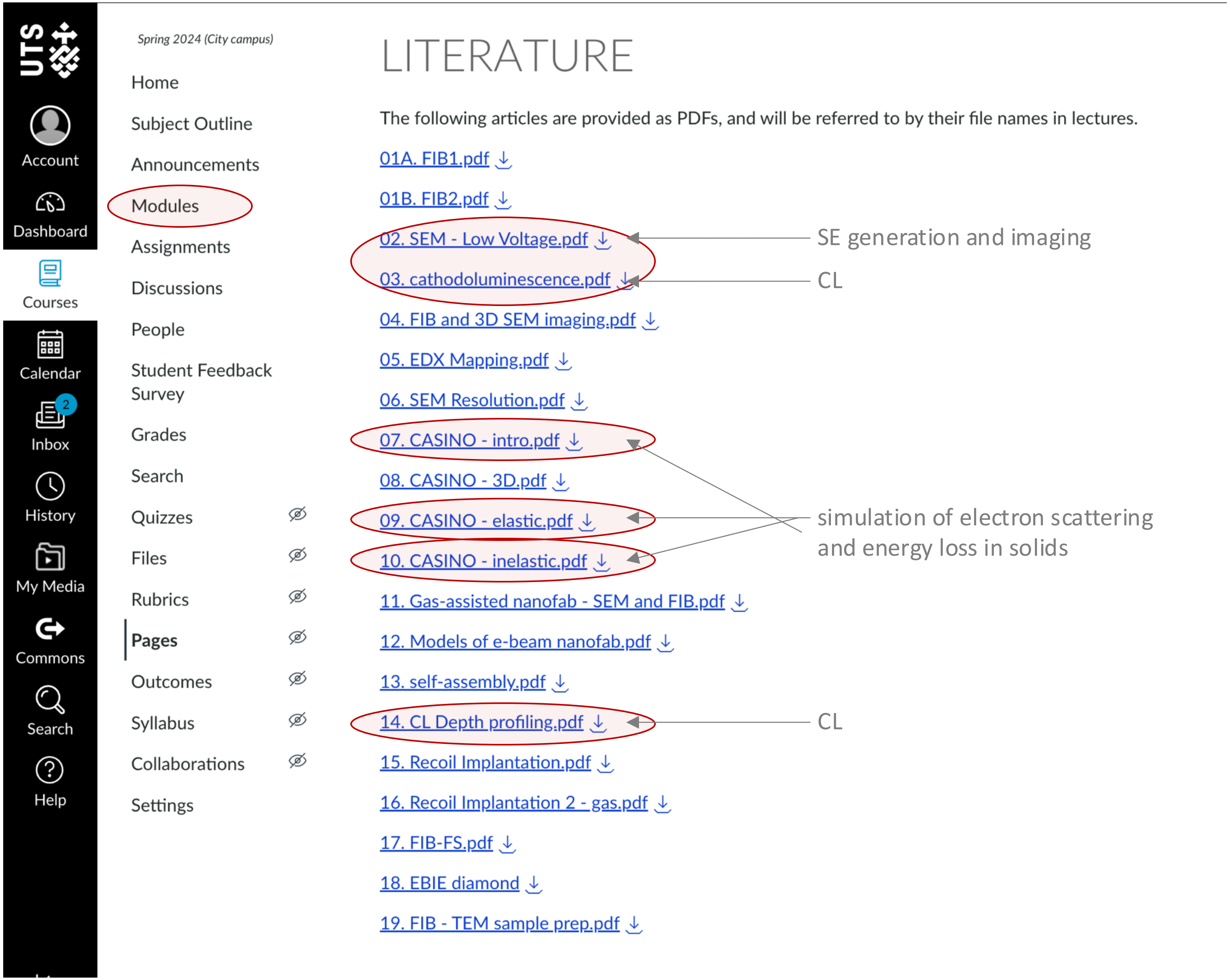



All SE electrons generated below the SE escape depth are absorbed in the specimen

**SE generated within the SE escape depth produce SE signal** and are most relevant at high magnification within the probe diameter

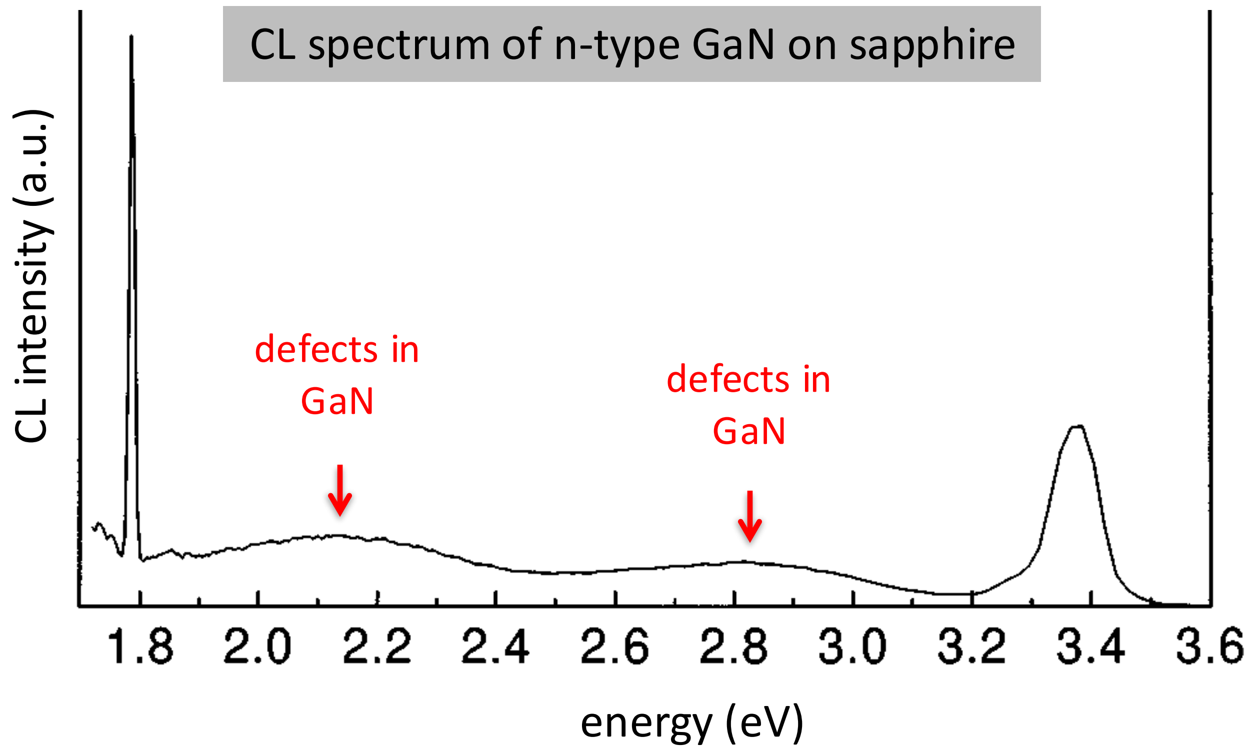
Hence, to a first approximation, the **diameter of the probe determines the spatial resolution** in the image.

# Reading material



# Sample class test questions

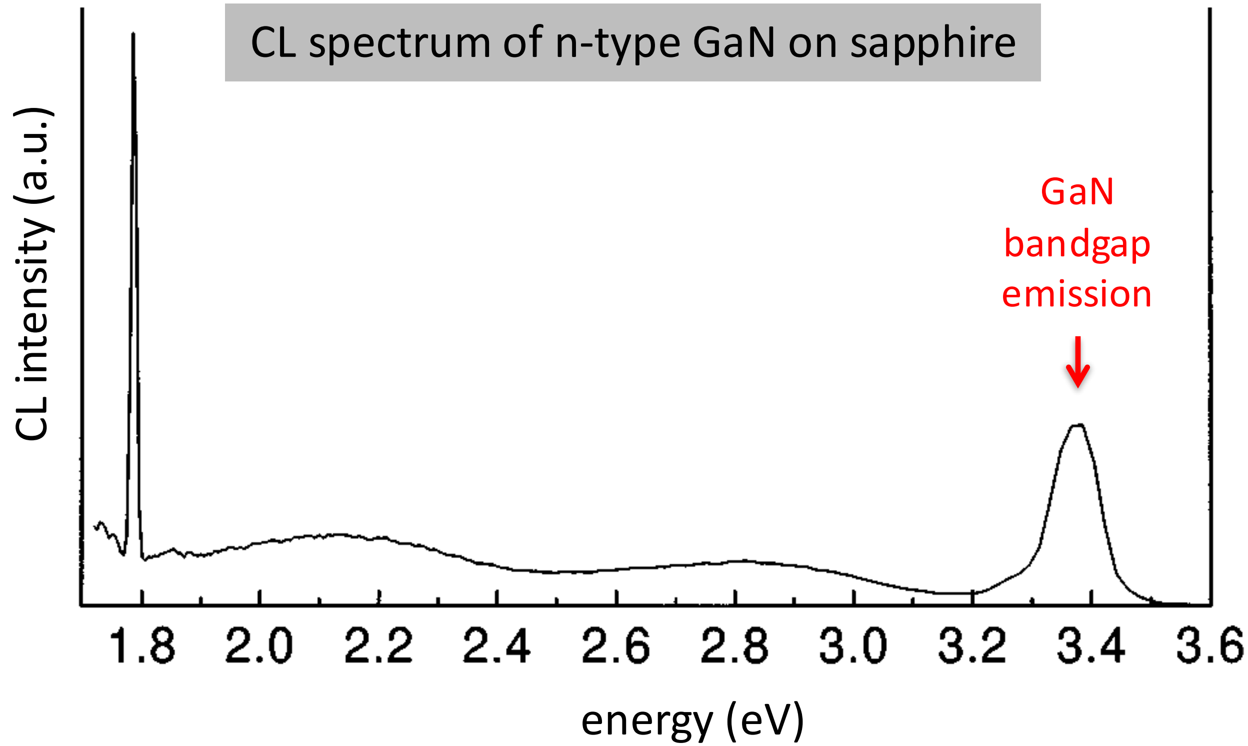
# CL 1




Consider this cathodoluminescence (CL) spectrum from the semiconductor GaN. The GaN thickness is 2 microns and the electron beam energy is 30 keV. Which of the following limits the spatial resolution of CL images generated using the CL emissions indicated in red on the spectrum?

a) Electron beam energy.
b) Energy of the CL photons.
c) Absorption of light by GaN.
d) Wavelength of the CL photons.
e) Electron-hole pair recombination rate.
f) Atomic weight of the defects responsible for the CL emissions.
g) Bandgap of GaN.

# CL 2



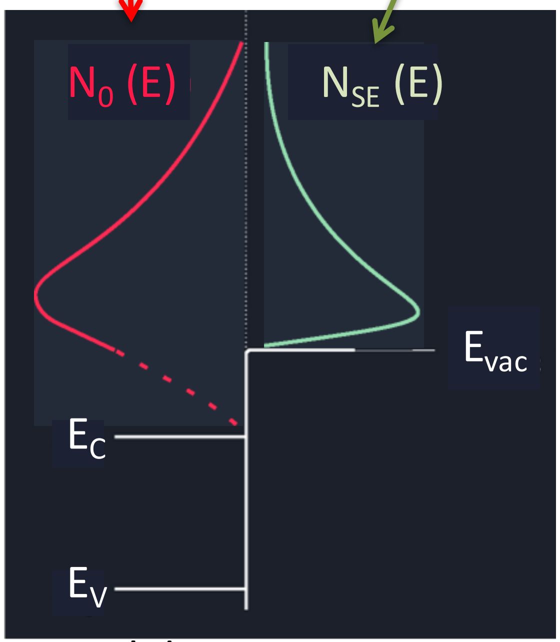

Consider this cathodoluminescence (CL) spectrum from the semiconductor GaN. The GaN thickness is 2 microns and the electron beam energy is 30 keV. Which of the following limits the spatial resolution of CL images generated using the bandgap emission indicated in red on the spectrum?

a) Electron beam energy.
b) Energy of the CL photons.
c) Absorption of light by GaN.
d) Wavelength of the CL photons.
e) Electron-hole pair recombination rate.
f) Atomic weight of the defects responsible for the CL emissions.
g) Bandgap of GaN.

# Sample class test question

energy spectrum of electrons excited in the solid

energy spectrum of electrons emitted into vacuum




solid vacuum

Consider this electron energy diagram of the sample-vacuum interface. Superimposed on the diagram are plots of the energy spectra of secondary electrons excited in the sample by an electron beam, and secondary electrons emitted from the sample and used to form an image.

**Why are the two energy spectra not identical?**

a) Because emitted secondary electrons are accelerated towards a detector.
b) Because of electron-hole pair recombination in the sample.
c) Because of electron diffusion in the sample.
d) Because the electron image is out of focus.
e) Because the electron beam energy is smaller than the bandgap energy.