ASBeST

A 7-Beryllium electron capture STudy for nuclear and solid state physics

CNRNANO

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Istituto di Nanoscienze

CNR, Pisa

Optical Characterization of Implantation Defects: the case study of sulphur implanted silicon

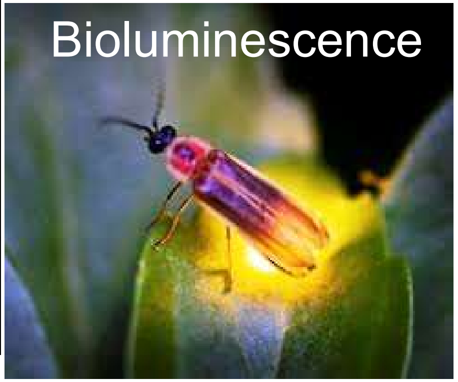
NPMET Summer School, Rome

What is LUMINESCENCE?

IUPAC says the spontaneous emission of radiation from an electronically excited species not in equilibrium with its environment

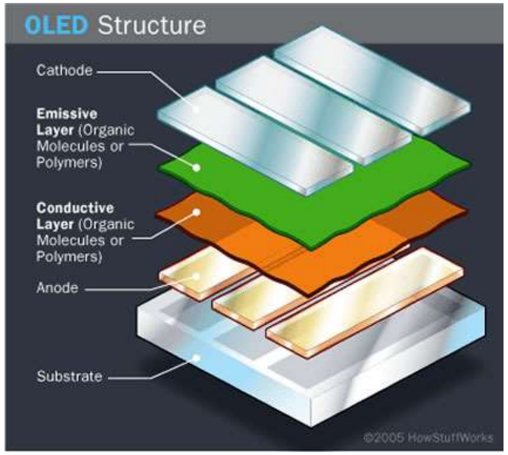
But there are several modes to excite radiation emission

as a result of a chemical reaction



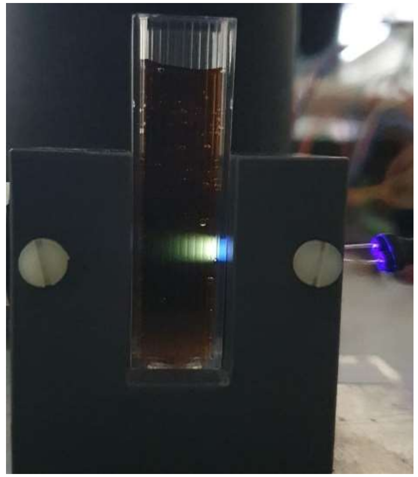
a result of biochemical reactions in a living organism

Electroluminescence



a result of an electric current passed through a substance

Photoluminescence

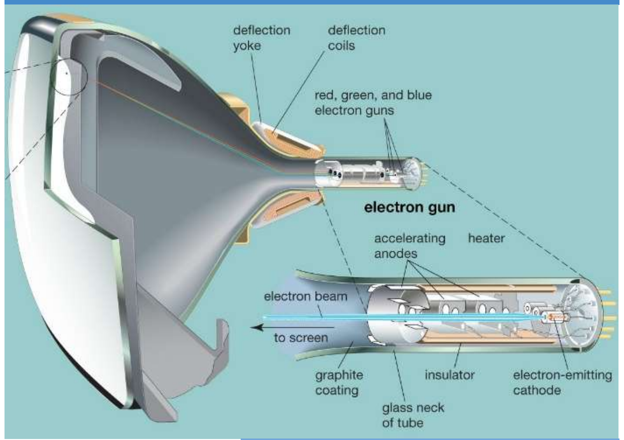


What is Cathodoluminescence?

Definition

Cathodoluminescence is the physical process by which a system, excited by **high energy impinging electrons**, **emits photons during relaxation** to a lower energy state.

Funny Notes:
Defined as cathodoluminescence because electrons were called cathode rays

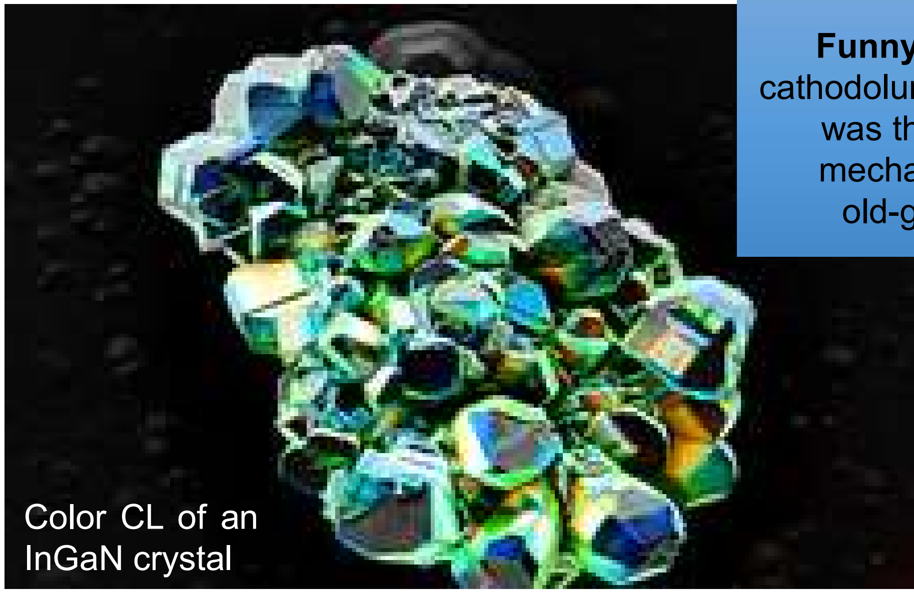


Main applications

Geology / Gemology


Color cathodoluminescence of a diamond

Material Science

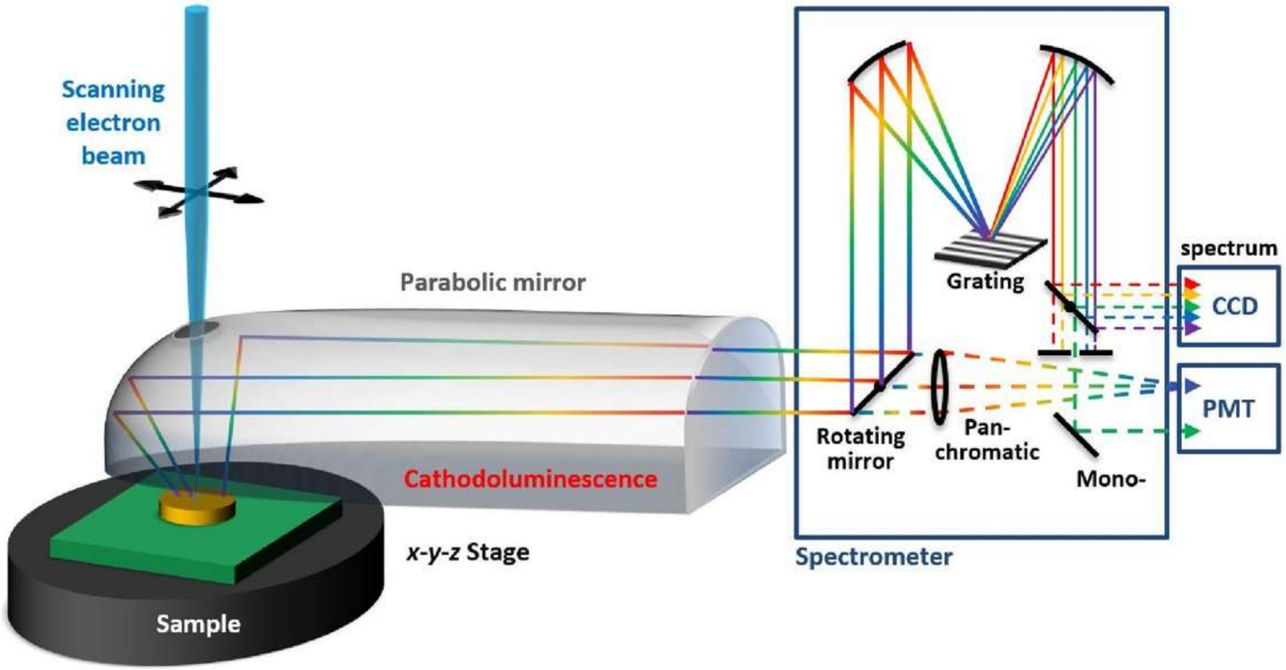

Color CL of an InGaN crystal

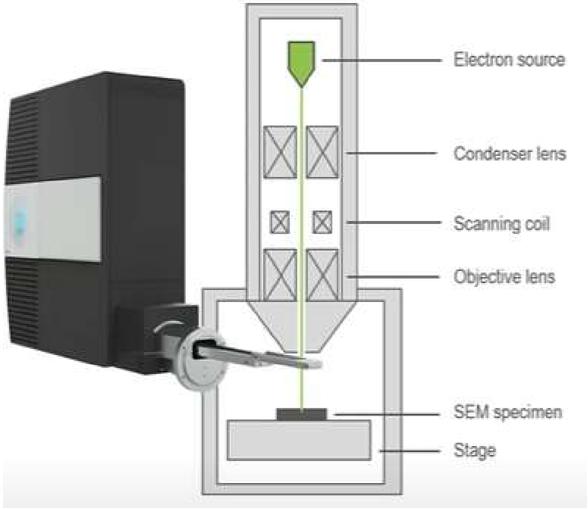
Funny Notes:
cathodoluminescence was the basic mechanism of old-gen TV

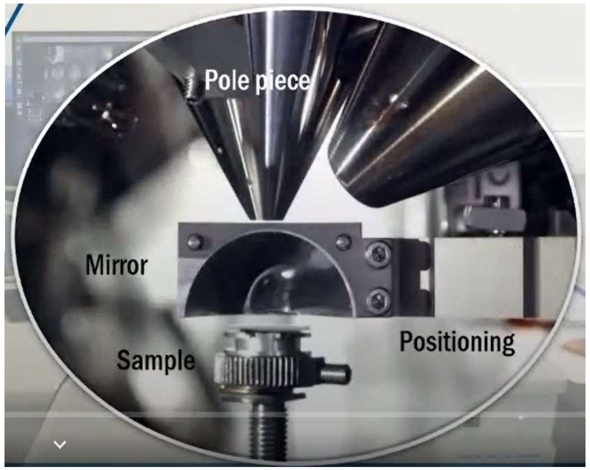
How to acquire Cathodoluminescence?

CL experiments can be carried out in:

- **Scanning Electron Microscope (SEM)**



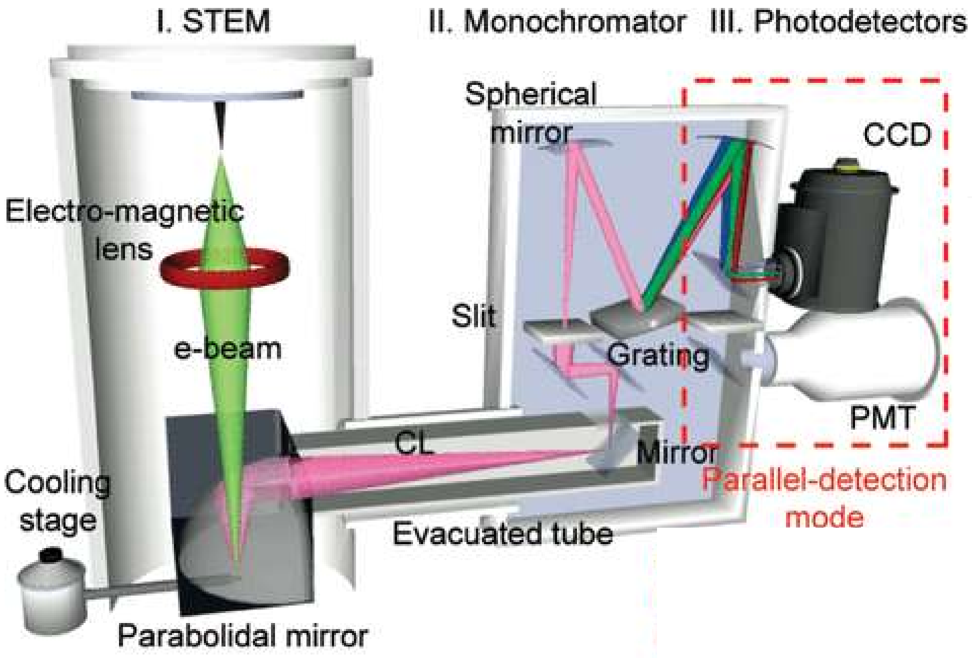


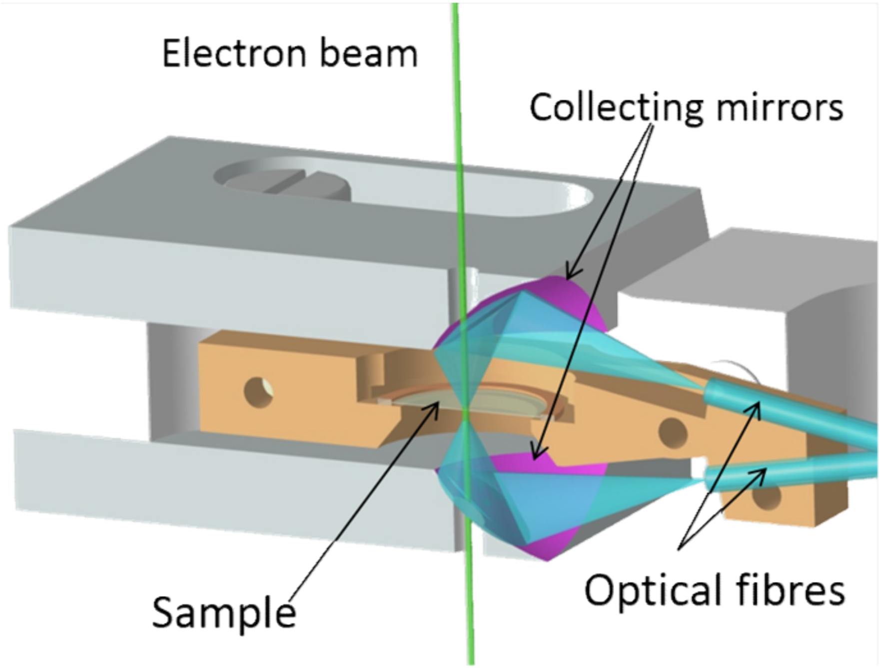


How to acquire Cathodoluminescence?

CL experiments can be carried out in:

- **Scanning Transmission Electron Microscope (STEM)**





How to acquire Cathodoluminescence spectrum or map?

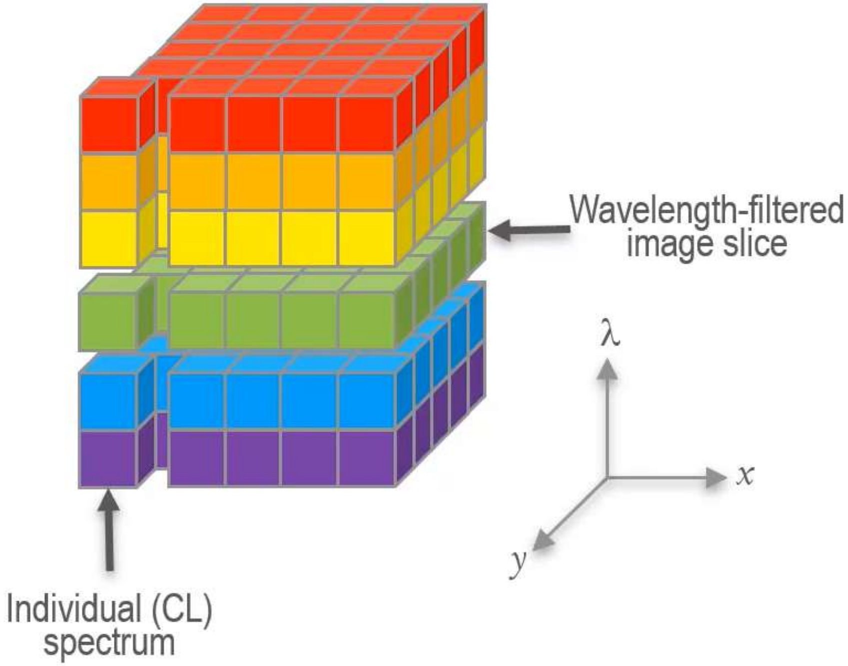
Hyperspectral Data Cube (Spectrum Image)

A 3D dataset (data cube) containing both spatially- and spectrally- resolved information

- A two-dimensional array of spectra
- An aligned stack of wavelength-filtered images; typically > 20 wavelength slices

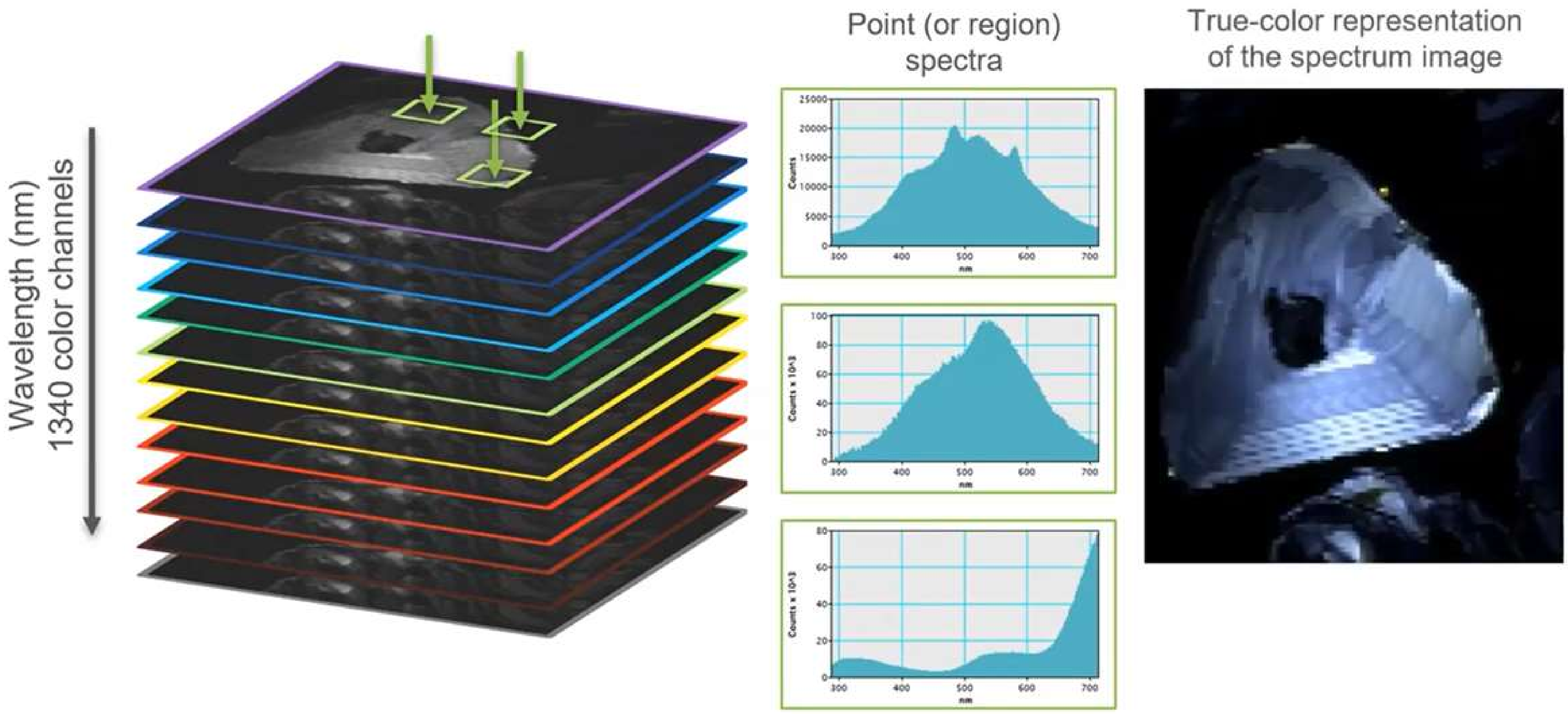
Advantages include:

- All spatial and spectral information captured; no *a priori* knowledge required
- Spectra or wavelength-filtered images may be extracted in post processing analysis
- Quantitative mapping using mathematical processing; correlation with other hyperspectral data techniques

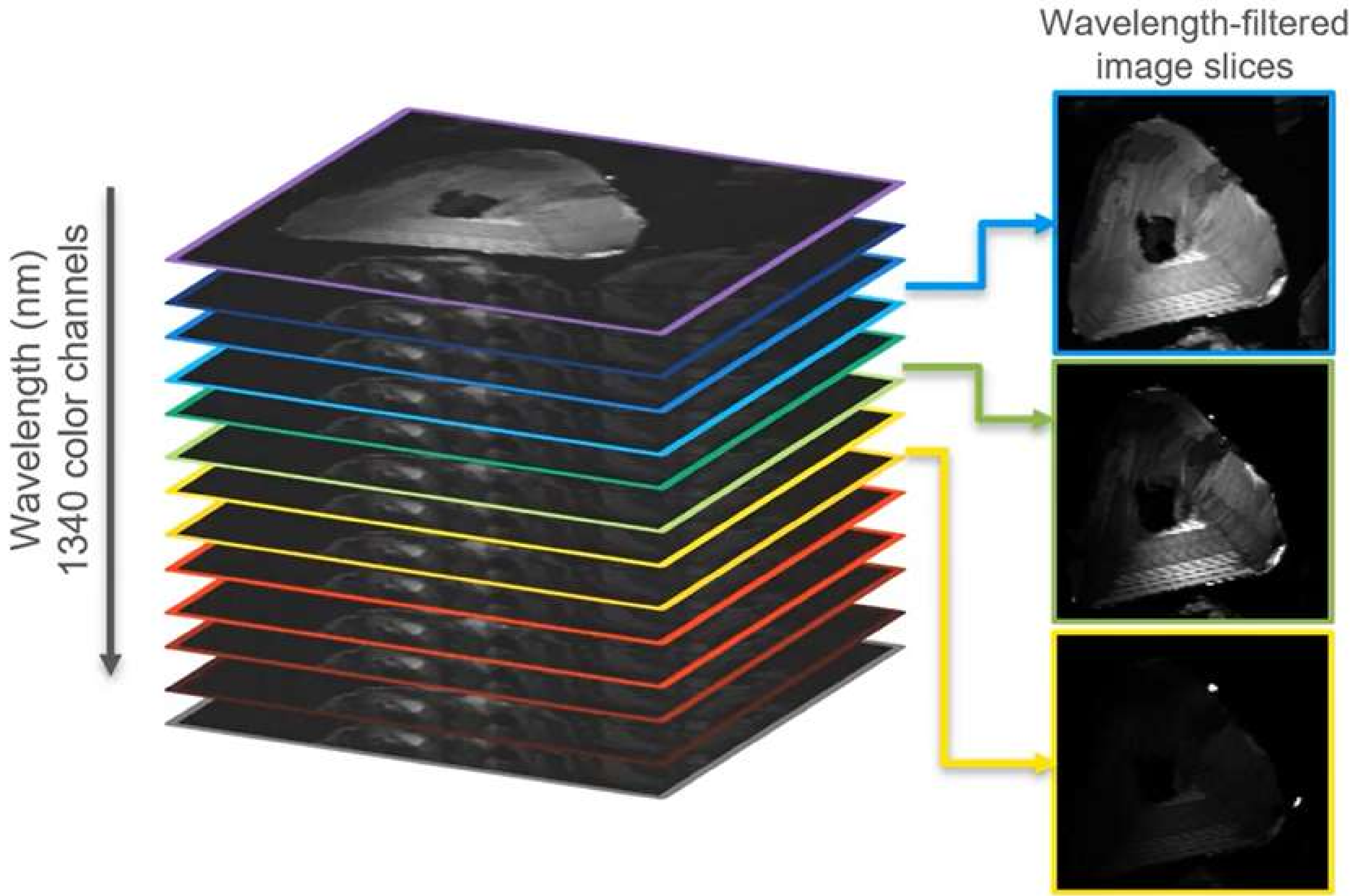


Hyperspectral 'data cube'

How to acquire a Cathodoluminescence spectrum?



How to acquire a Cathodoluminescence map?



What are the ADVANTEGES of CL spectroscopy and imaging?

Detection of luminescence with different nature and their interaction

Correlative analysis with other electron excitation based techniques

Electron penetration depth is variable:
depth-resolved studies, imaging buried structures

Nanoscale lateral resolution based on electron excitation

***In-Situ* CL analysis of electron irradiated materials**

CL study of ion implanted materials

The case study: the luminescence of sulphur implanted silicon

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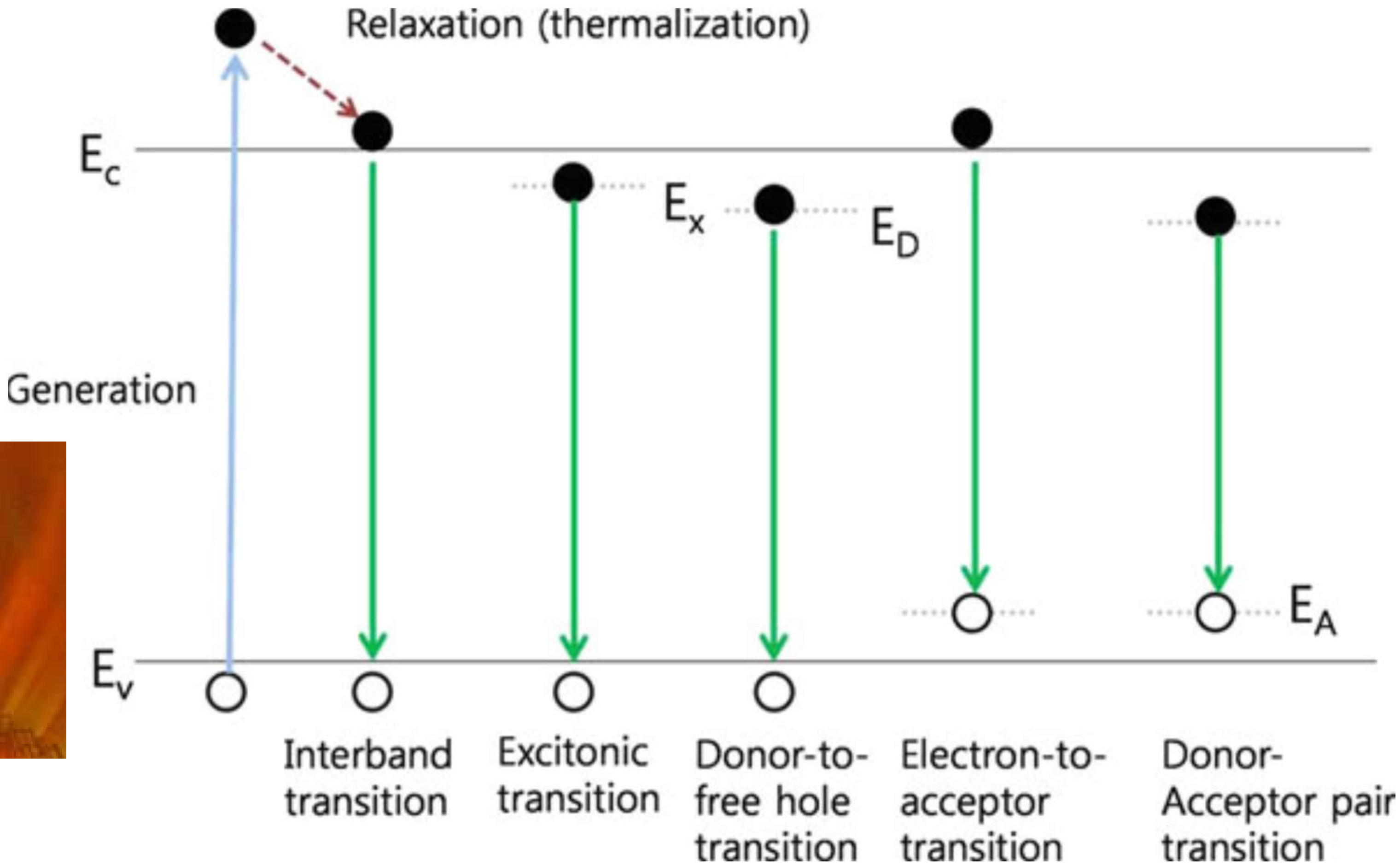
Detection of luminescence with different nature and their interaction

High energy electron probe allows the excitation of insulators and wide bandgap semiconductor

SiO_2 $E_g \approx$ 9eV
hBN $E_g \approx$ 6eV
Ga_2O_3 $E_g \approx$ 5.5eV

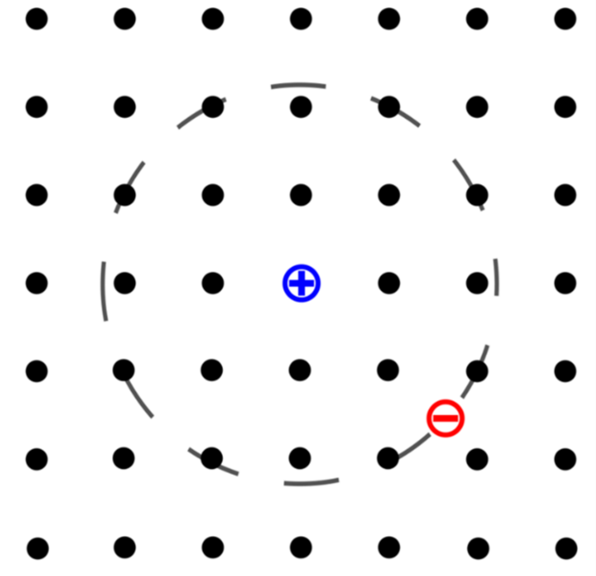


Detection of luminescence with different nature and their interaction

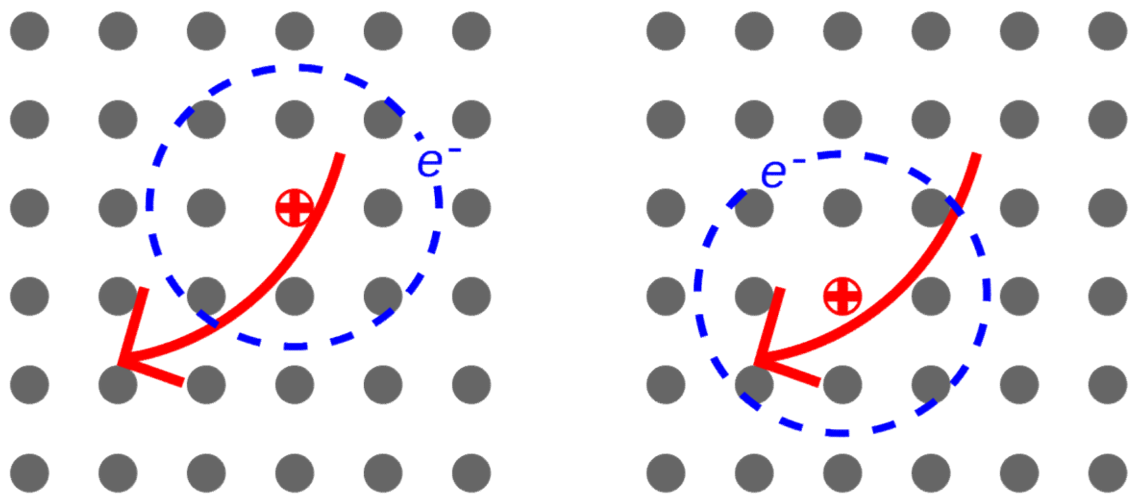
What is an exciton?

An exciton is a bound state of an electron and an hole which are attracted to each other by the electrostatic Coulomb force.

Frenkel exciton



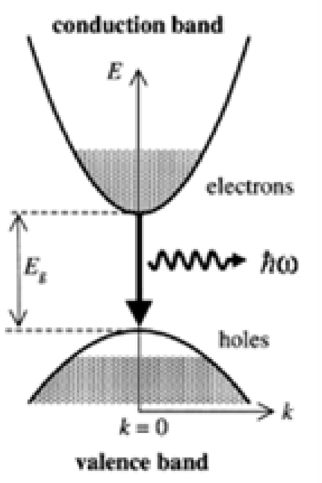
Wannier – Mott exciton

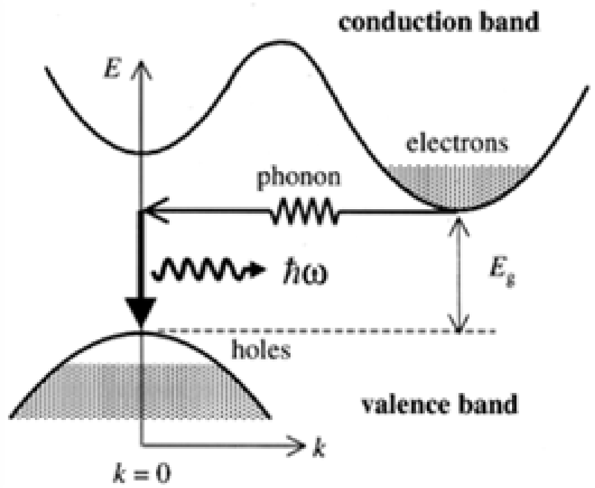


In materials with a relatively **small dielectric constant**, the Coulomb interaction between electron and hole may be strong and the excitons thus tend to be small, of the same order as the size of the unit cell.

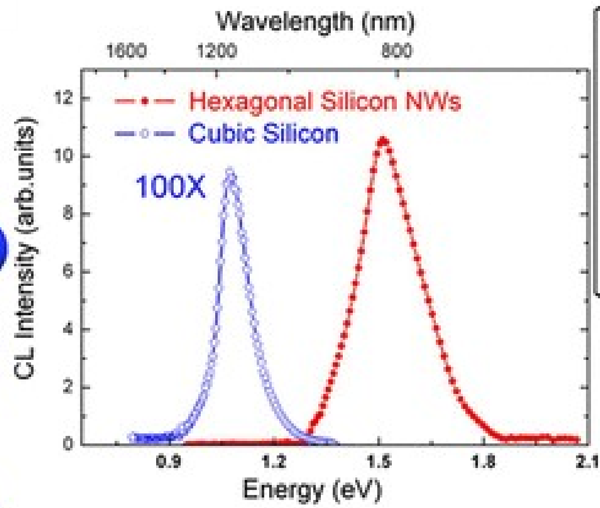
In semiconductor, the **high dielectric constant** decreases the Coulomb interaction between the electron and the hole therefore the exciton radius is bigger than the unit cell.

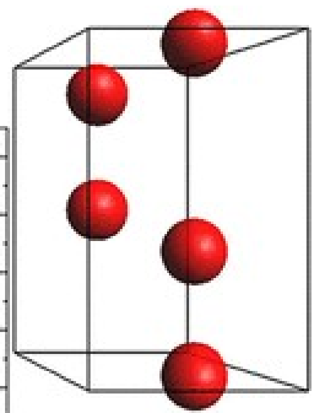
Detection of luminescence with different nature and their interaction



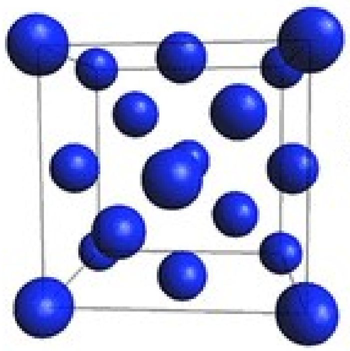


In CL experiments is possible to detect indirect bandgap transition due to the local generation of thermal phonons.





The direct bandgap radiative recombination are more intense than the ones related to indirect bandgap: the example of silicon in different crystalline lattice.

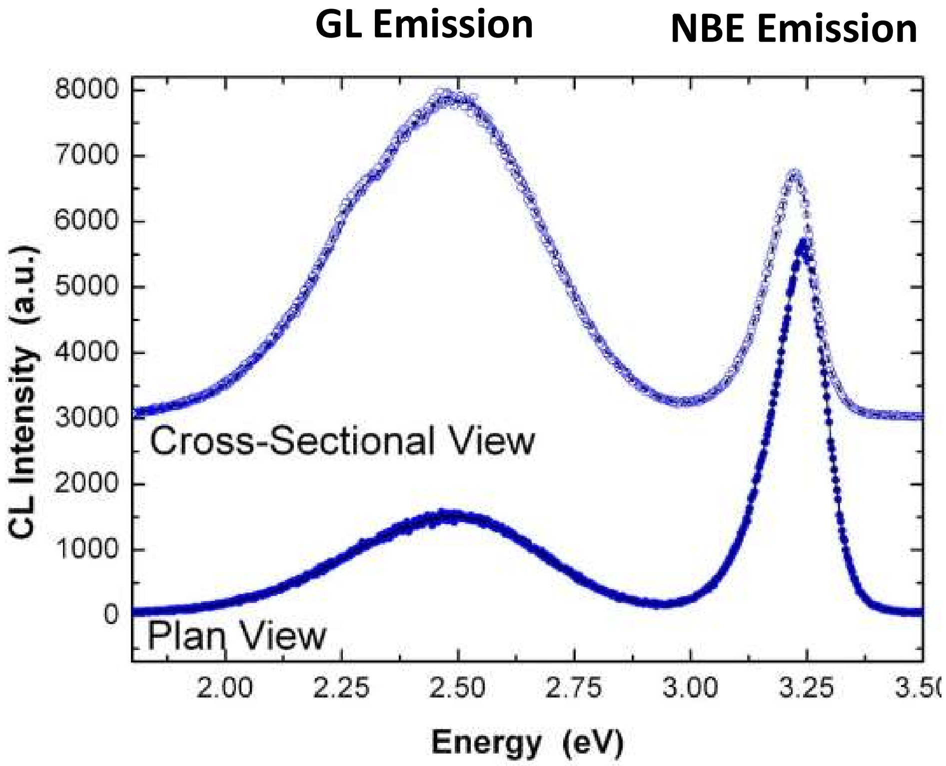


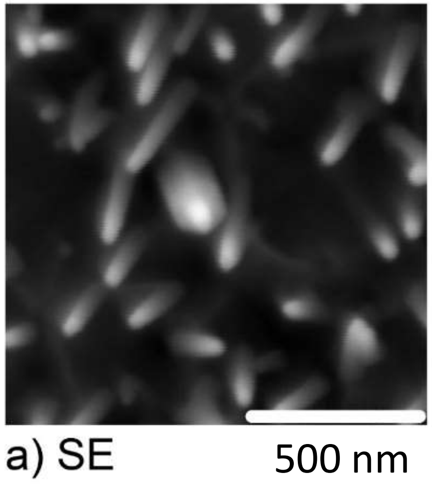
Nano Lett. 2013, 13, 5900–5906

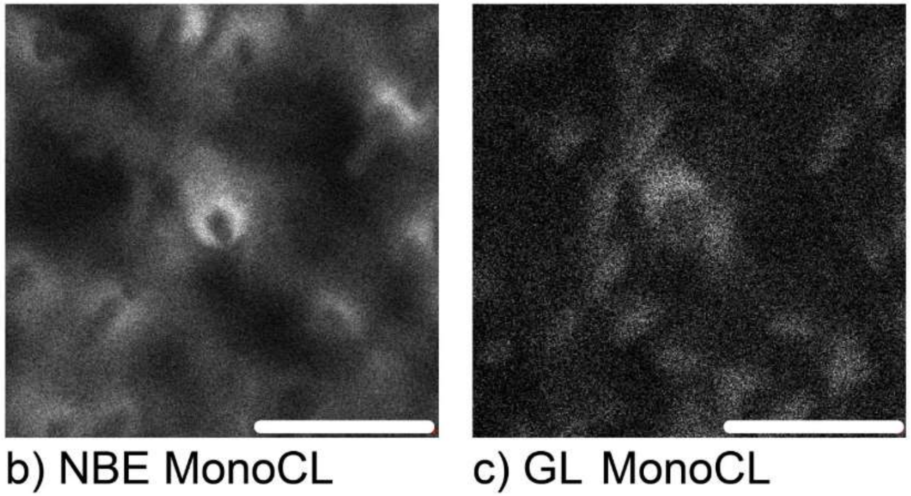
Optical Characterization of Implantation Defects

Detection of luminescence with different nature and their interaction

SEM-CL: Detection of defect related emission (GL) on lateral surface of ZnO NanoRod



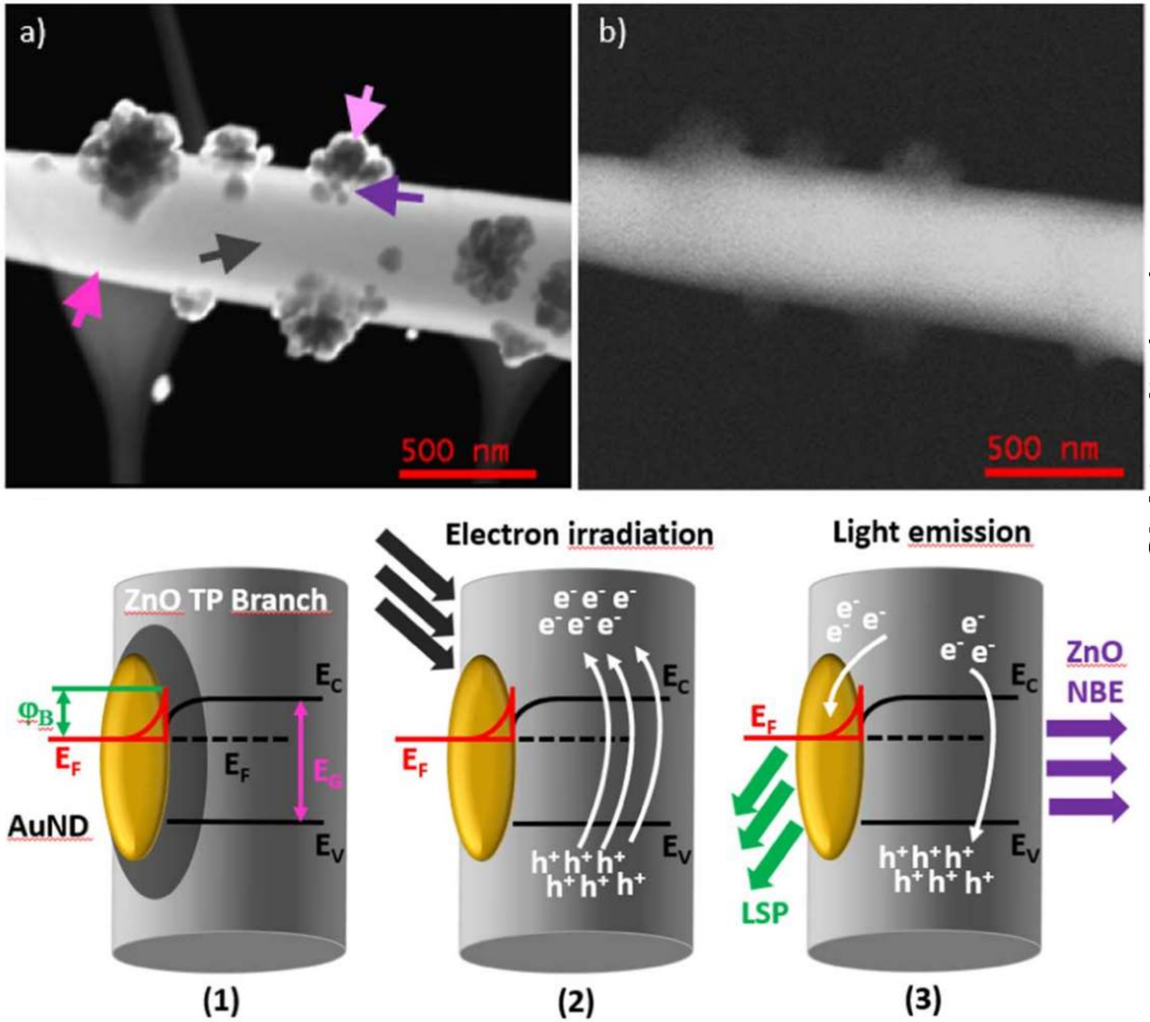


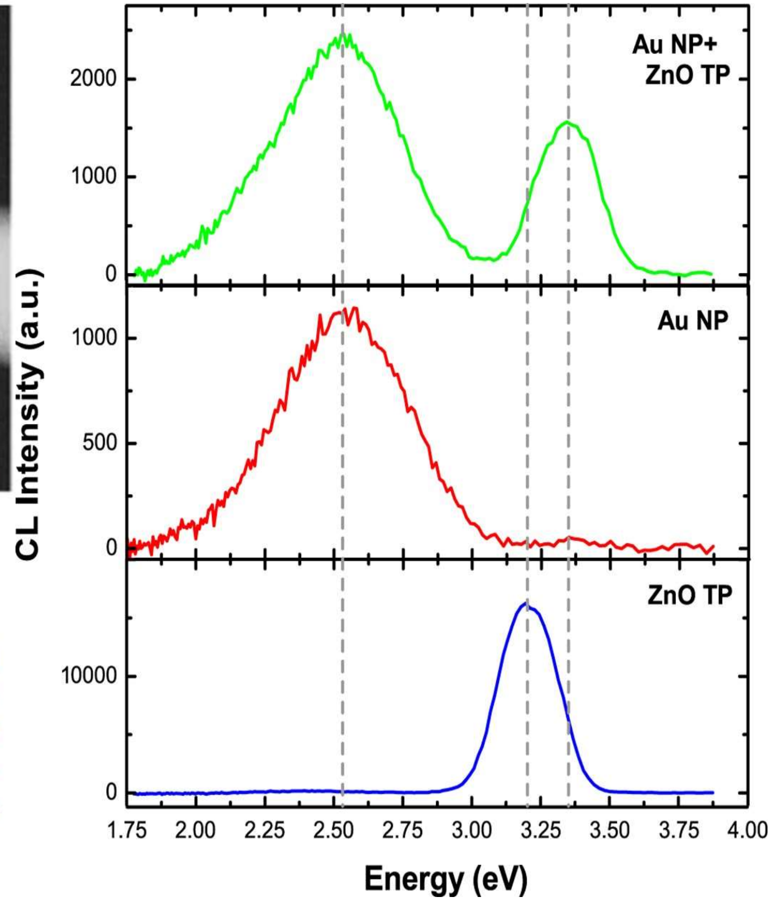


Scientific Reports **4**, 5158 (2014)

Detection of luminescence with different nature and their interaction

STEM-CL: Interaction of ZnO exciton with gold nano-aggregate surface plasmon.





Nano Express **2** 014004 (2021)

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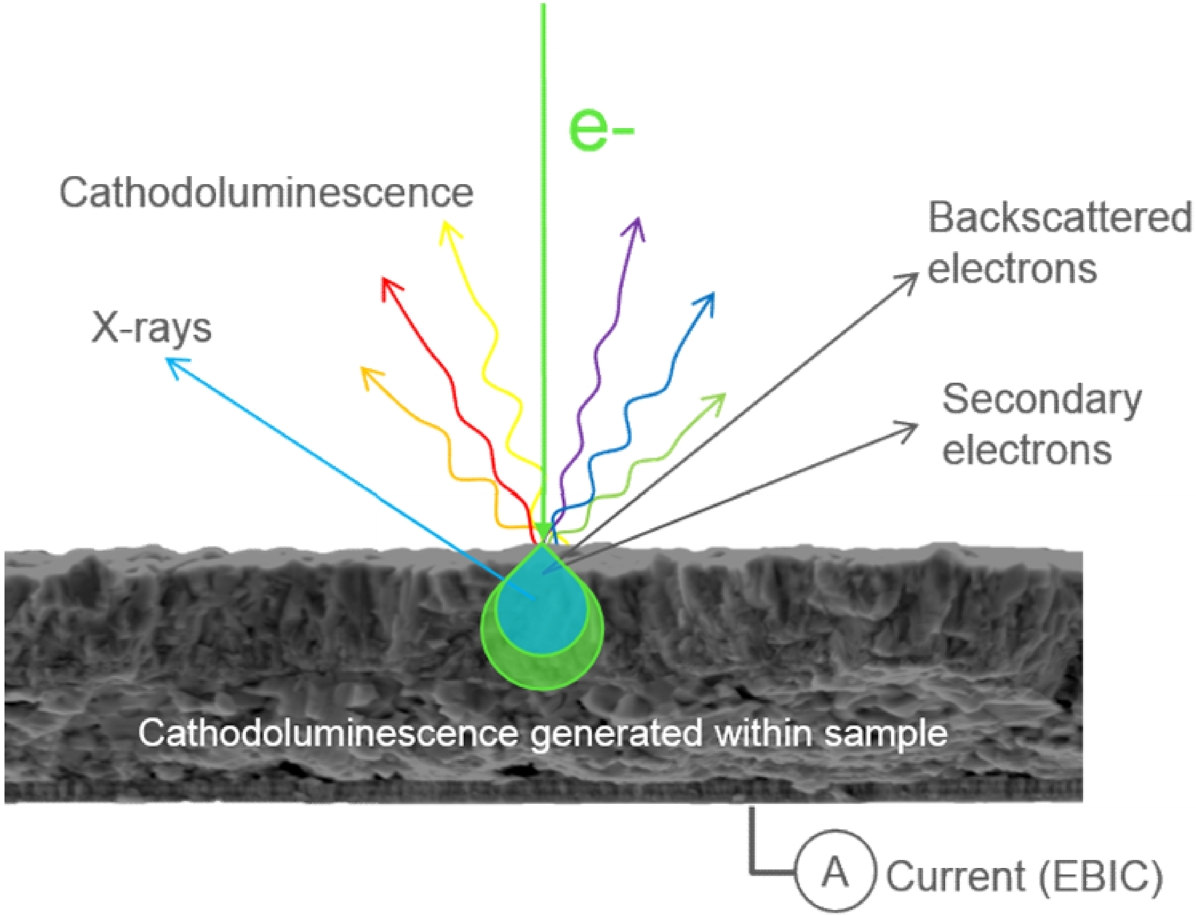
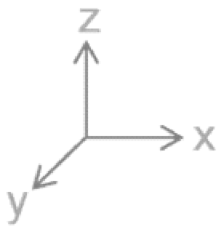


The interaction of the primary electron beam with the sample gives rise to several results (SE, BSE, X-ray), therefore it is possible to take advantages of the different signals to carry out correlative analyses in terms of:

- **morphology,**
- **composition**
- **optical properties**.



Correlative analysis with other electron excitation based techniques

Composition Mapping of Cadmium Telluride/Sulphide Alloy

- CL maps the bandgap
- Estimate Sulphur content $CdTe_{1-x}S_x$

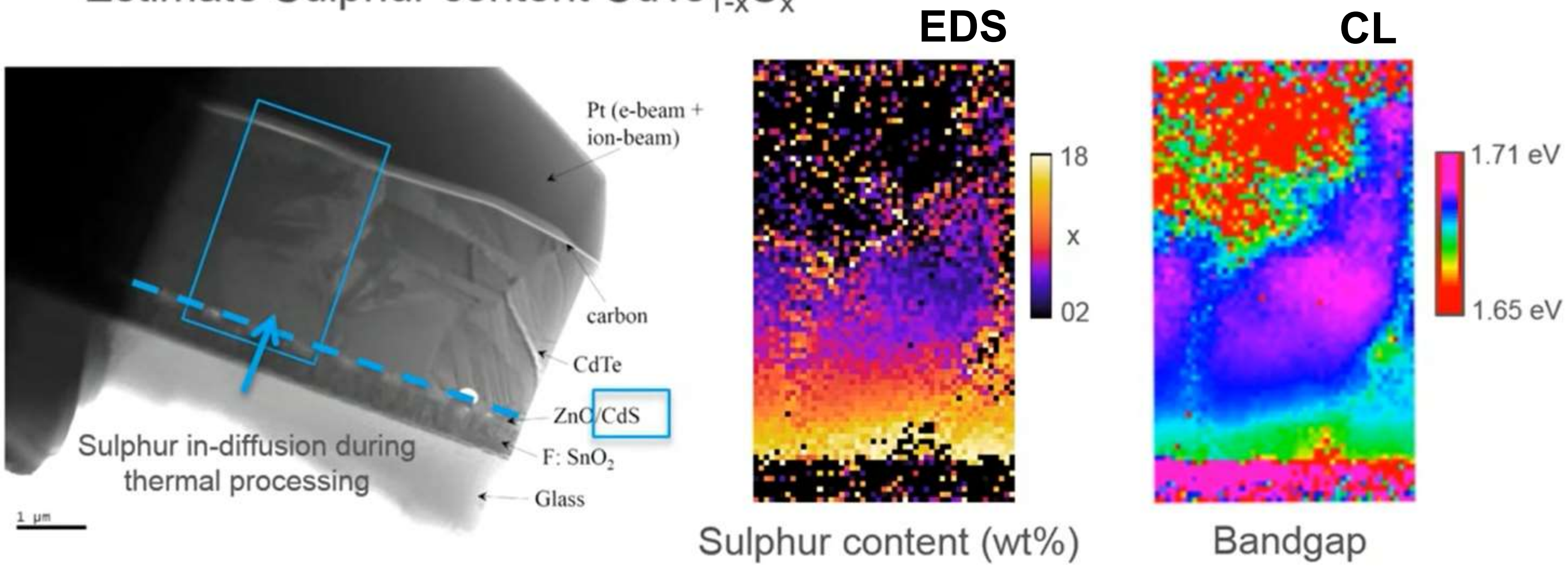
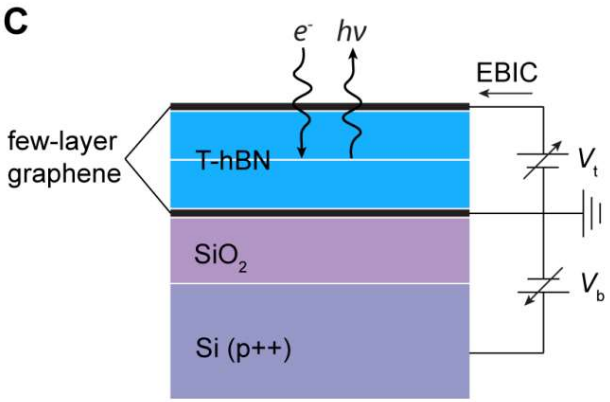


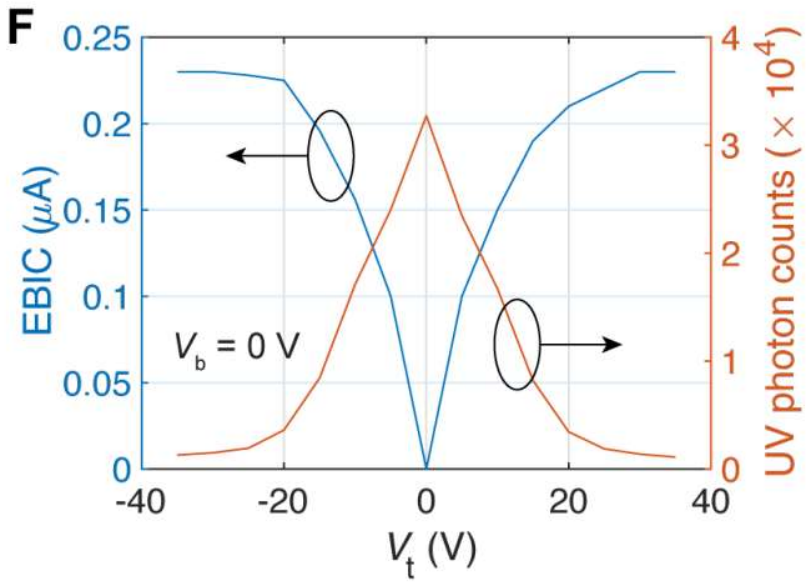
Image information: Band gap map of $CdTe_{1-x}S_x$ alloy extracted by Gaussian fitting from CL spectrum-image, courtesy of Dr B. Mendis, Durham University

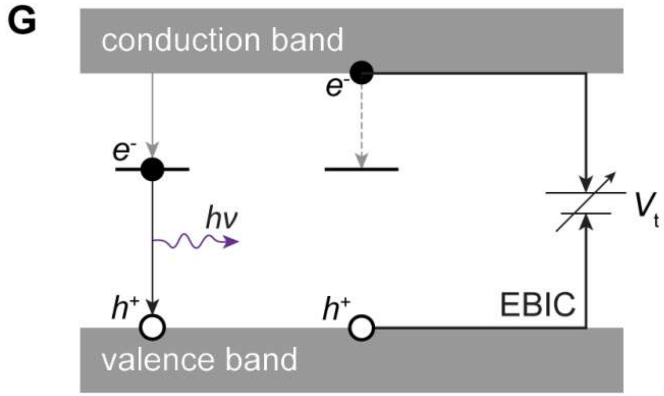
Correlative analysis with other electron excitation based techniques

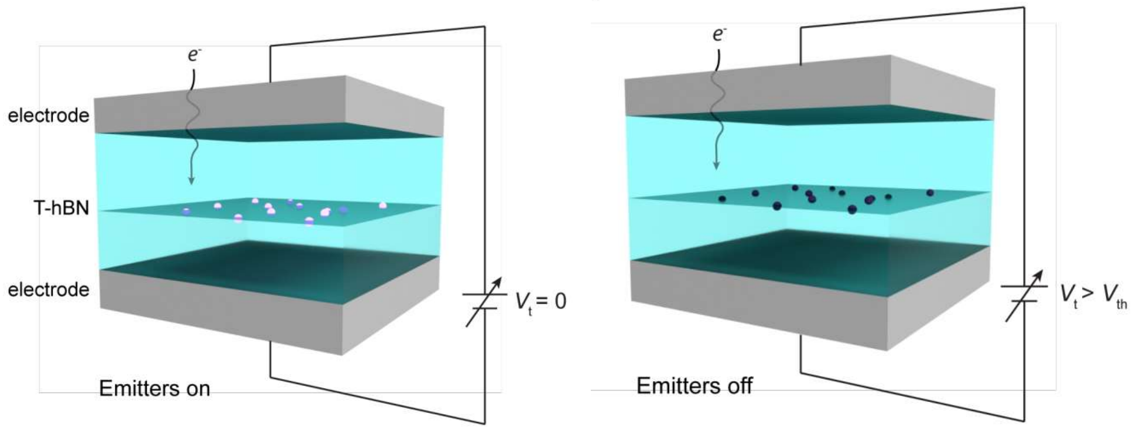
This is not true for every SEM base techniques, in fact EBIC and CL are based on two different way to collect the electron excited carriers:

Nature Materials **21**, 896–902 (2022)









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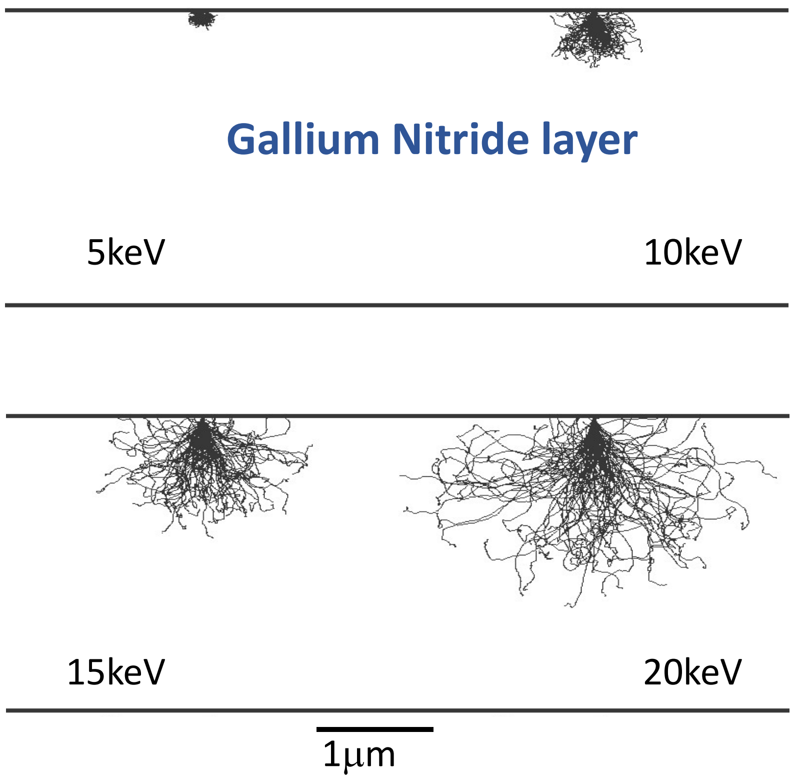
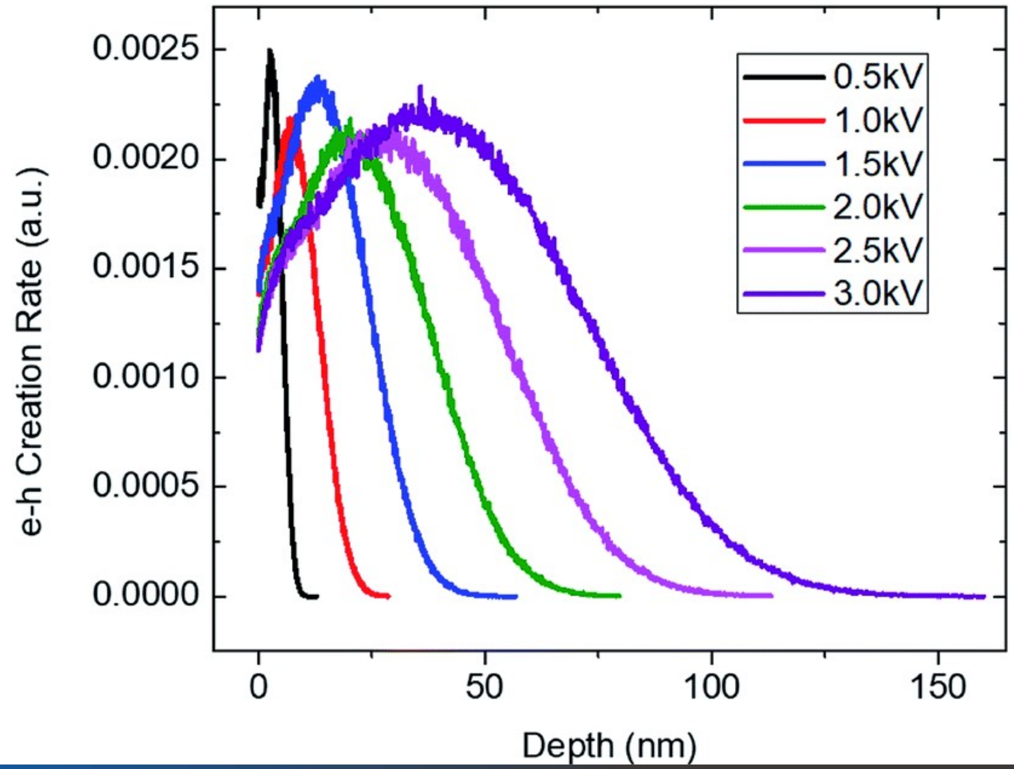
Electron penetration depth is variable

Generation volume in a material



It is possible to simulate the stochastic scattering events of the primary electron beam with atoms composing a material depending on the material density by means of classical Monte Carlo Simulation (MCS).



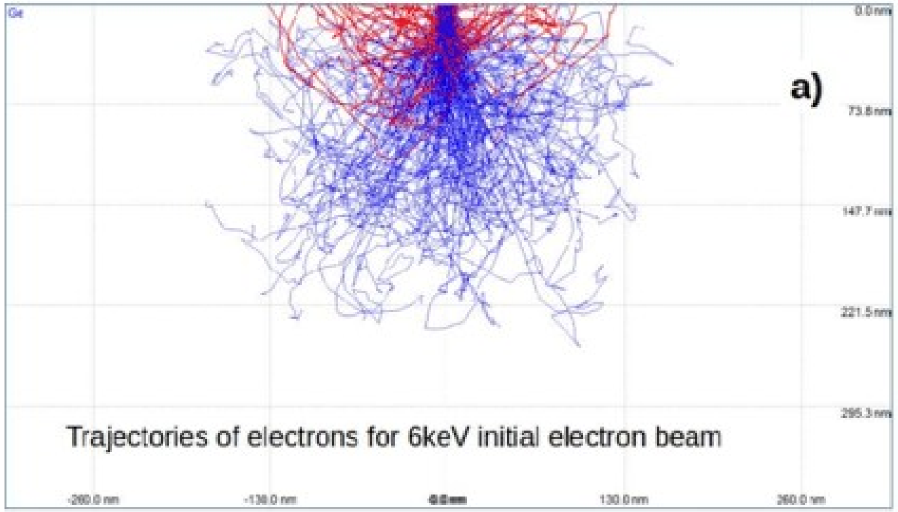
How to perform Monte Carlo simulations

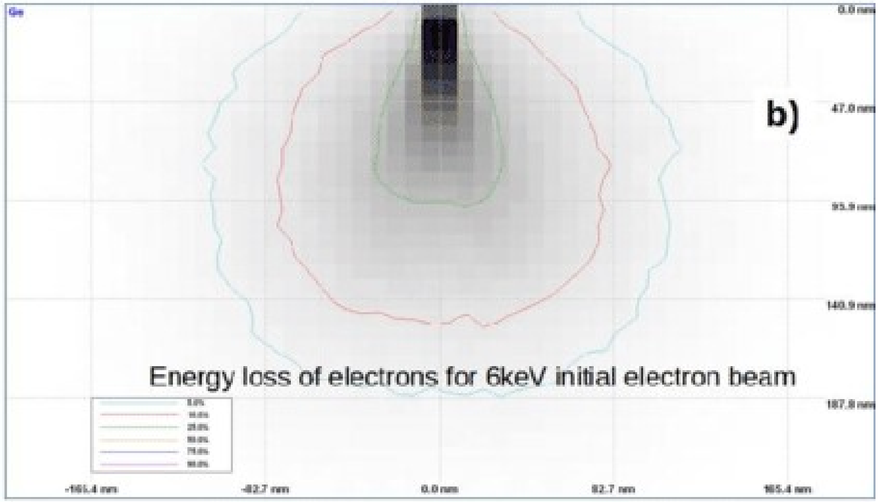
2. **Casino**
   A free software package for Monte Carlo simulation of electron trajectories in solids

Authors: Dominique Drouin, Alexandre Real Couture, Raynald Gauvin, Pierre Hovington, Paula Homy and Hendrix Demers
Platform: Windows
Citations:

1. P. Hovington, D. Drouin and R. Gauvin, "CASINO: A New Monte Carlo Code in C Language for Electron Beam Interaction - Part I: Description of the Program", *Scanning*, **19** (1997), 1-14.
2. D. Drouin, P. Hovington and R. Gauvin, "CASINO: A New Monte Carlo Code in C Language for Electron Beam Interaction - Part II: Tabulated Values of the Mott Cross Section", *Scanning*, **19** (1997), 20-28.
3. D. Drouin, P. Hovington, R. Gauvin, D.C. Joy and N. Evans, "CASINO: A New Monte Carlo Code in C Language for Electron Beam Interaction - Part III: Stopping Power at Low Energies", *Scanning*, **19** (1997) 29-35.
4. D. Drouin, A.R.Couture, D. Joly, X. Tastet, V. Aimez and R. Gauvin, "CASINO V2.42 - A Fast and Easy-to-use Modeling Tool for Scanning Electron Microscopy and Microanalysis Users", *Scanning*, **29** (2007), 92-101.

Link: http://www.gel.usherbrooke.ca/casino/What.html





The last version of CASINO has a CAD based system for simulating 3D structures!

If you don't want to run Monte Carlo simulations

The maximum effective penetration depth (Grün range, R_G) to which energy dissipation (and e-h pairs generation) extends is a function of the beam energy (E_B) and of the material density (ρ). This is in general parameterized as:

$$R_G = \frac{k}{\rho} {E_B}^{\alpha}$$

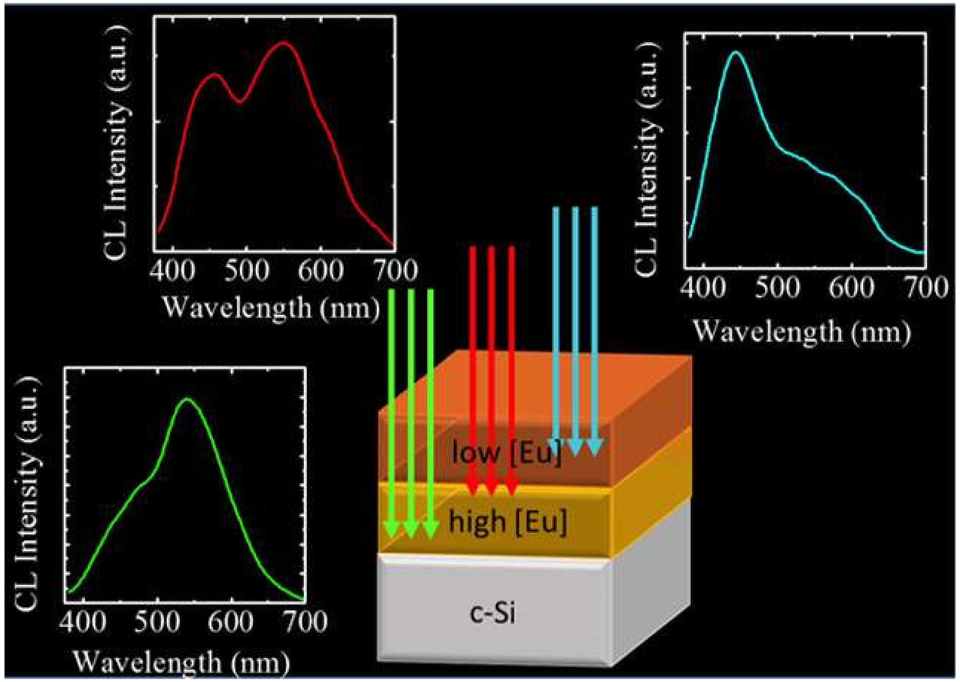
For a uniform single-type material:
Everhart and Hoff (1971) derived $k=3.98 \times 10^{-2}$ and $\alpha=1.75$ valid for $5<E_B<25$ keV and $10<Z<15$,

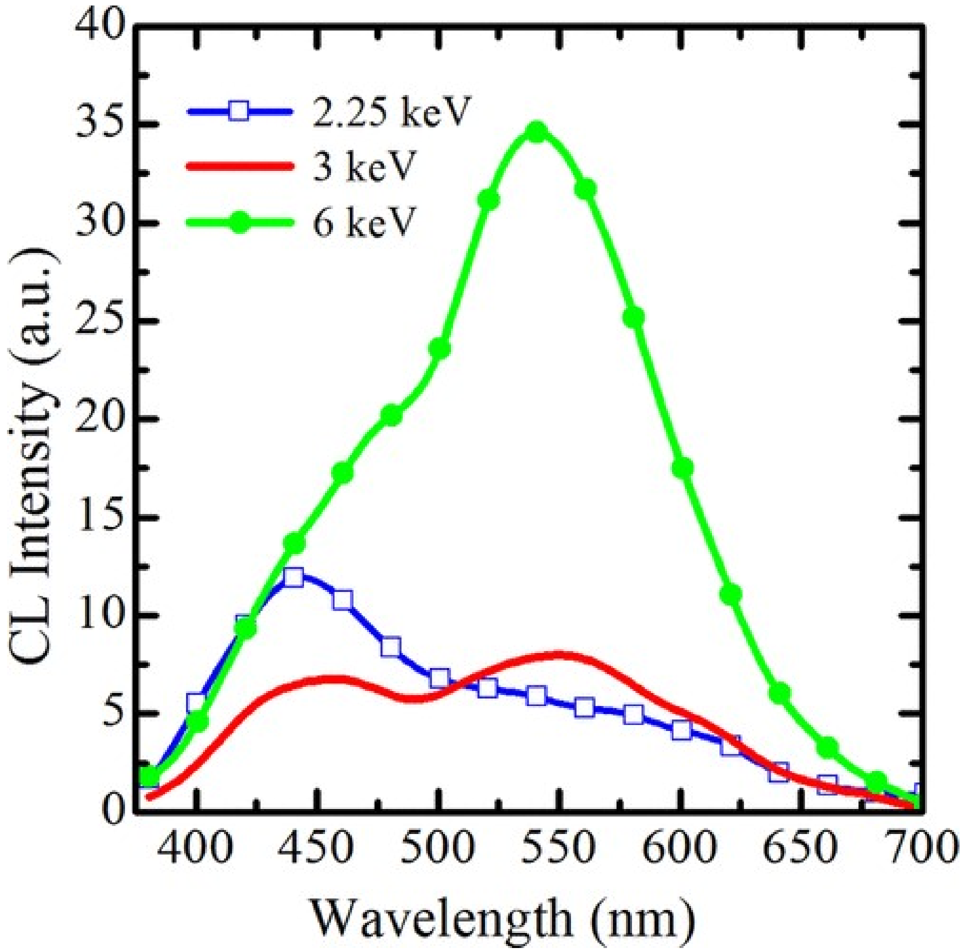
Kanaya and Okayama (1972) derived a more general expression with $\alpha=1.67$ and $k=2.76 \times 10^{-2} \times (A/Z^{0.889})$, having a wider applicability and in good agreement with experimental data.

Electron penetration depth is variable: depth-resolved studies

ACS Appl. Mater. Interfaces 2015, 7, 18201–18205

Multicolor Depth-Resolved Cathodoluminescence from Eu-Doped SiOC Thin Films

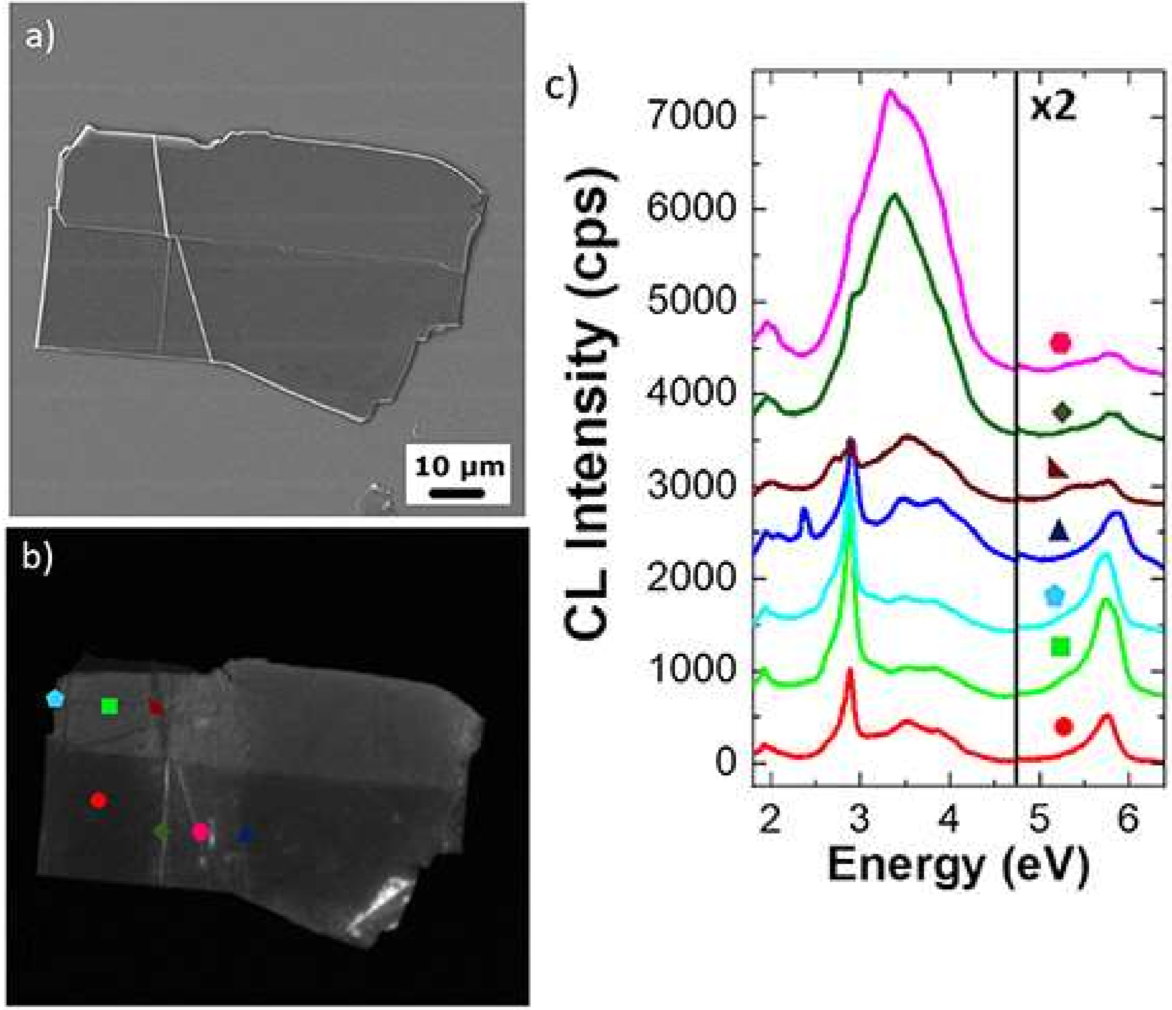


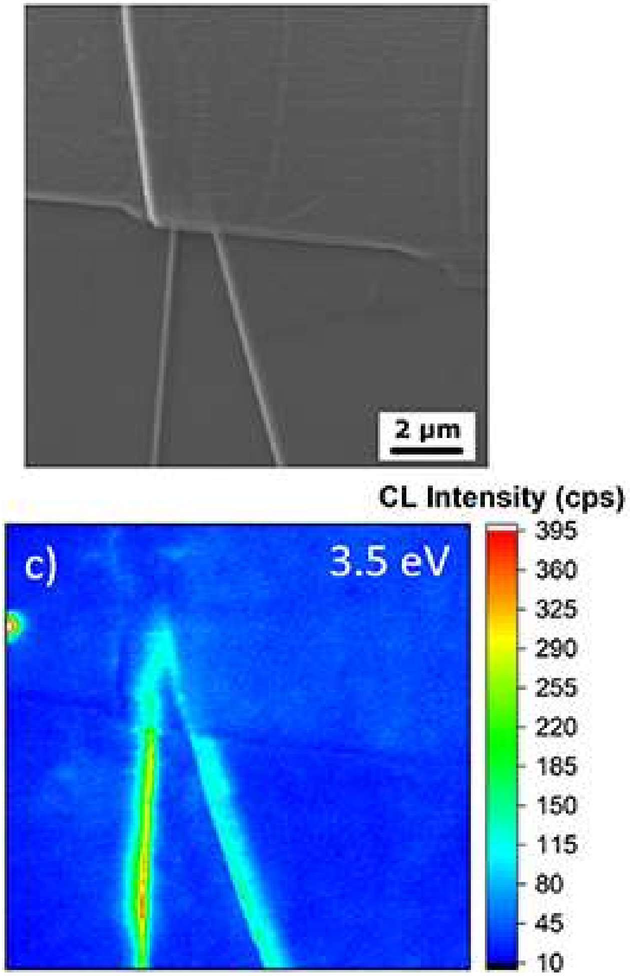


Electron penetration depth is variable: imaging buried structures

2D Materials 2022, **9**, 035018

Light emission properties of mechanical exfoliation induced extended defects in hexagonal boron nitride flakes





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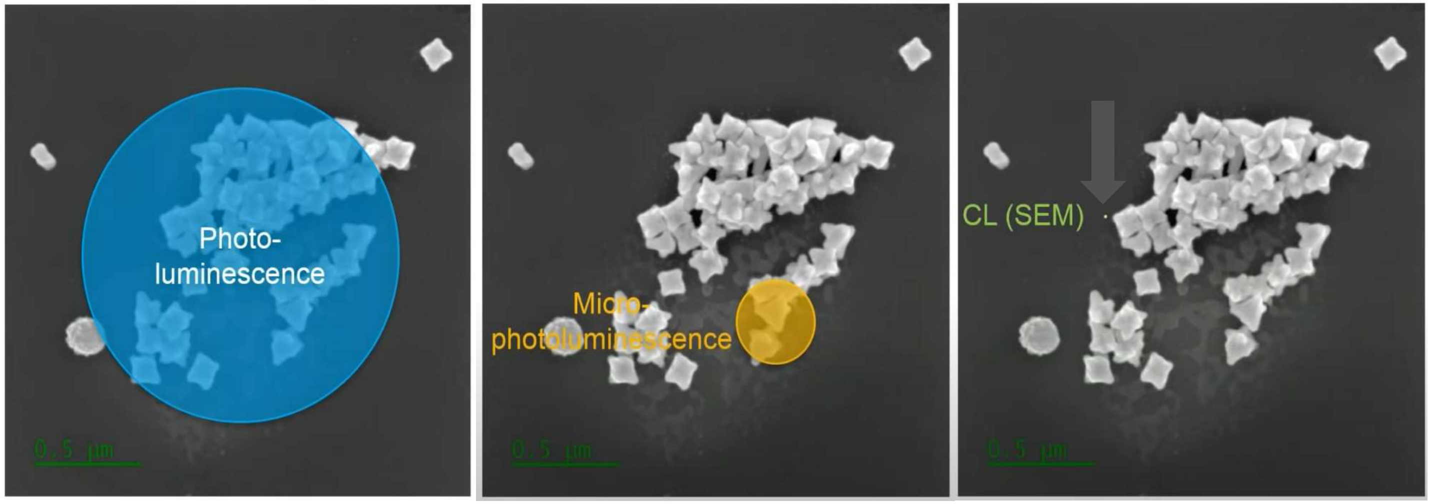
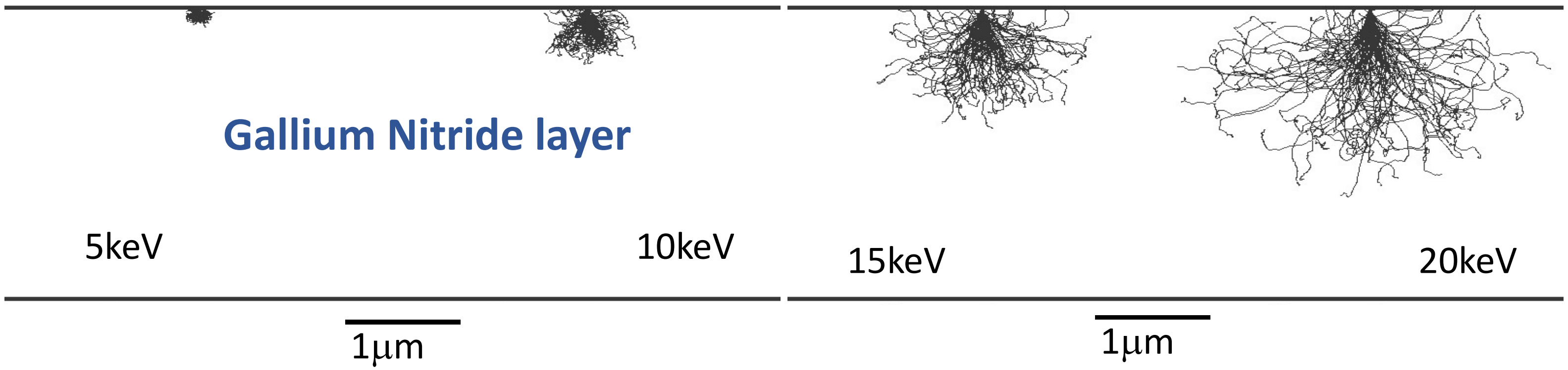
Nanoscale lateral resolution based on electron excitation

The main feature, that allows the nanoscale lateral resolution of CL, is the size of the primary electron beam

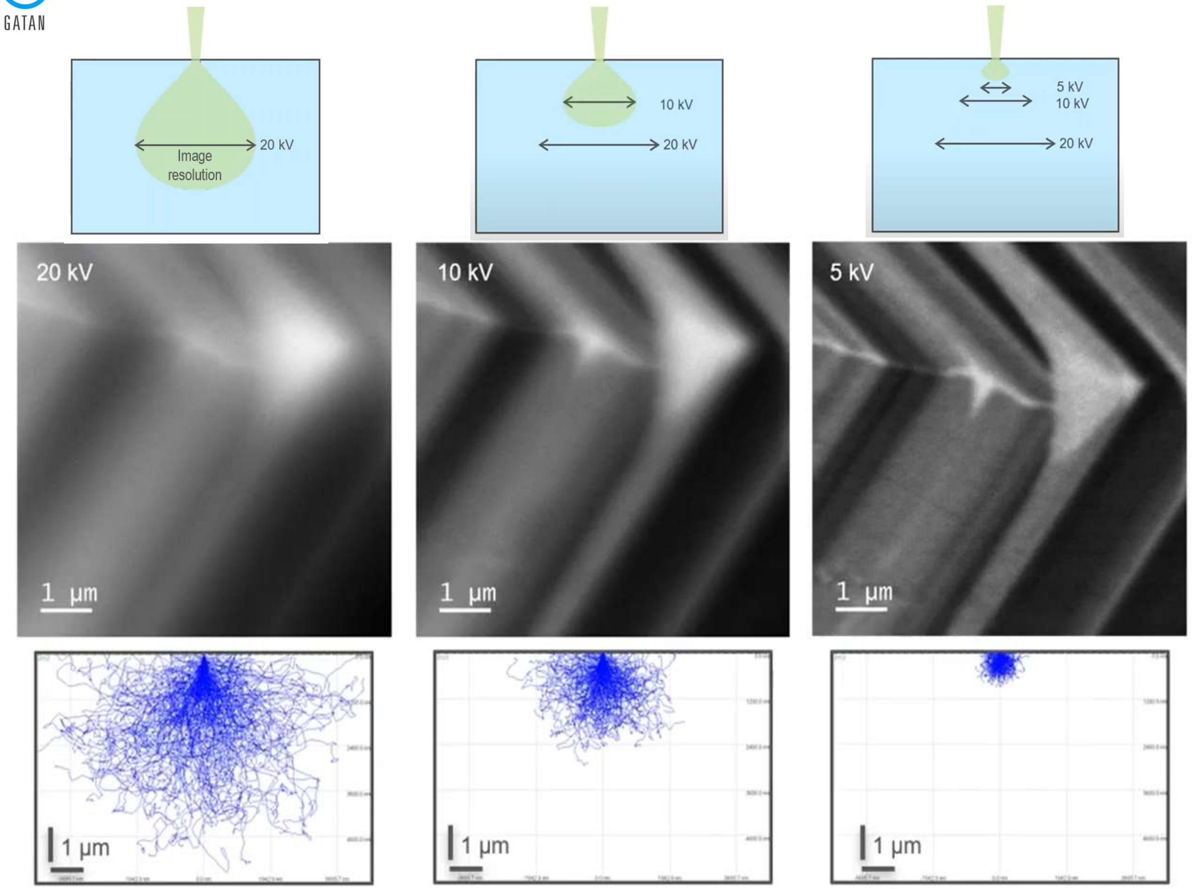




The main limiting factor is the interaction of the primary beam with the sample in analysis

Nanoscale lateral resolution based on electron excitation

CL Mapping of a Geological Sample

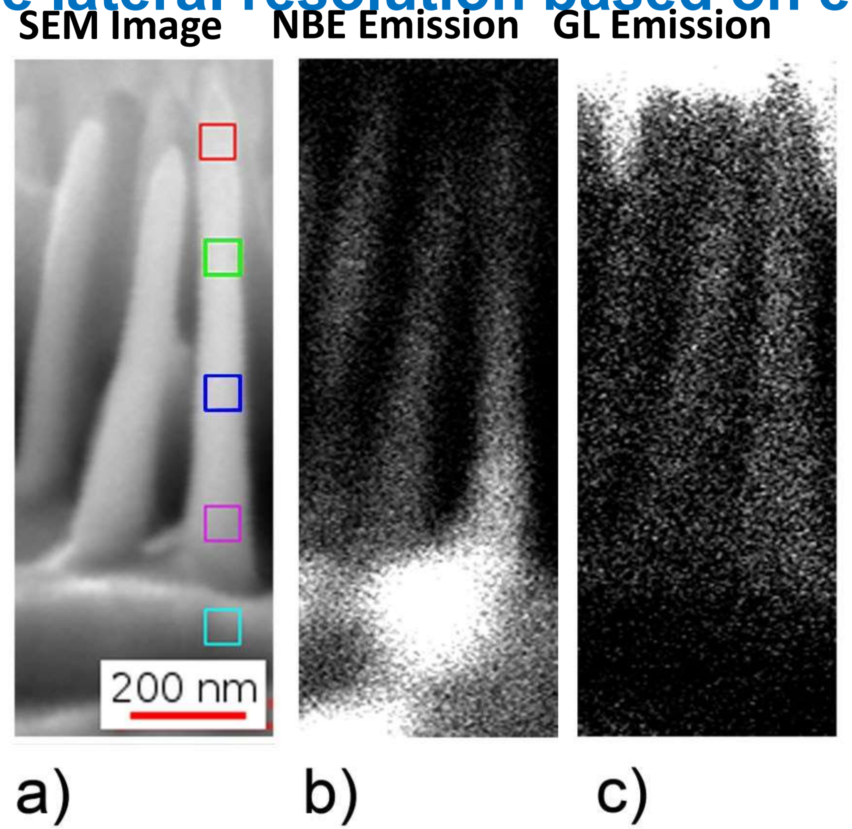


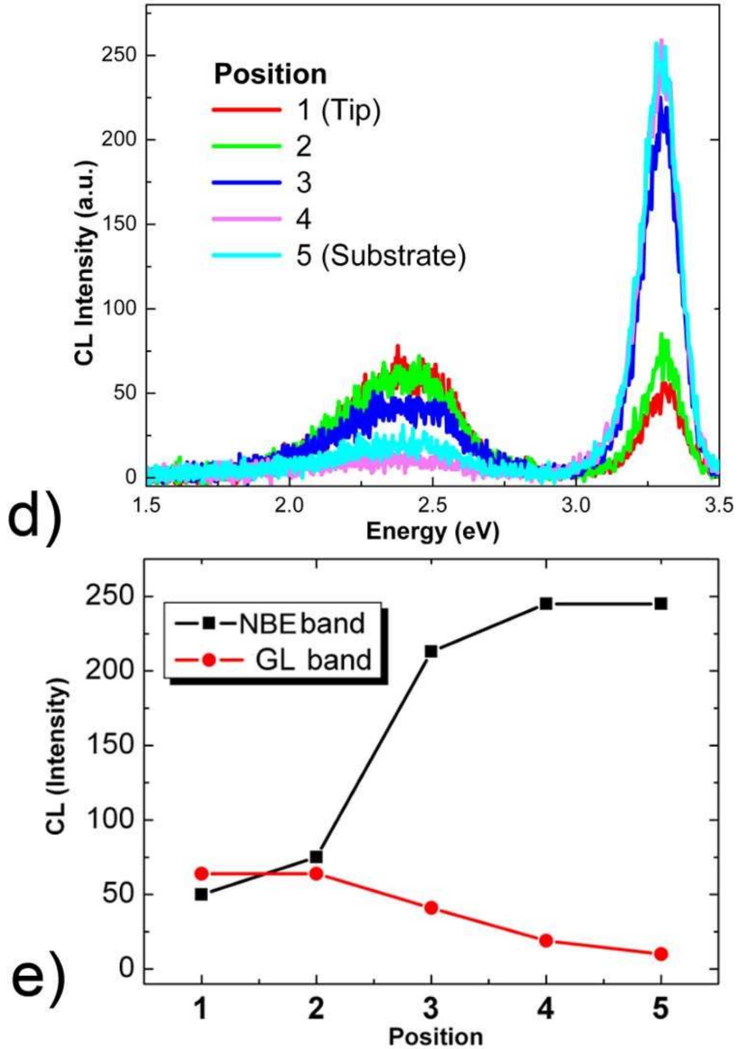
SPATIAL RESOLUTION IMPROVEMENT WITH LOWER ACCELERATING VOLTAGES

LATERAL RESOLUTION : the minimum detectable distance between two regions presenting different CL intensity.

It depends mainly on the size of the recombination volume (generation volume broadened for the diffusion length) of e-h pairs inside the material.

Nanoscale lateral resolution based on electron excitation



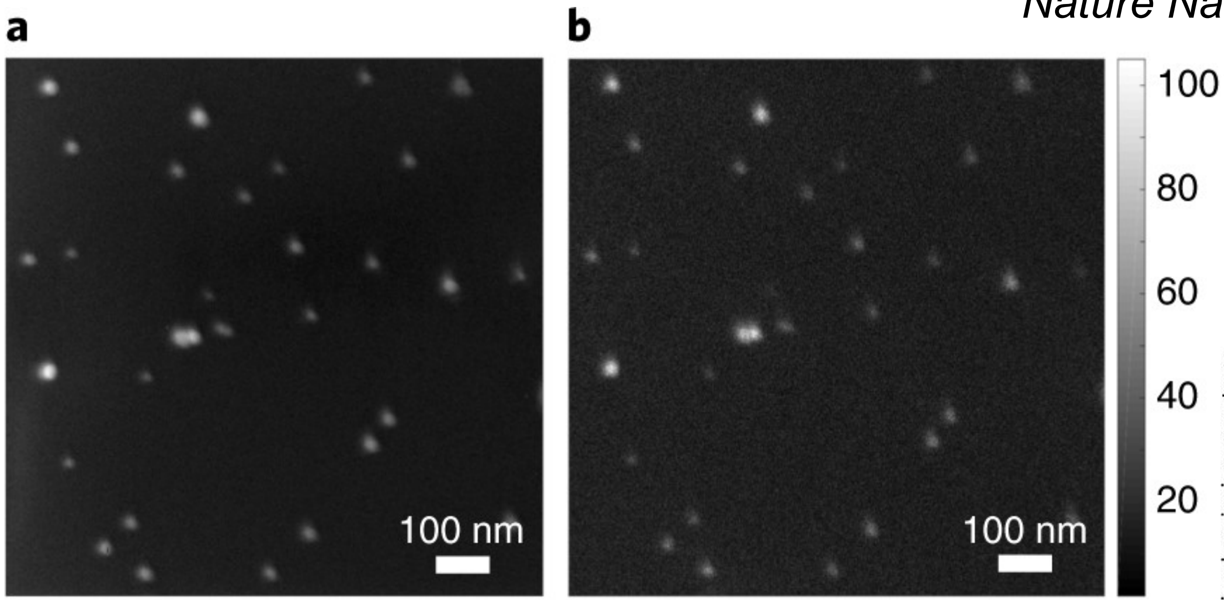


The nanoscale resolution of CL allows us to collect the CL spectra along a 100 nm ZnO NRs.

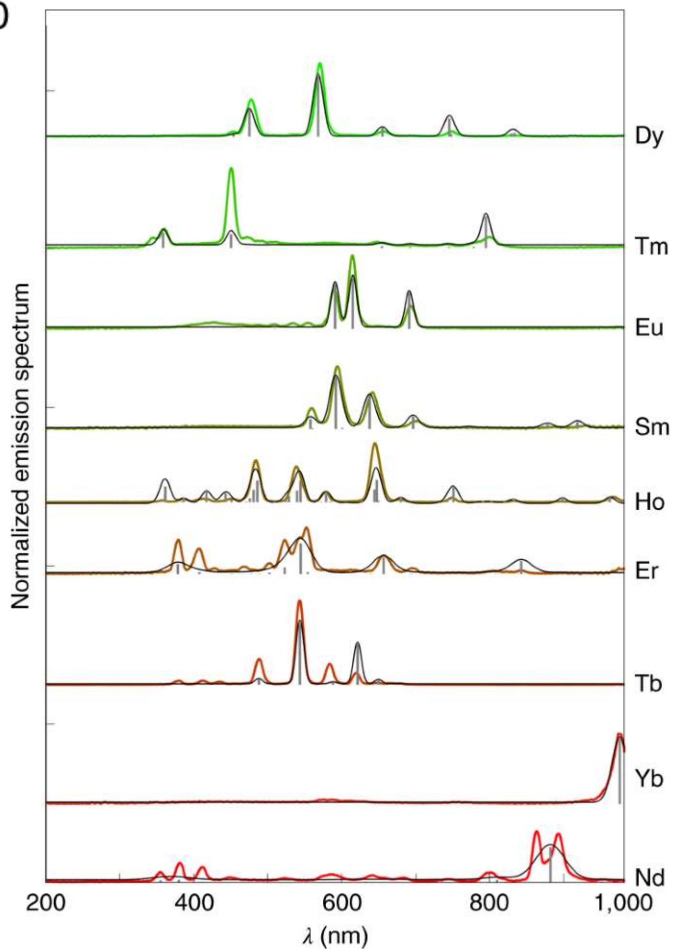
What is the limit of nanoscale detection resolution of SEM-CL?

Bright sub-20-nm cathodoluminescent nanoprobes for electron microscopy

Nature Nanotechnology 14, 420–425 (2019)



CL imaging of single nanoparticle composed of $NaGdF_4$:5% Eu^{3+}



Multicolor imaging of lanthanide-based nanoprobes

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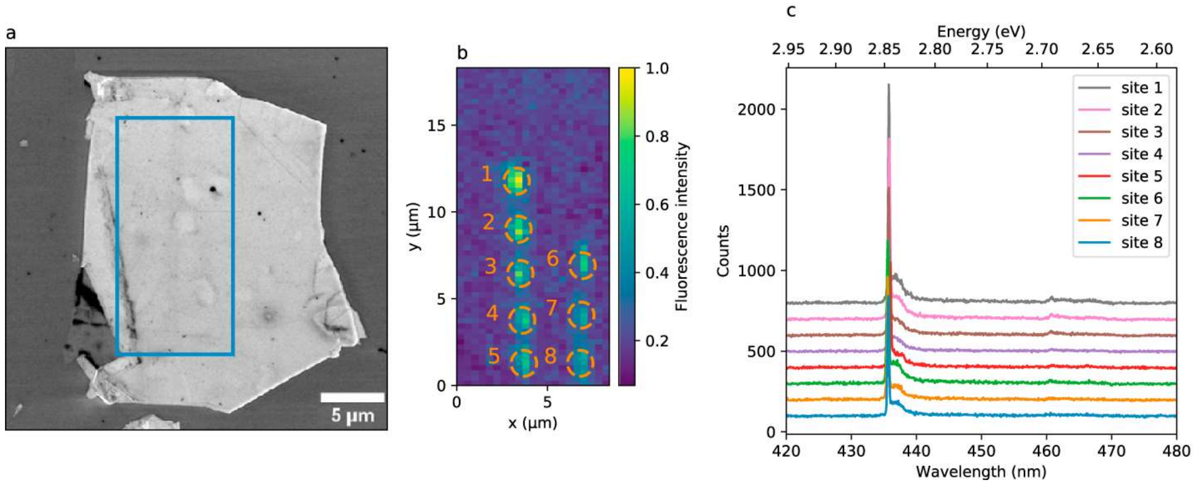
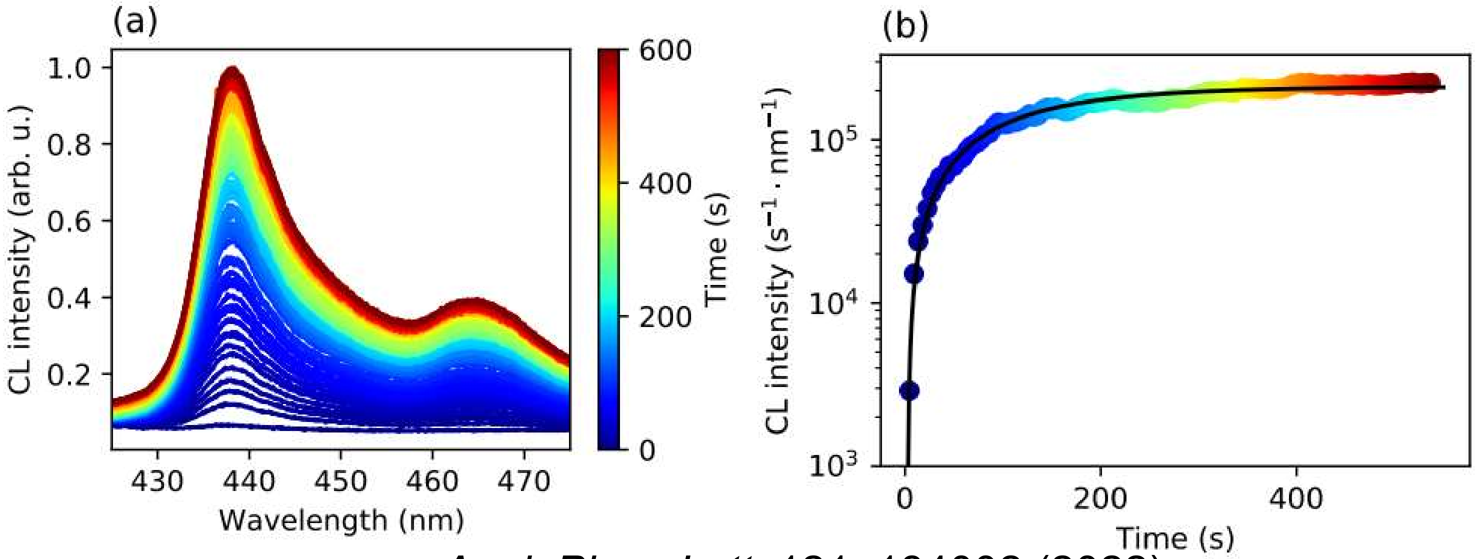


Single photon emitter (SPE), emitting in the blue, can be generated in hBN by electron beam irradiation.

Nature Communications **12**, 3779 (2021)

In-Situ CL has been used to monitor the generation of the blue emitting center in electron irradiated hBN.



Appl. Phys. Lett. 121, 184002 (2022)

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Electron penetration depth is variable:
depth-resolved studies, imaging buried structures

Nanoscale lateral resolution based on electron excitation

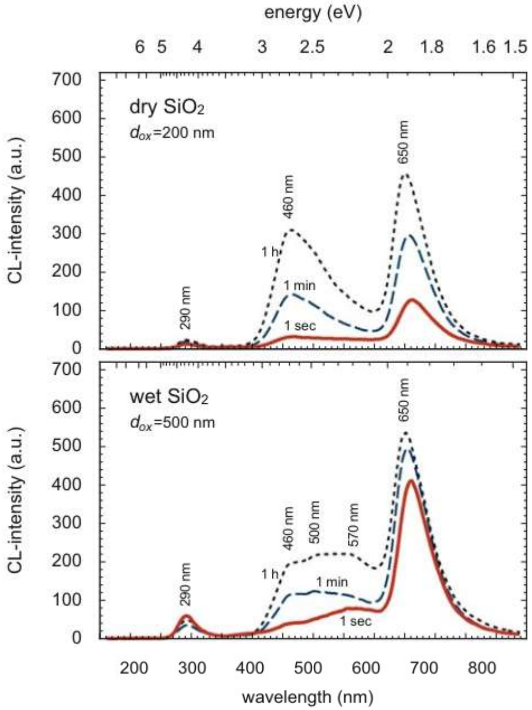
***In-Situ* CL analysis of electron irradiated materials**

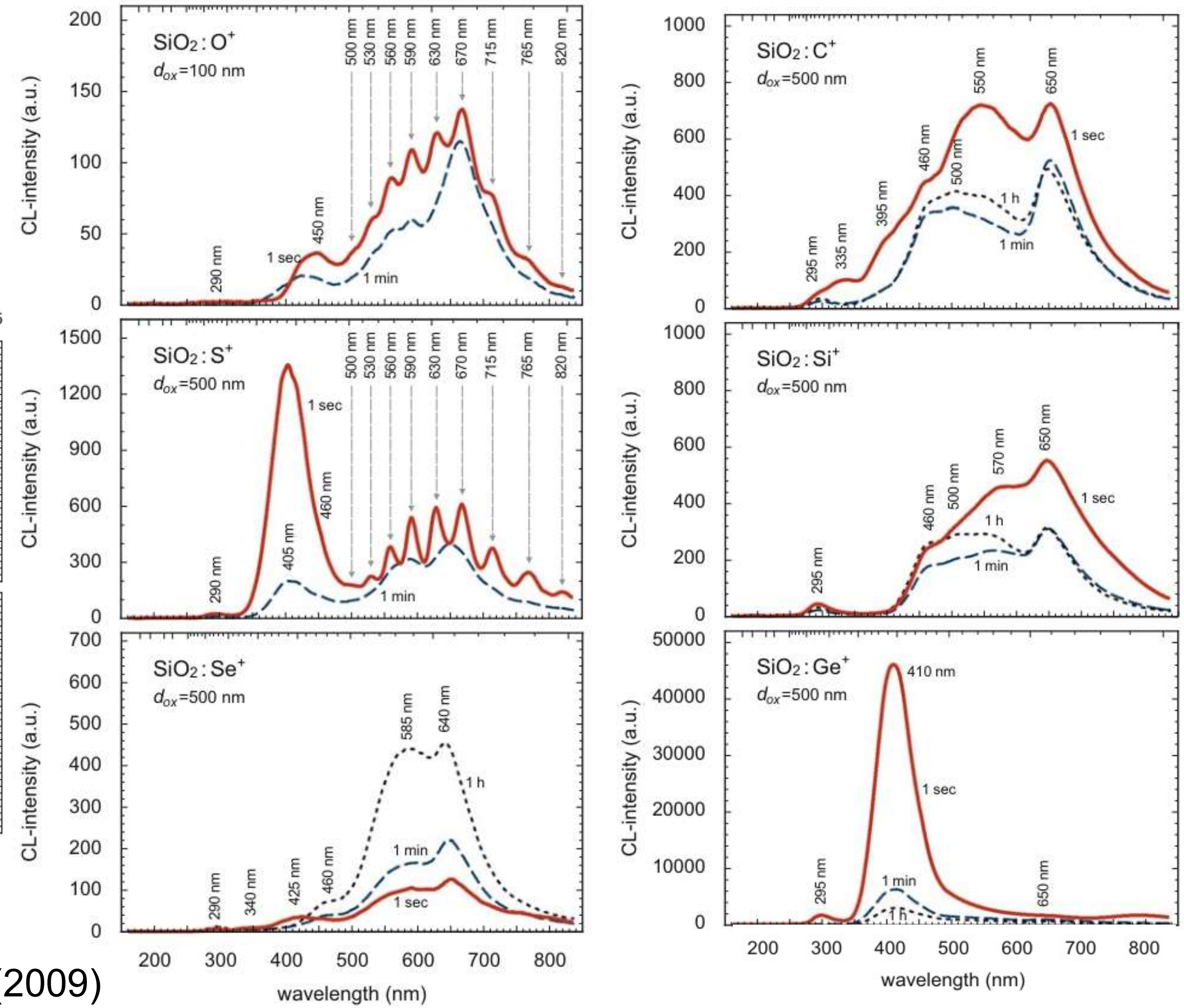
CL study of ion implanted materials

The case study: the luminescence of sulphur implanted silicon

CL study of ion implanted materials: Silicon Dioxide

SiO_2 is one of the most studied materials where the luminescence properties change drastically with ion implantation

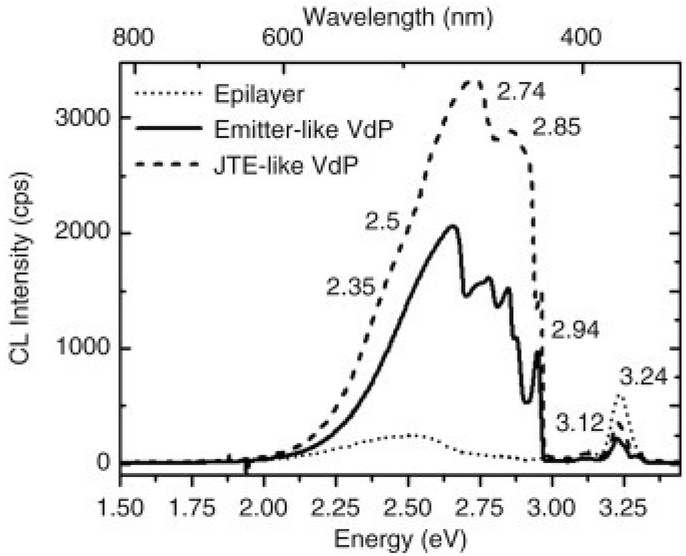




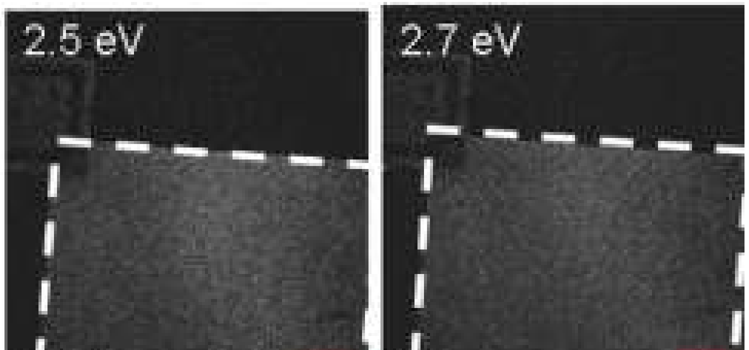
Jour. of Lum. **129**, 1488 (2009)

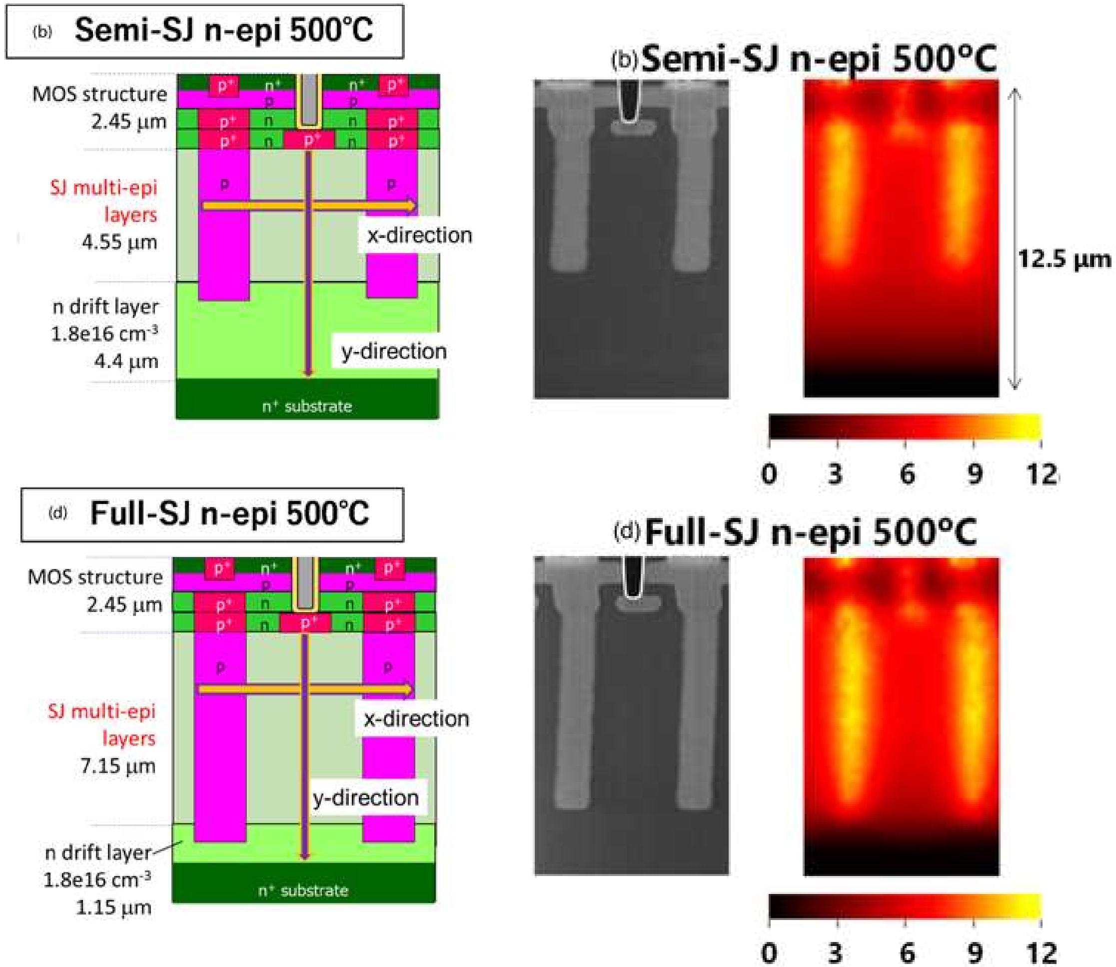
CL study of ion implanted materials: Silicon Carbide (4H-SiC)

Superlat & Microstrut. **45,** 383 (2009)



The Aluminum implantation in 4H-SiC, (employed for *p* doping) gives rise to a bright emission in the visible range, detectable in CL maps.

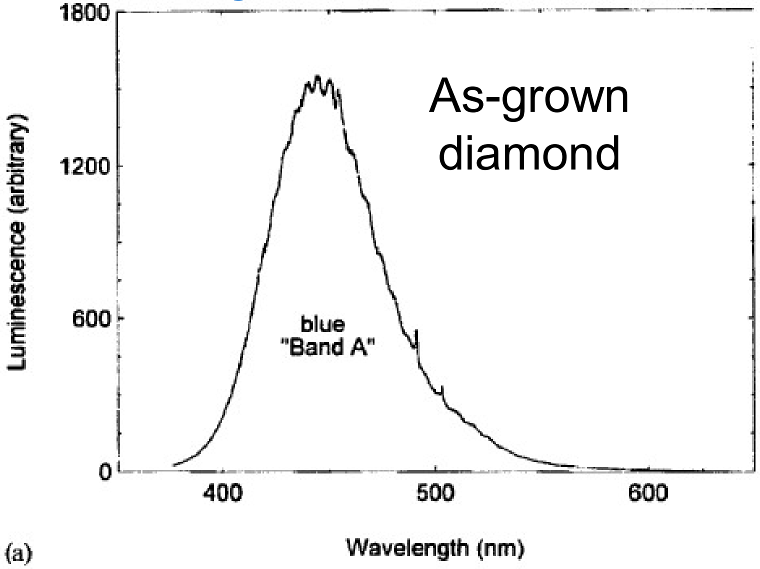


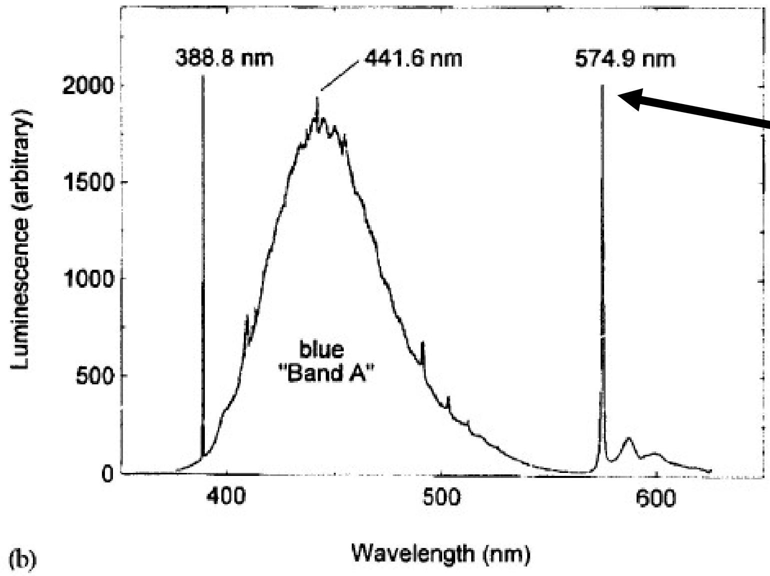


Cross-sectional CL maps are employed for quality benchmarking of complex 4H-SiC device fabrication

JJAP **62**, 016508 (2023)

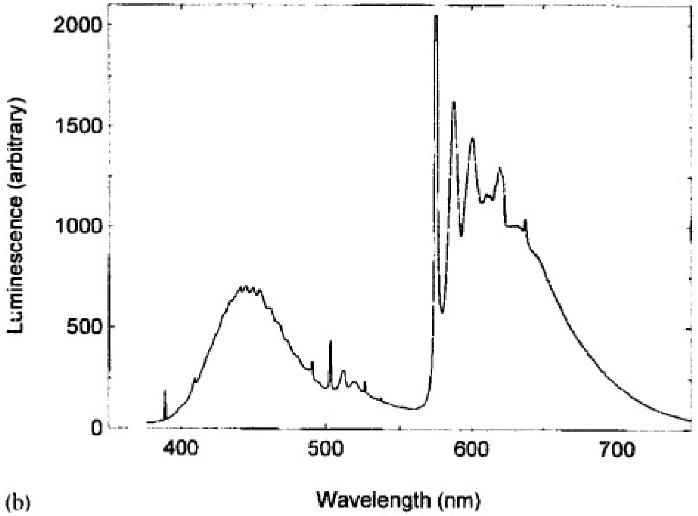
CL study of ion implanted materials: Diamond





After first round of N implantation $(N\text{-}V)^0$

After second round of N implantation



Diamond **6**, 516-520 (1997)

Diamond (bandgap E_g= 5.5 eV) is a peculiar material, because the nitrogen ion implantation has a double purpose:

- First, the *n* type doping with high concentration

-Second the possible generation of sharp emission due to nitrogen related complex with single photon emission properties, employed in quantum cryptography

What are the ADVANTEGES of CL spectroscopy and imaging?

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Examples: CL study of ion implanted materials

The case study: the luminescence of sulphur implanted silicon

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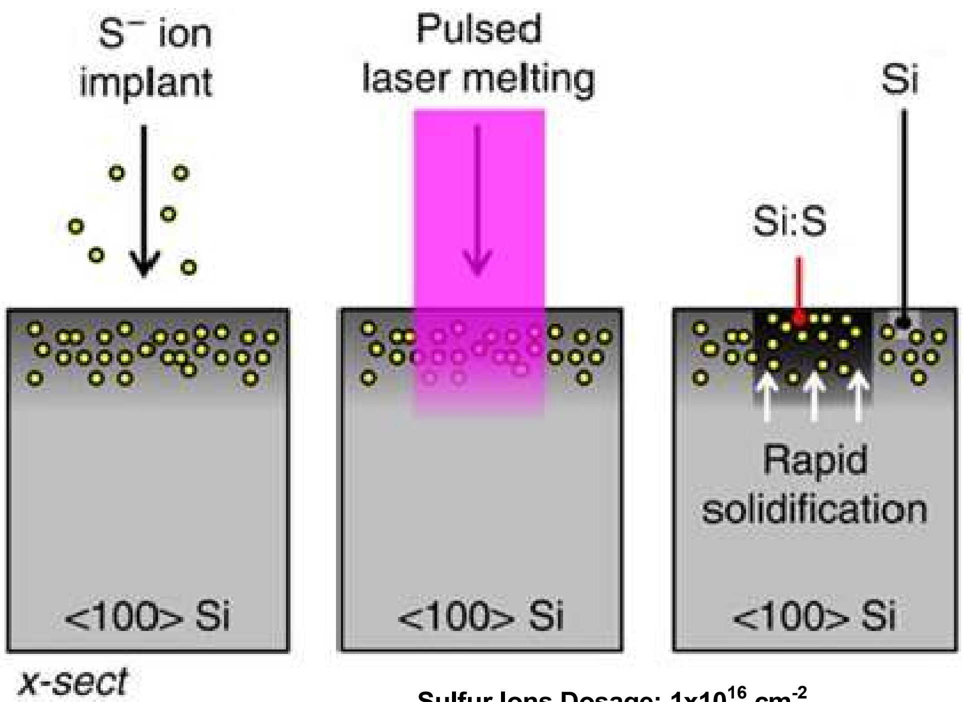
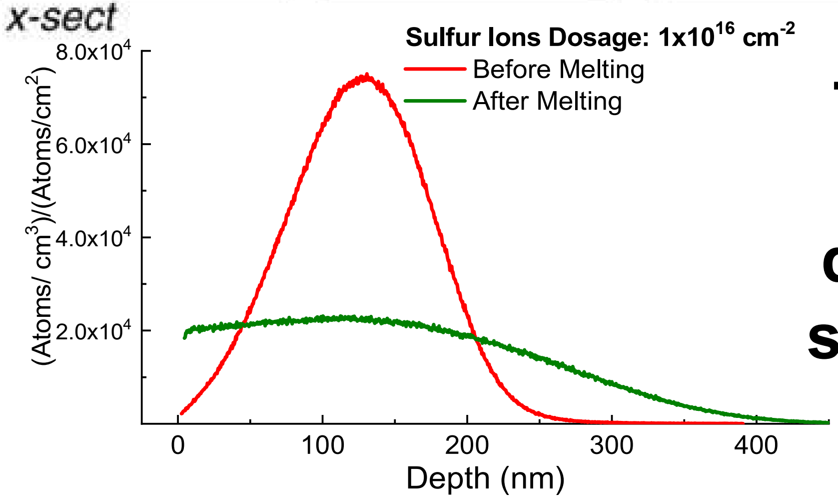


Fabrication steps:

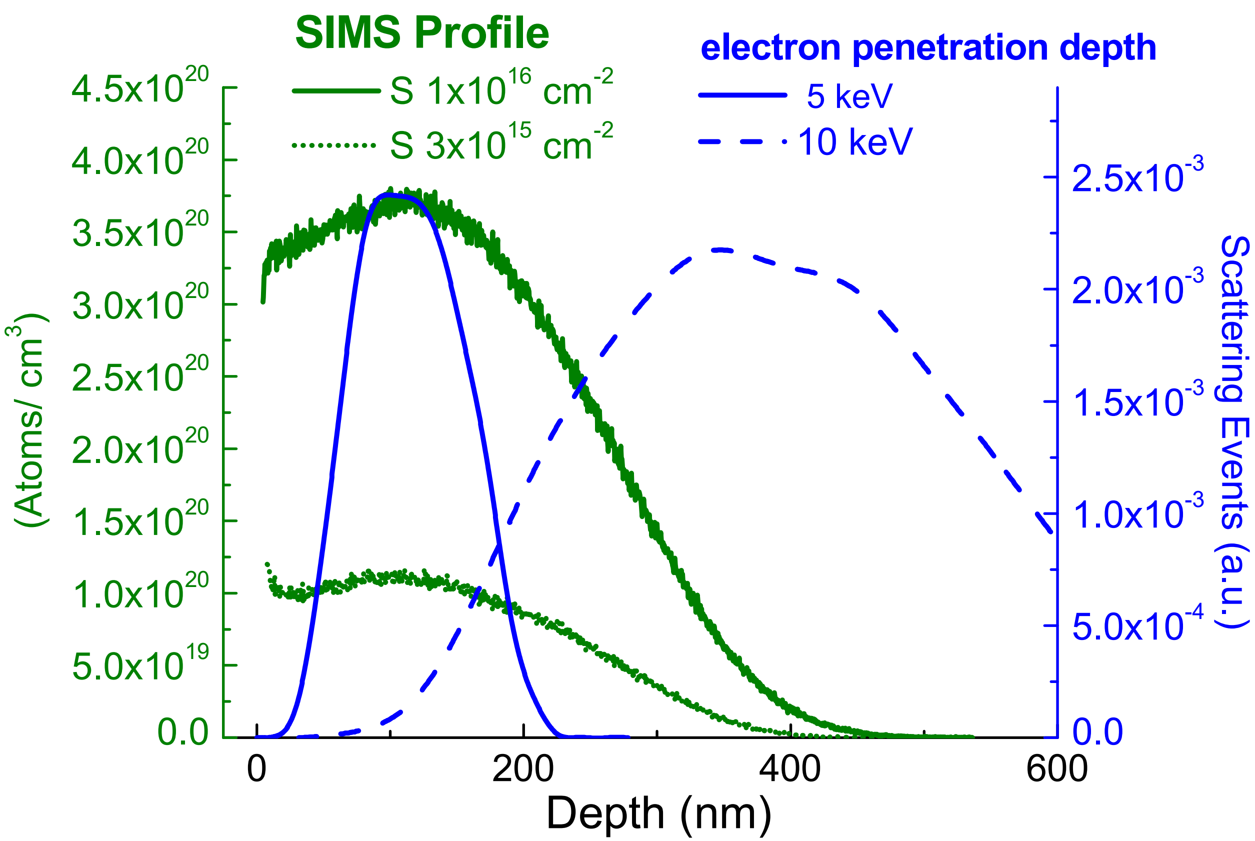
1- Ion implantation of sulphur ($^{32}S^{+}$) with a energy of 95 keV and 7° off-normal to prevent channeling.

2- Pulsed laser melting (PLM) using a XeCl laser (308 nm, 4 50 ns long pulses with a power of 1.7 Jcm^{-2}).



This process results in a sulfur hyperdoping of silicon, with a doping concentration above the solubility limit of sulfur in silicon

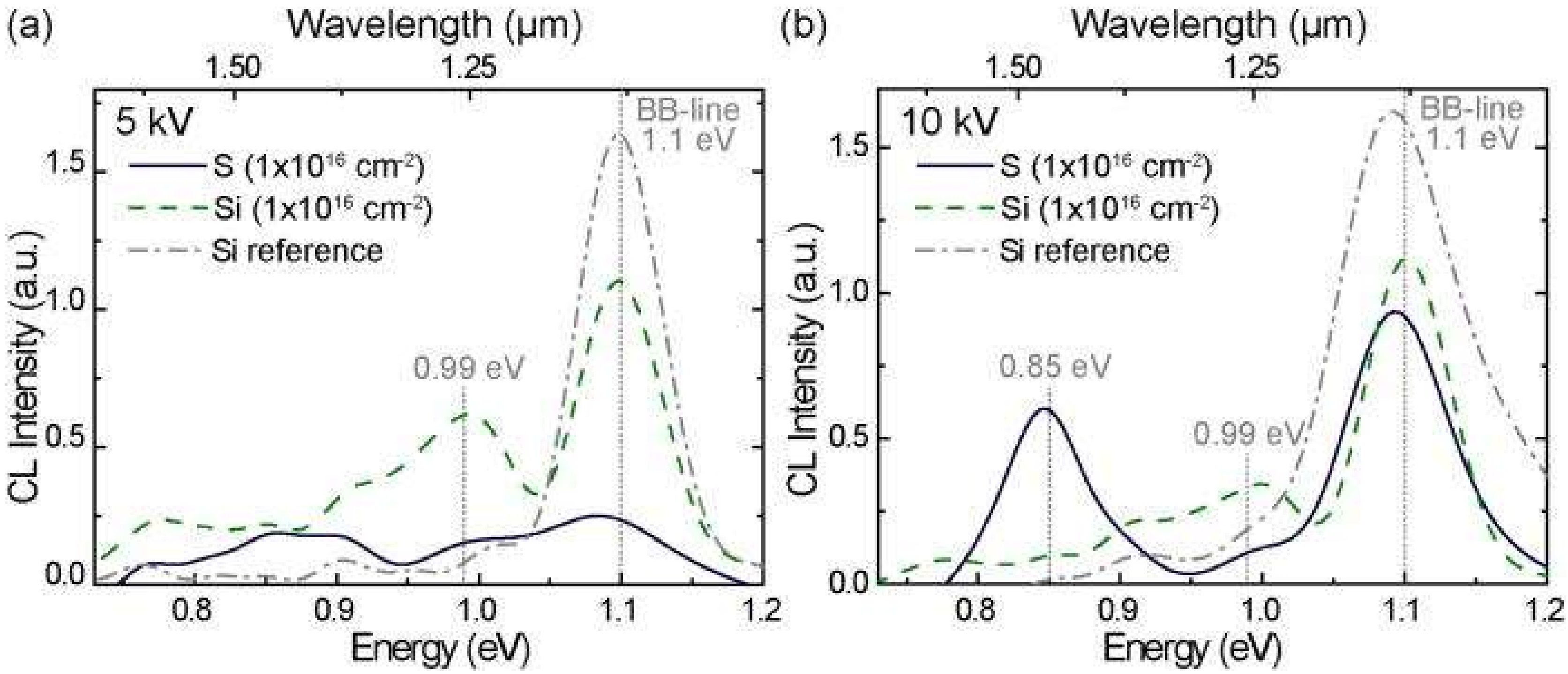
The case study: the luminescence of sulphur implanted silicon



Montecarlo simulations are used to evaluate the electron penetration depth for choosing the accelerating voltage for cathodoluminescence analysis of the samples. We choose 5 keV and 10 keV CL analyses for probing the implantation plateau and implantation tail, respectively

Secondary ion mass spectroscopy (SIMS) is employed to determine the resulting sulfur concentration profiles for two different implantation doses.
SIMS reveals a sulfur concentration above 10^{20} cm^{-3} with a hyperdoped layer thickness of 400 nm.

The case study: the luminescence of sulphur implanted silicon



In order to determine the intragap states caused by sulfur hyperdoping, we compare the CL spectra of the Si reference, Sulfur implanted Si and Silicon implanted Si to rule out the possible attribution to irradiation induced defects.

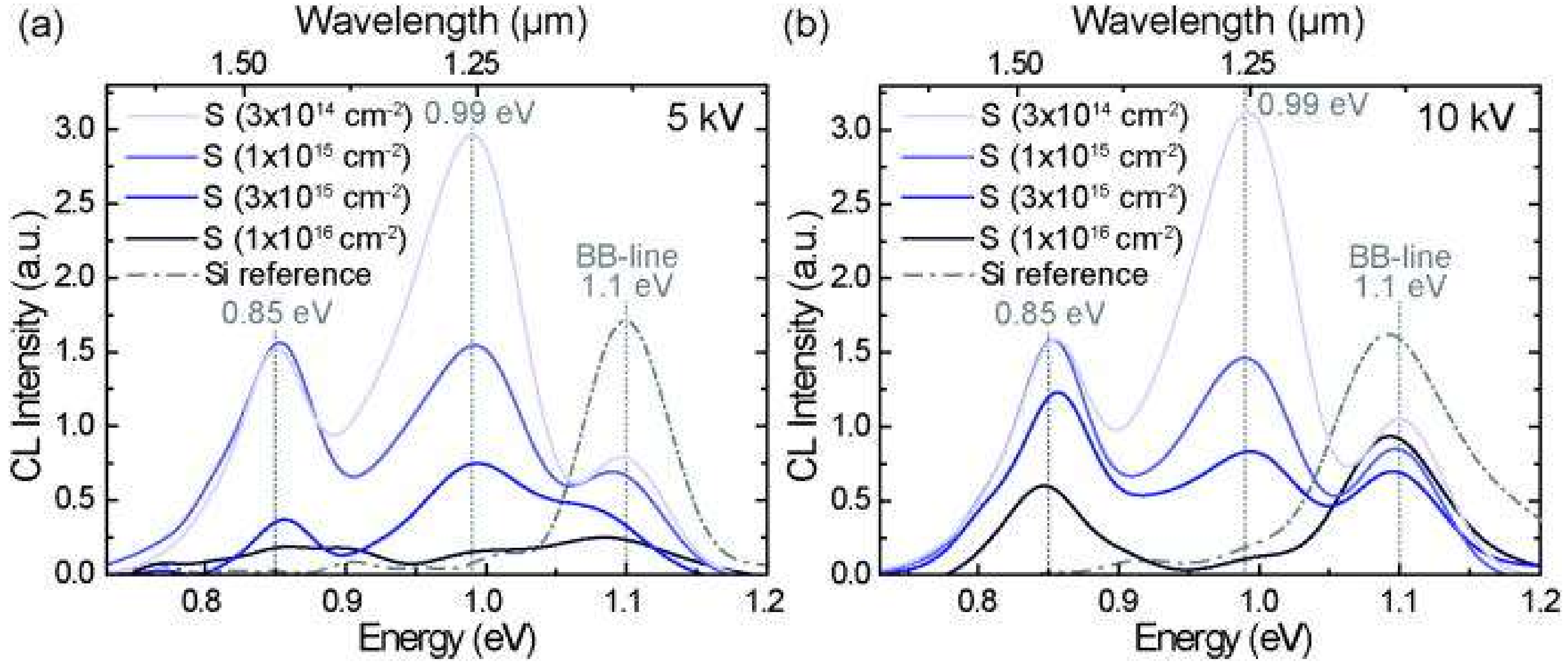
In particular:

the 1.1 eV emission is the band-to-band recombination of silicon,

The 0.99 eV emission is assigned to silicon interstitial atoms,

The 0.85 eV emission is attributed the sulfur intragap state.

The case study: the luminescence of sulphur implanted silicon

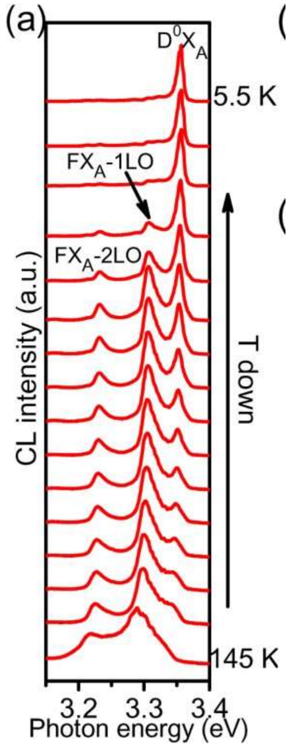


Decreasing the sulfur concentration, we found the presence of irradiation induced deep levels, while the S related luminescence is maxed out in the implanted layer with the lowest S implantation dose.

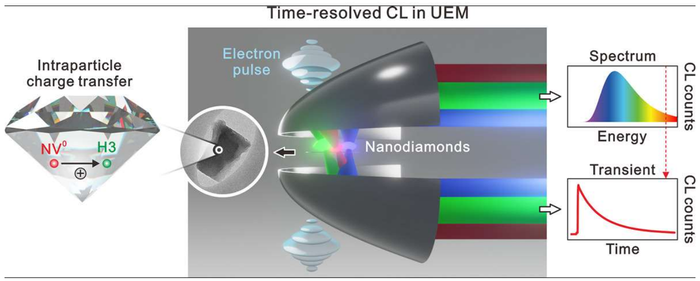
The decrease and broadening of the BB-line with the highest S dose in the implantation plateau is due to the presence of **strain** that cause the quenching of all the light emission. This effect does not occur in the implantation tail area due to the lower local concentration of S.

Optical Characterization of Implantation Defects

In this lesson, we only scratched the surface of the possible opportunities given by
cathodoluminescence spectroscopy and imaging



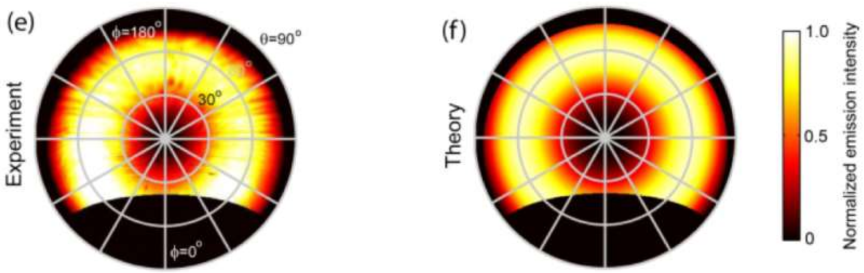
Time resolved Cathodoluminescence



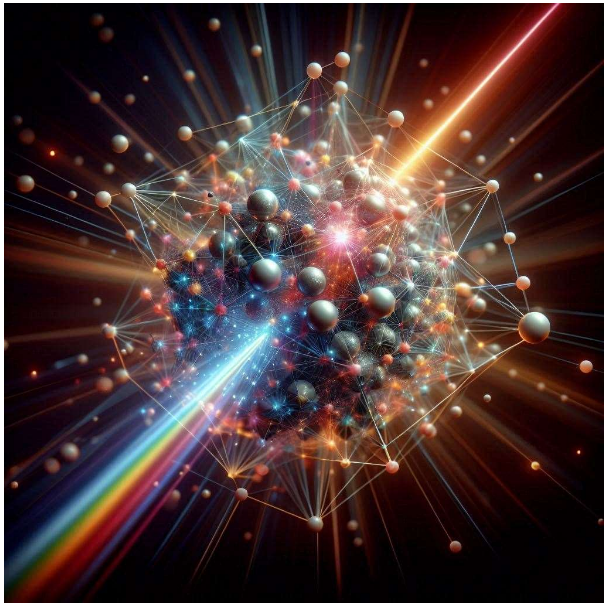
Temperature dependent Cathodoluminescence

Angle resolved Cathodoluminescence

Power dependent Cathodoluminescence



Thank you for your attention



If you are interested in CL experiments, please contact me:

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ASBeST

A 7-Beryllium electron capture STudy for nuclear and solid state physics