Structural origins of light emission in Germanium quantum dots

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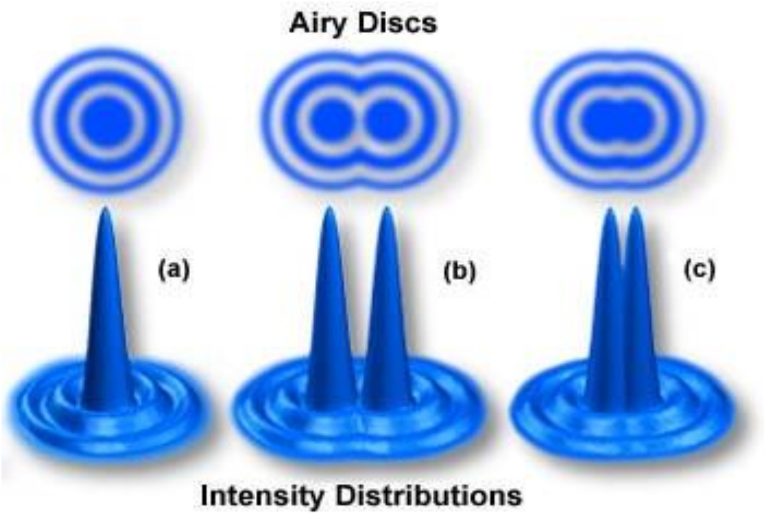
What's the problem in optical imaging ?

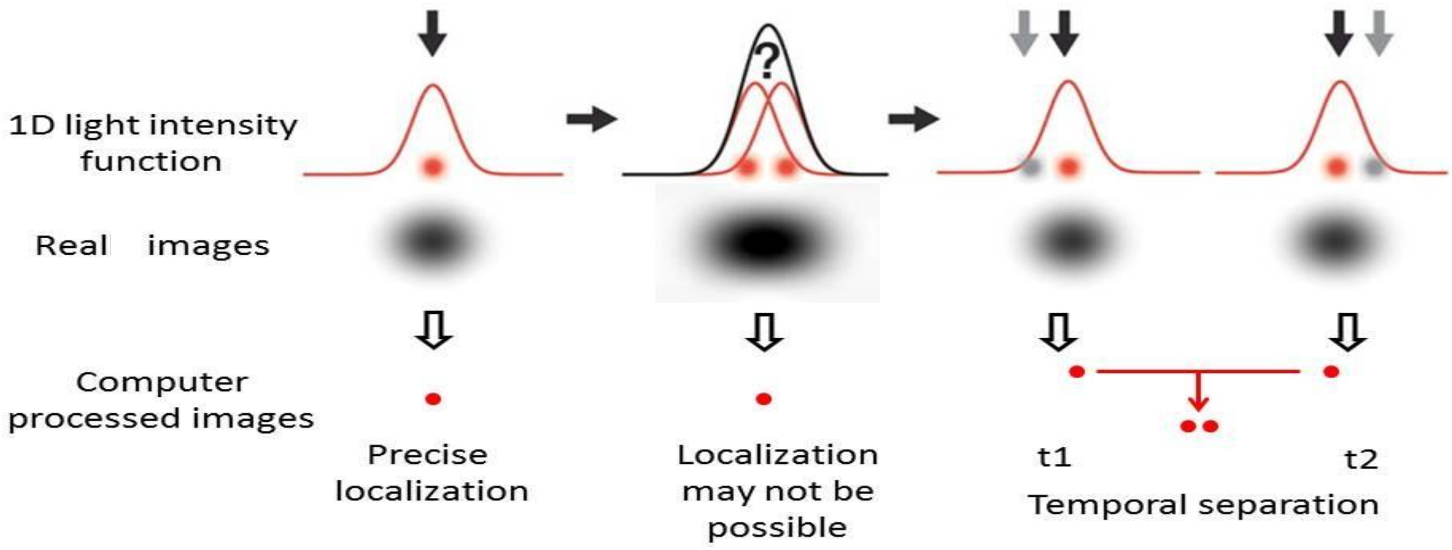
Abbe's law sets the resolution limit - diffraction limit:

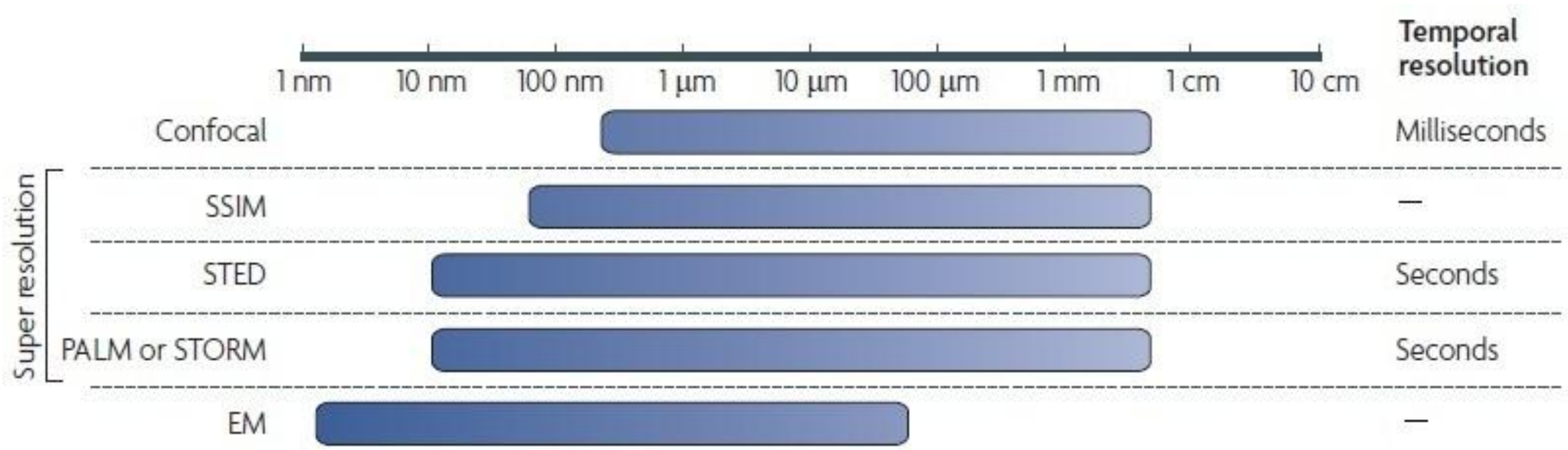
$d = \lambda / 2NA$



Solutions - super-resolution:fluorescent super-resolution
SSIM, STED, PALM, STORM

Super-resolution





Cell imaging

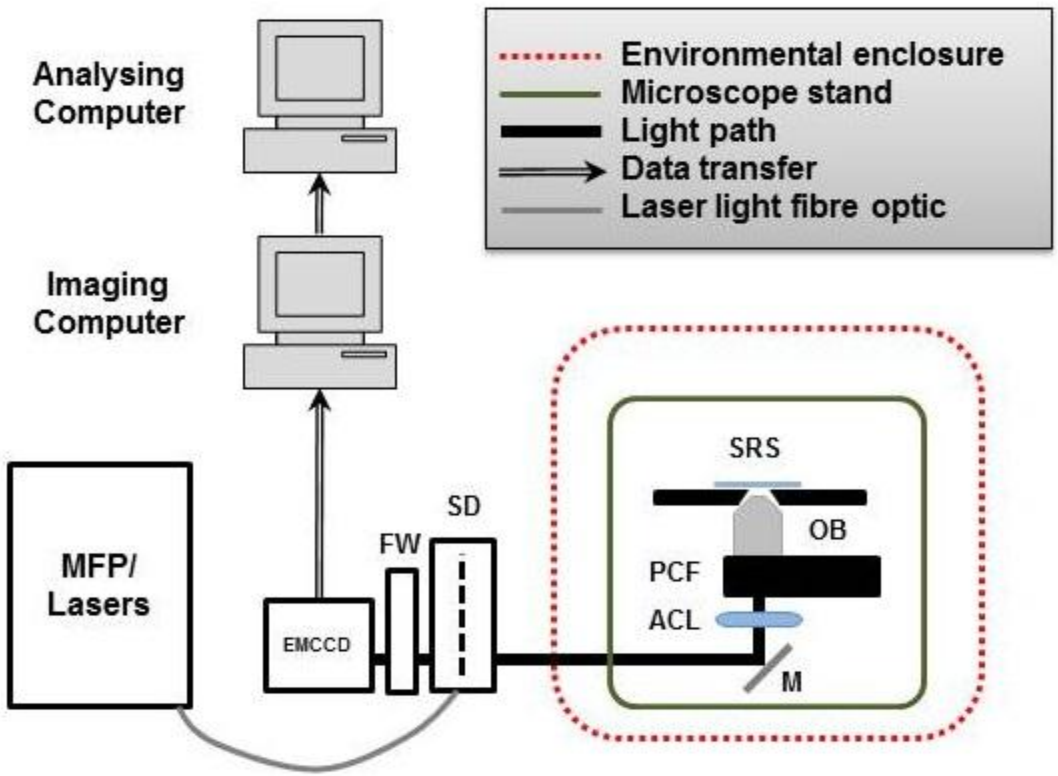
Imaging system

Image processing

Fluorophores

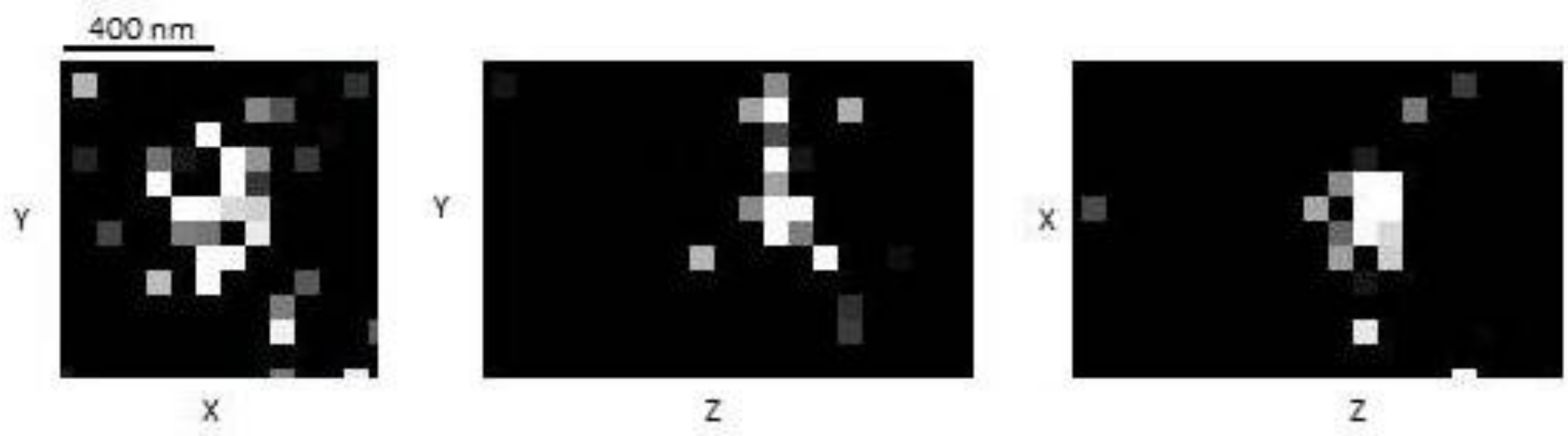
Cell Imaging - Imaging system

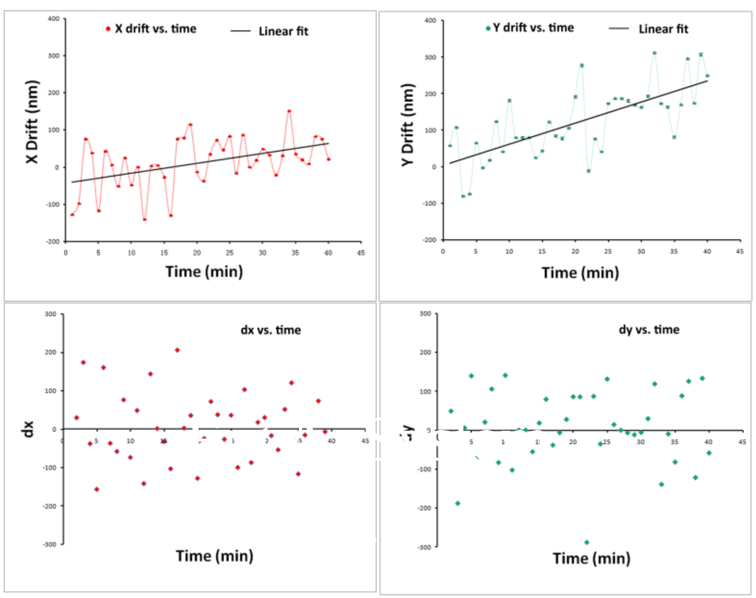
Spinning Disk Confocal Microscopy



Component elements of the imaging system

Imaging system assessment





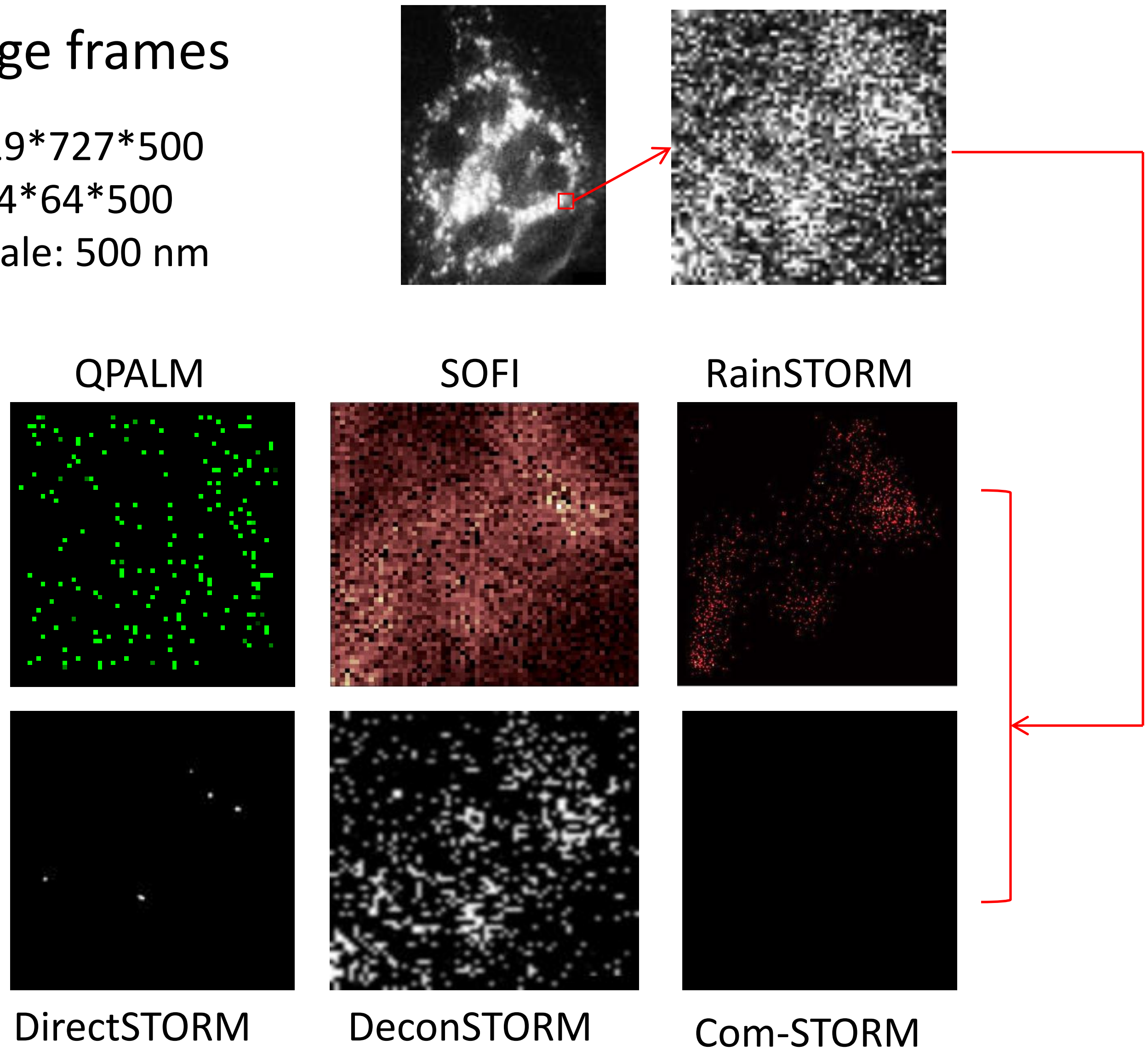
Excitation wavelength (nm)	405	488	561	640
FWHM of PSF(nm)	92 m	96 nm	115 nm	110 nm

Cell imaging → Image Processing

Raw image frames

Left : 529*727*500
Right: 64*64*500
Right Scale: 500 nm

Processed image



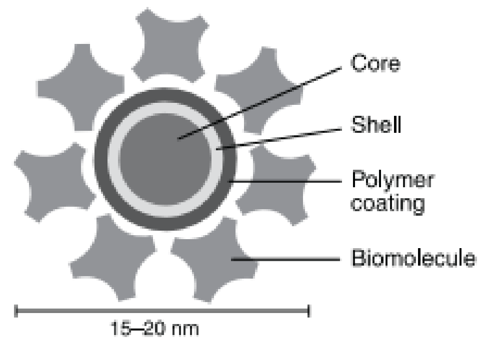
Cell imaging → Algorithm comparison

Algorithm	Description	Resolution	Data test (Image size)	Data test (Time)
QPALM	ImageJ plugin	40nm	64*64*500	1 minute
SOFI	Matlab	20nm	64*64*500	1.5 minutes
Rain-STORM	Matlab	Pixel size	64*64*500	1.5 minutes
Direct-STORM	C	20nm	64*64*500	7 minutes
Decon-STORM	Matlab	<50nm	64*64*500	20 minutes
Compress-STORM	Matlab	<40nm	64*64*500	>3 hours

Cell imaging

Fluorophores : why use Qdots

Dyes

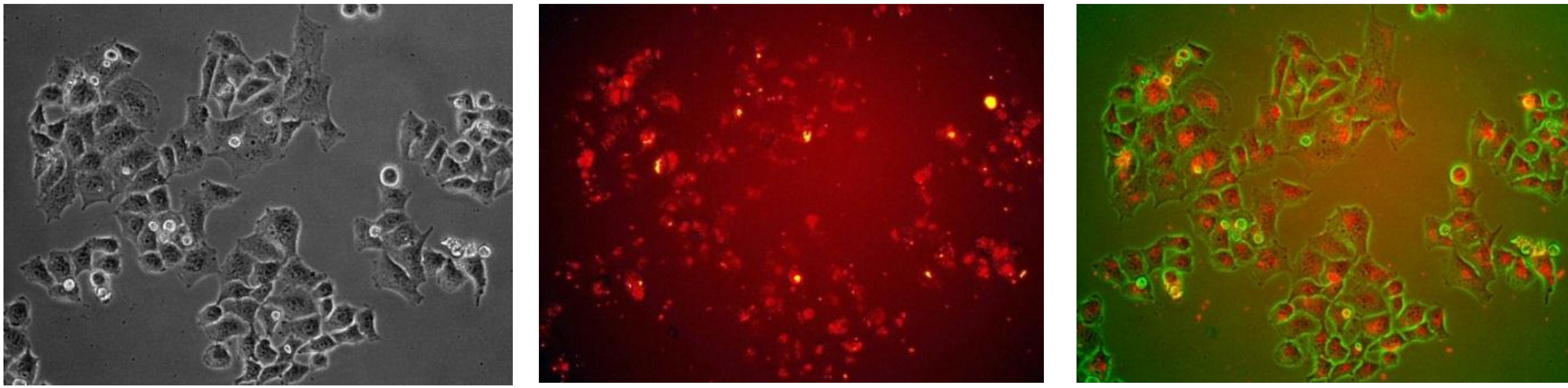


Qdots

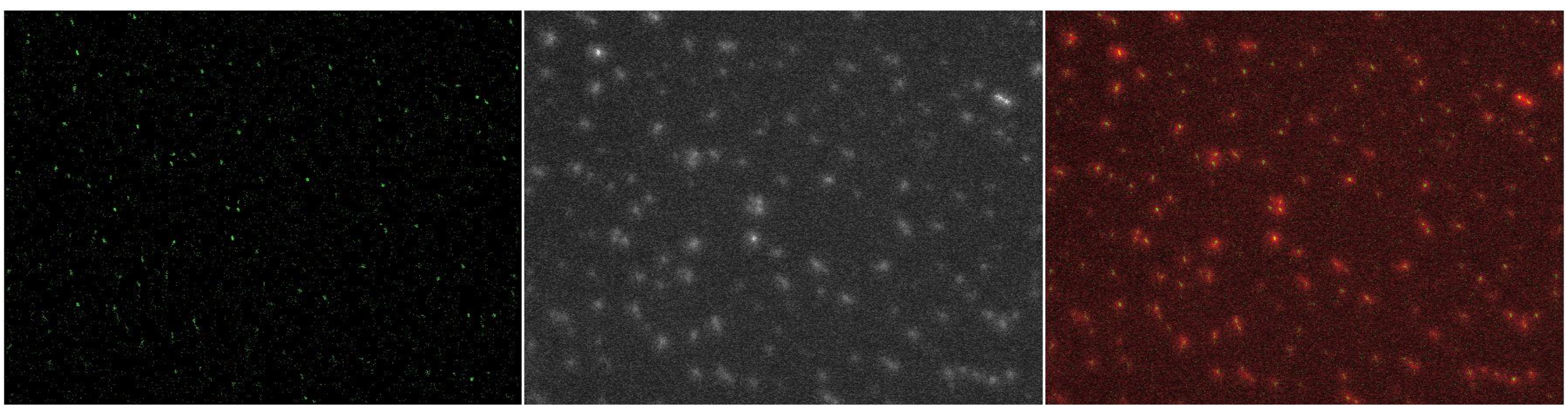
- *Improved optical characteristics*
- *Blinking*
- *Optically stable*
- *Biocompatibility*

Motivation

- Morphological super-resolution imaging
- Cell signal imaging

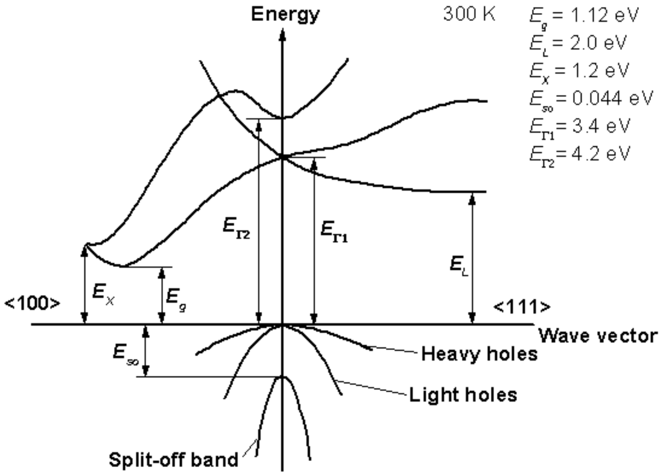


CdSe

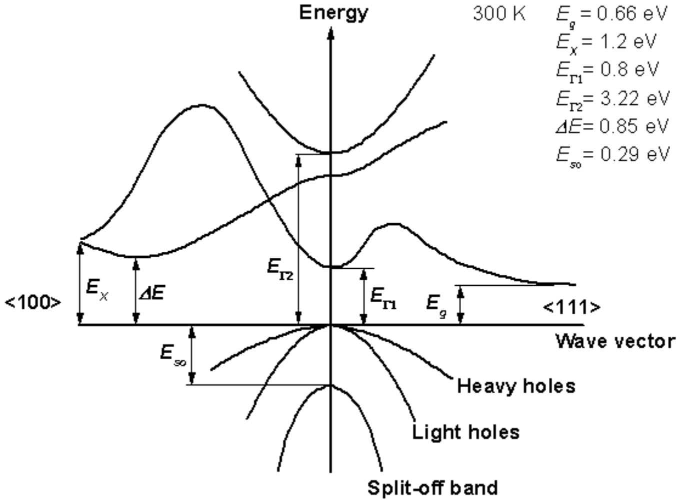


nc-Si

Si vs Ge

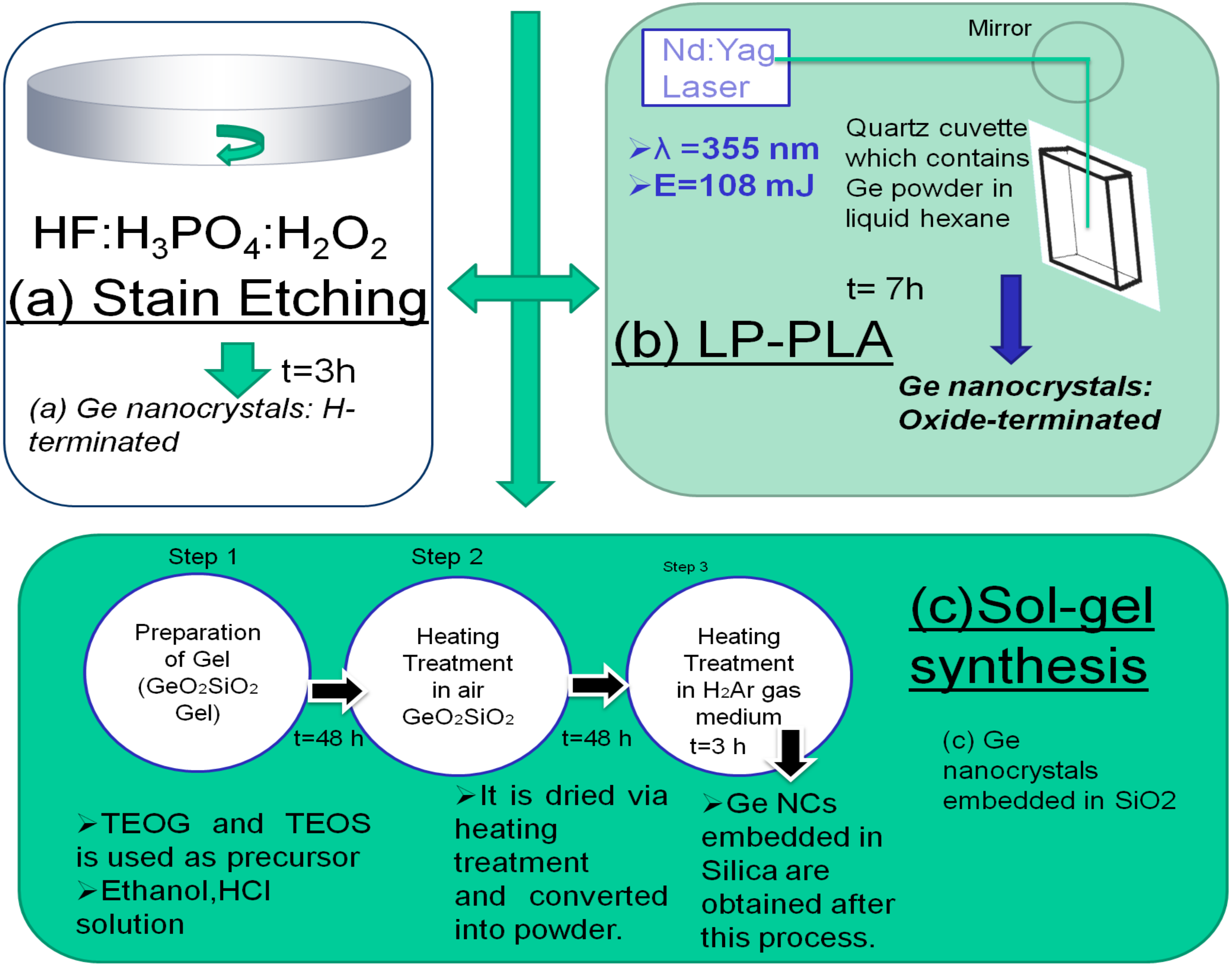


Energy
300 K
E_g = 1.12 eV
E_L = 2.0 eV
E_X = 1.2 eV
E_{so} = 0.044 eV
$E_{\Gamma 1}$ = 3.4 eV
$E_{\Gamma 2}$ = 4.2 eV
$E_{\Gamma 2}$
$E_{\Gamma 1}$
E_L
E_X
E_g
<100>
<111>
Wave vector
E_{so}
Heavy holes
Light holes
Split-off band



Energy
300 K
E_g = 0.66 eV
E_X = 1.2 eV
$E_{\Gamma 1}$= 0.8 eV
$E_{\Gamma 2}$= 3.22 eV
ΔE= 0.85 eV
E_{so} = 0.29 eV
$E_{\Gamma 2}$
E_X
ΔE
$E_{\Gamma 1}$
E_g
<100>
<111>
Wave vector
E_{so}
Heavy holes
Light holes
Split-off band

Sample Preparation



Characterisation

CHARACTERISATION TECHNIQUES:

- ✓ Raman
- ✓ PL
- ✓ TEM

→

- ✓ OD-XAS
- ✓ EXAFS
- ✓ XEOL

↓

beamline B18 at Diamond Light Source

←

Characterisation

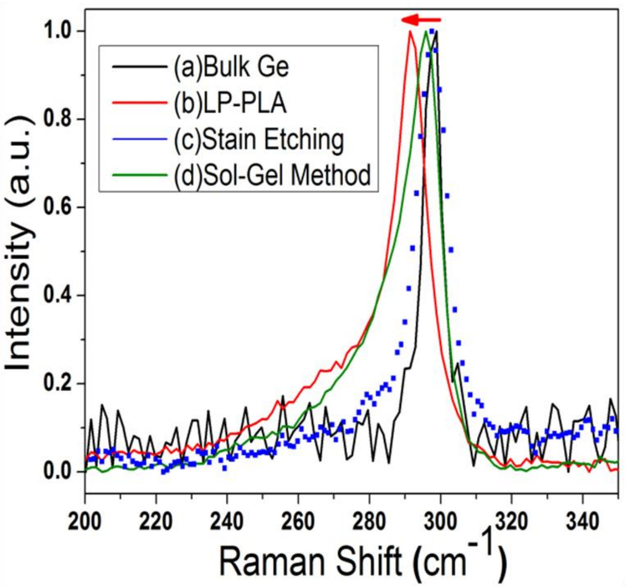


Figure 1 Normalised Raman Shift from right to left (a) bulk Ge and Ge nanoparticles formed by using (b) stain etching, (c) Sol-gel method and (d) LP-PLA.

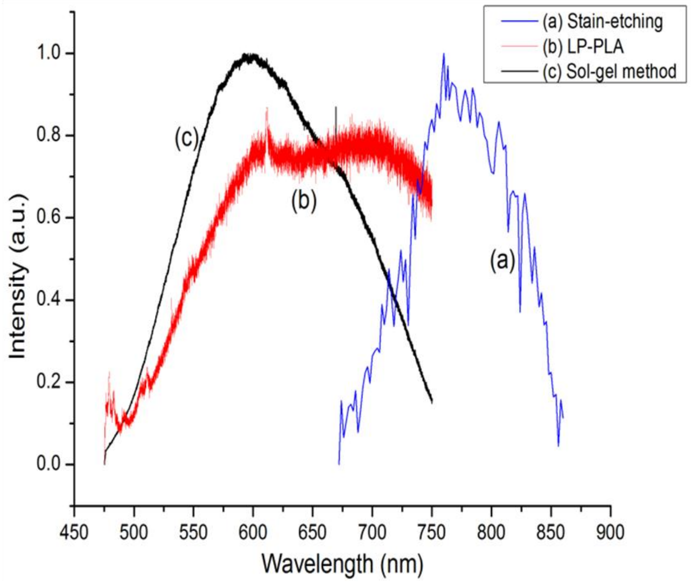


Figure 2 PL spectra of Ge nanoparticles formed by (a) stain etching (b) LP-PLA, (c) sol gel synthesis. Photoluminescence (PL) spectrum has been recorded from the each of the samples with excitation at 473 nm.

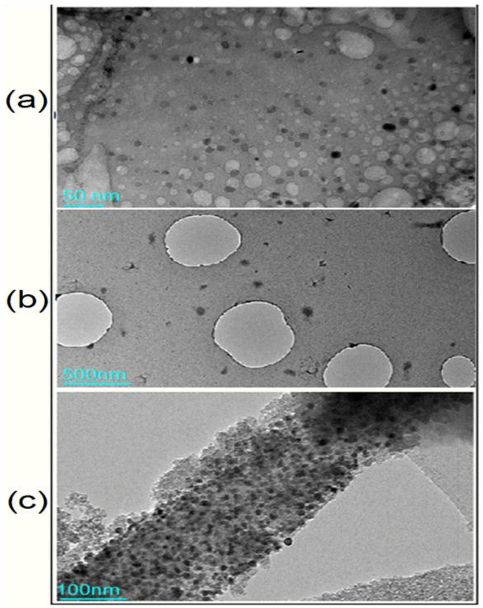
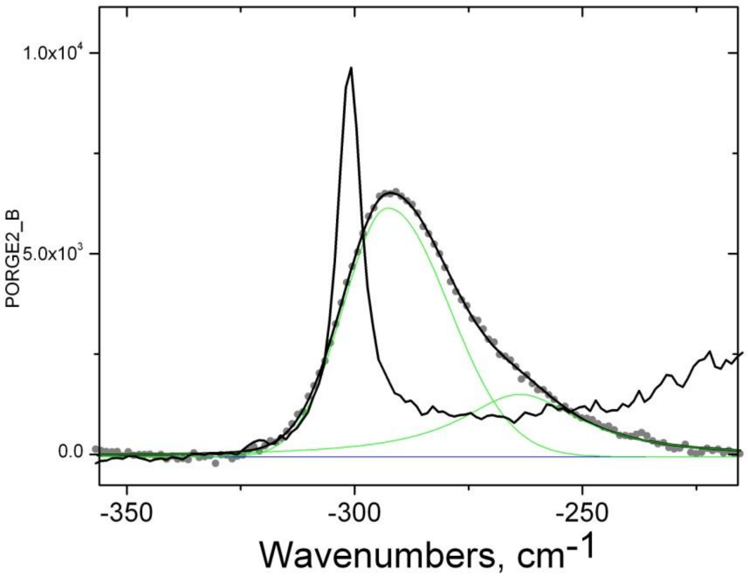


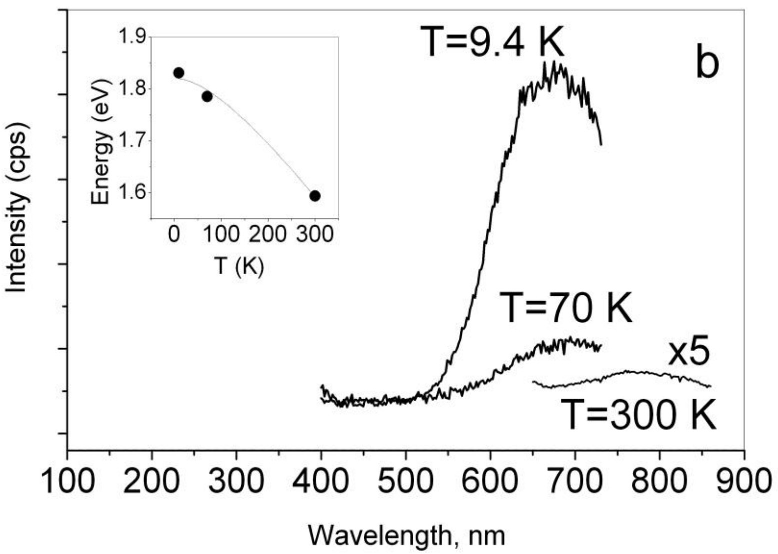
Figure 3 TEM micrograph of Ge nanoparticles from top to down prepared by (a) stain etching (b) LP- PLA and (c) Sol-Gel Method.

Characterisation

Raman



Photoluminescence



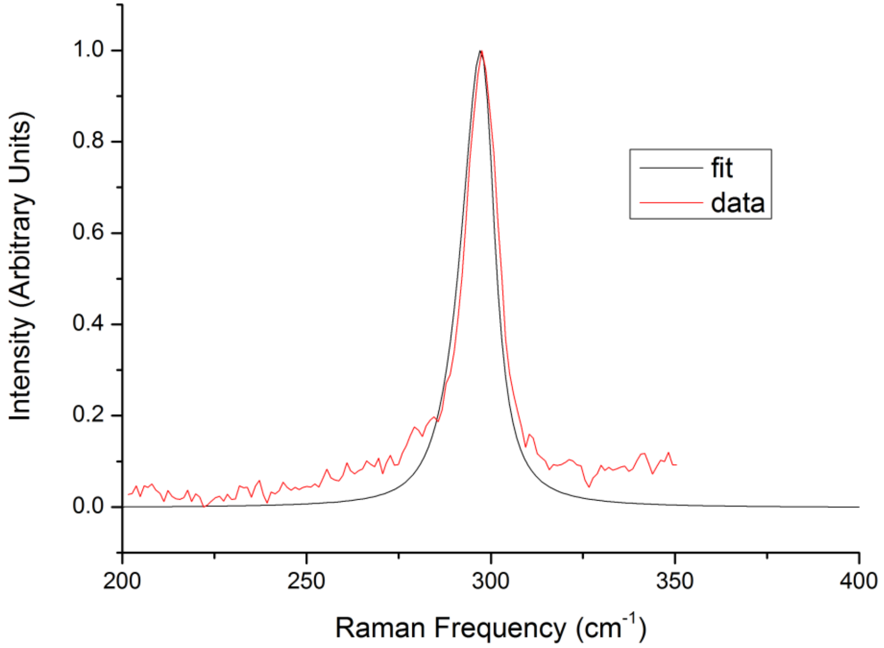
Raman Spectroscopy: the model for particle size evaluation

The Raman signal line shape can be described by the following expression, which includes phonon dispersion and natural line width:

$$I(\bar{v}) = I_0 \int \frac{d^3\vec{q}\,|C(0,q)|^2}{[\bar{v} - \bar{v}(\vec{q})]^2 + \left(\frac{\Gamma_0}{2}\right)^2}$$

The phonon confinement function which defines the area in the nanoparticle where phonons can exist. *r* is the radial position and *L* is the particle diameter.

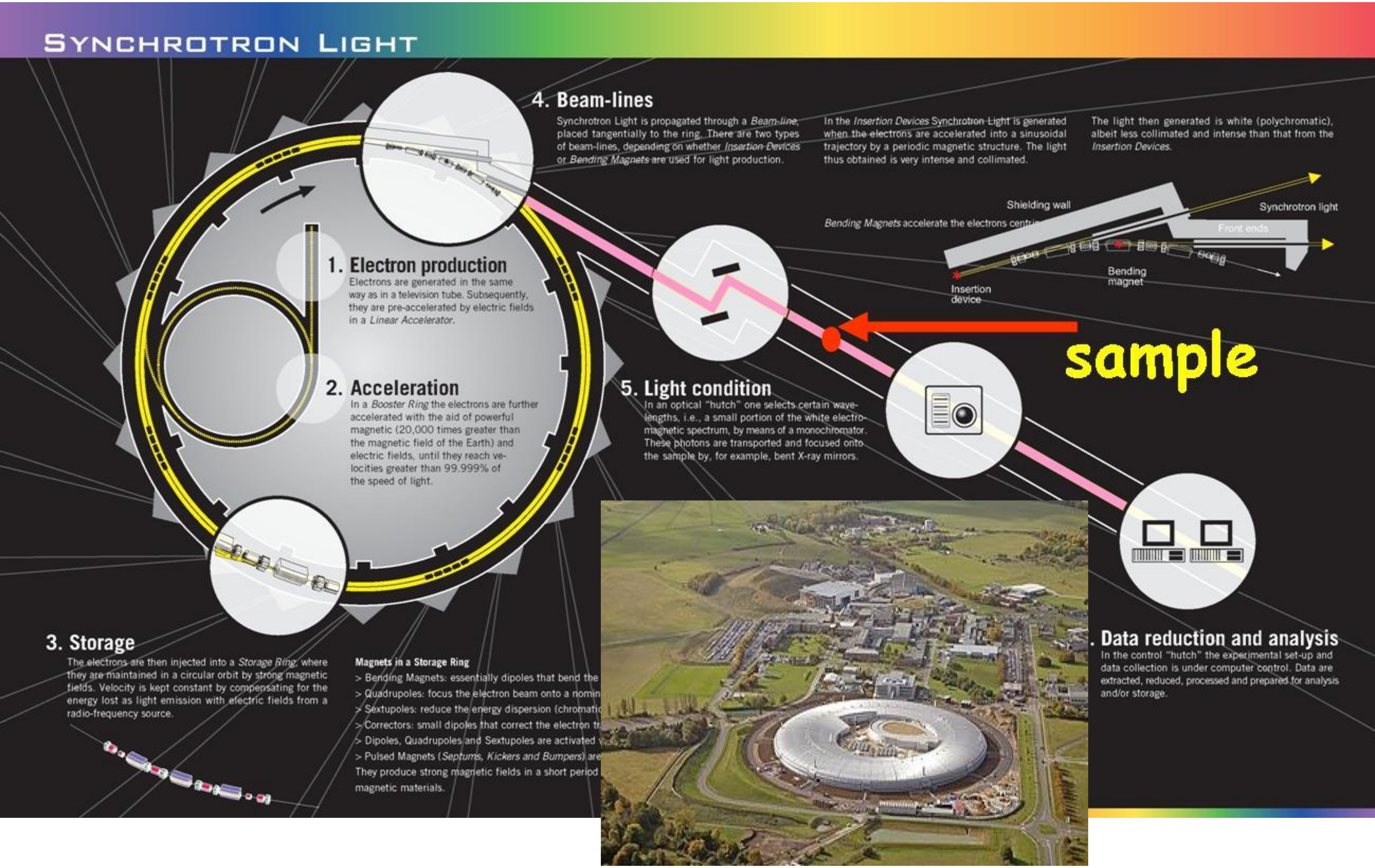
$$|C(0,q)|^2 = e^{-\frac{q^2L^2}{4}}$$



Size analysis results

Method	Technique	Transmission Electron Microscopy (nm)	Raman Spectroscopy	
			Size (nm)	FWHM (cm^{-1})
(a) Stain Etching		10 ± 4	6.9	10
(b) LP-PLA		41 ± 22	6.2	12
(c) Sol-Gel Method		10 ± 6	5.3	14

Structure of nanoGe



ODXAS measurements

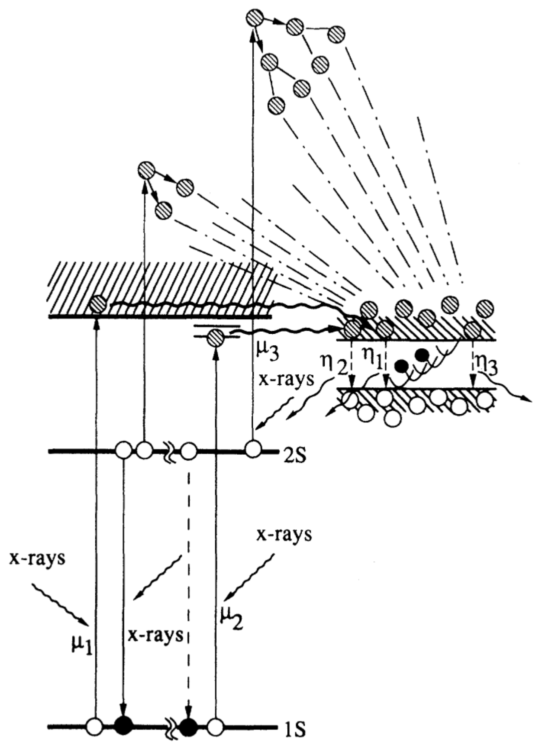
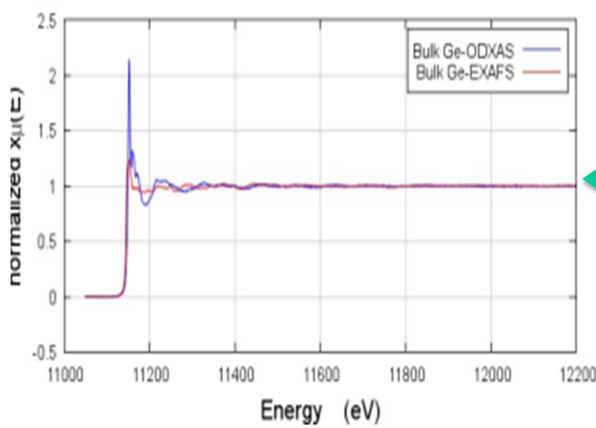
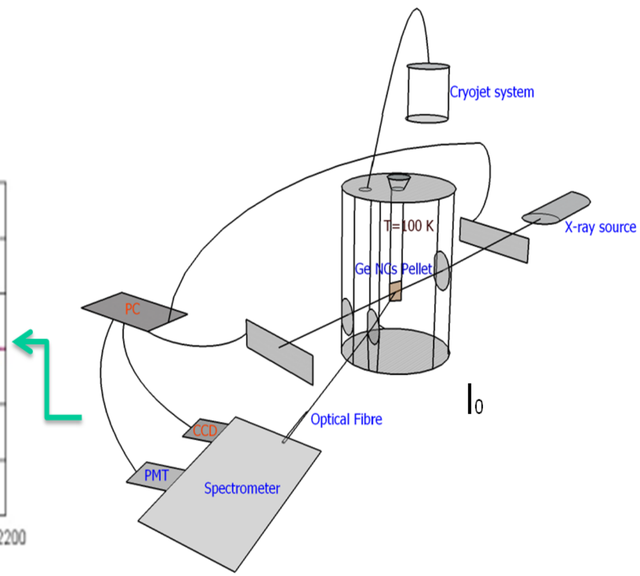


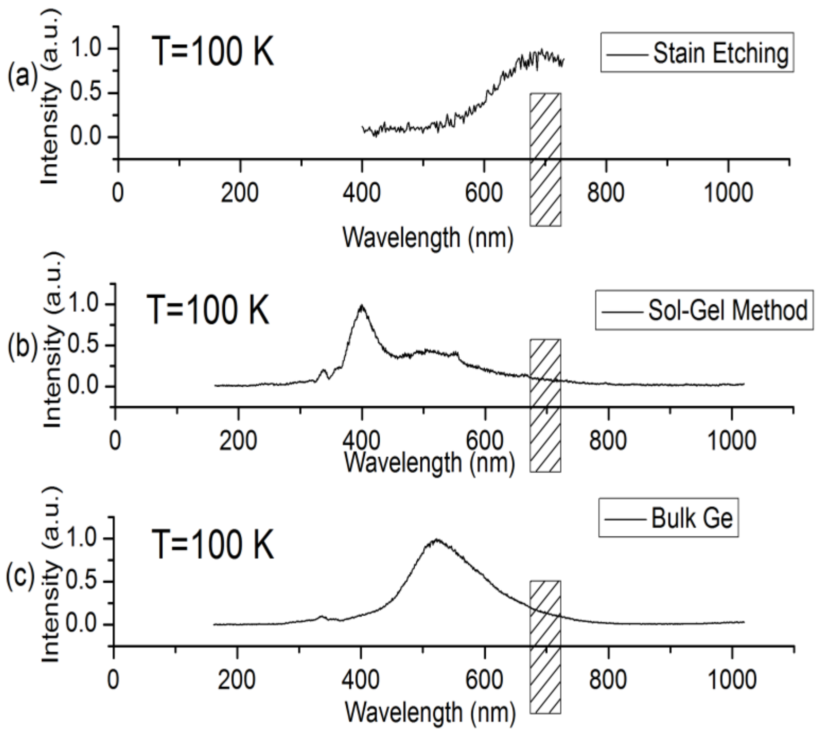
FIG. 1. A schematic diagram of the excitation-luminescence cycles. Three different excitations—from a 1*s* state (absorption coefficient μ_1) to a continuum state, a 1*s* state (μ_2) to a bound state, and a 2*s* (μ_3) to a continuum state—give rise to a single luminescence with the respective luminescence yields η_1, η_2, and η_3. The events of an x-ray fluorescence, a *KLL* Auger, electron multiscatterings, a nonradiative decay due to electron-phonon scattering, and radiative transitions are schematically depicted.

SCHEMATIC OF DETECTION SYSTEM AT DIAMOND LIGHT SOURCE (BEAMLINE B18)

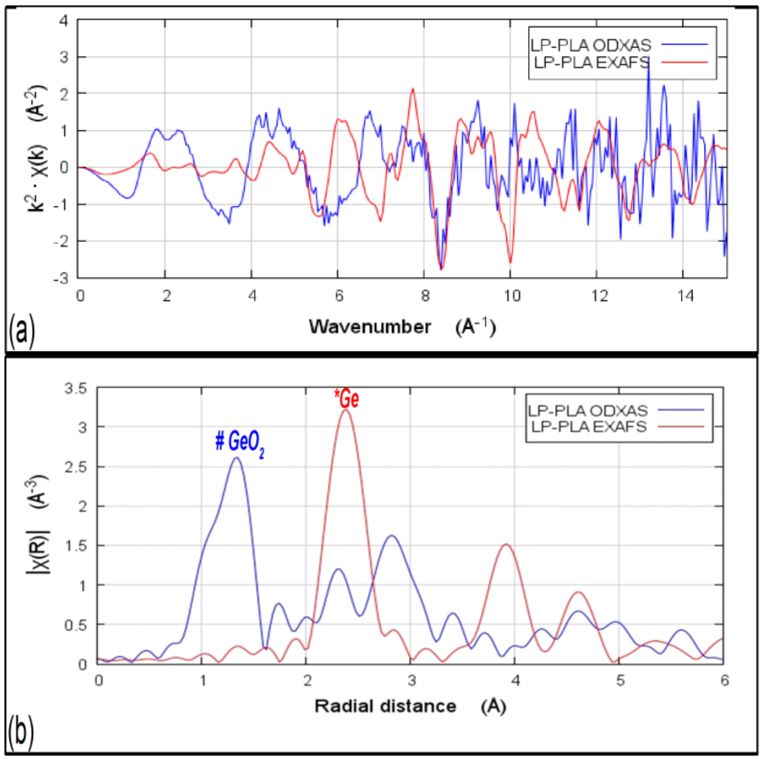




ODXAS and EXAFS

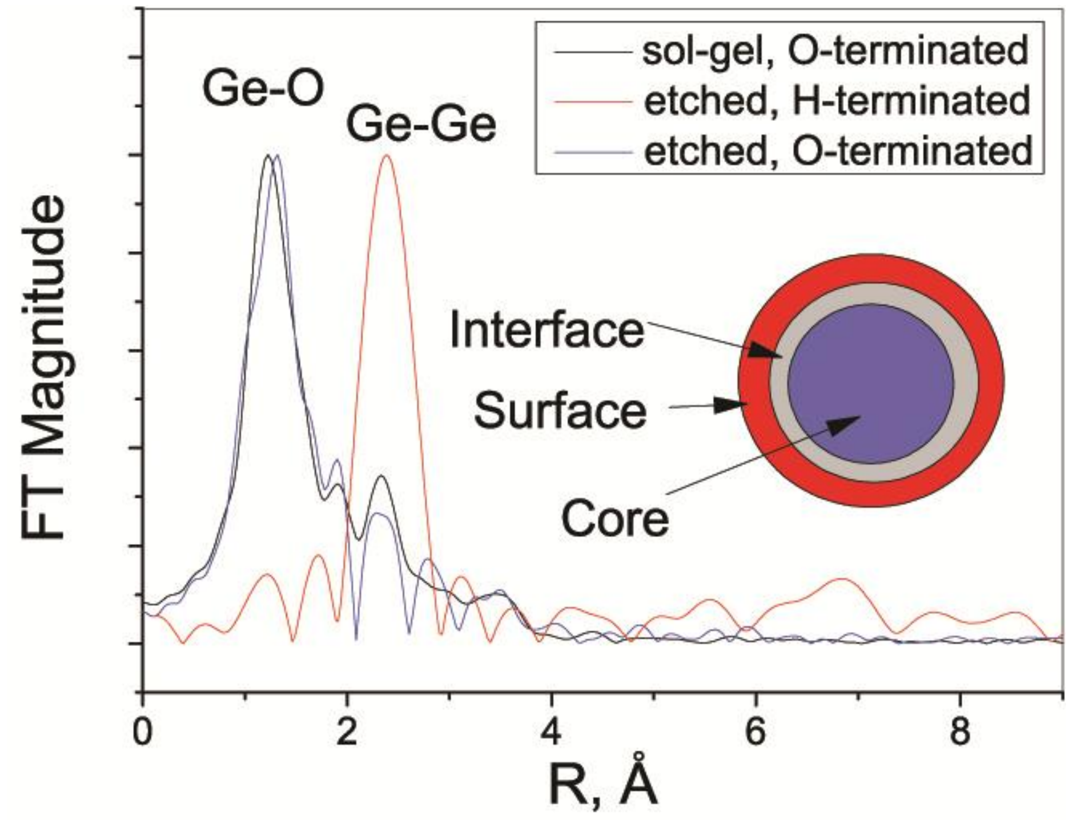


XEOL measurements of the Ge nanoparticles at 100 K.



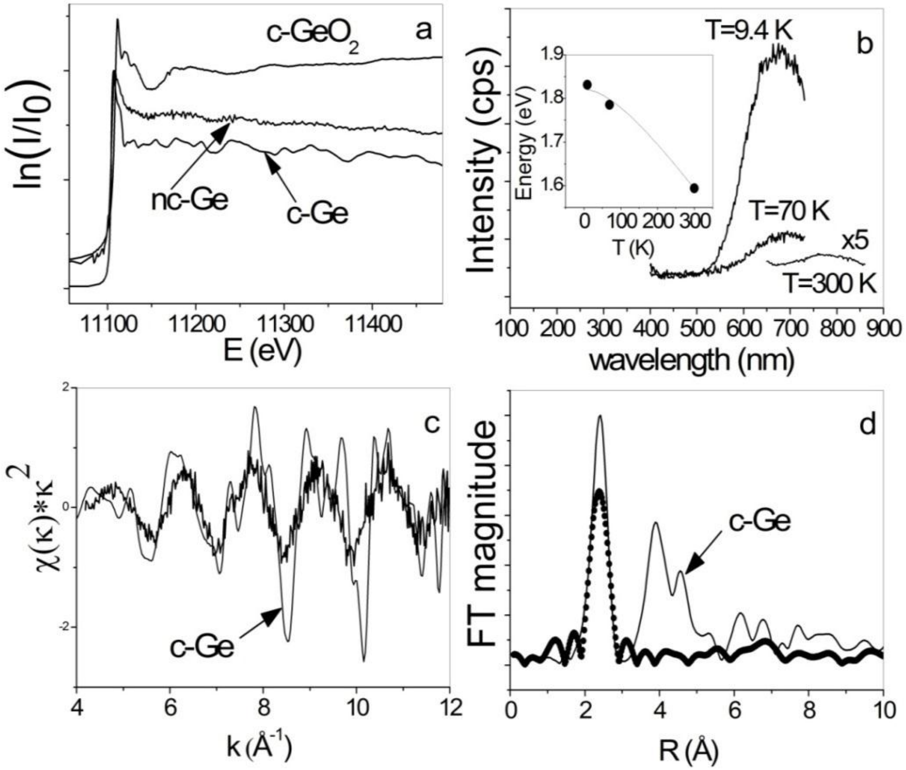
Comparison of OD-XAS and EXAFS of Ge K edge of LP-PLA (a) in k space (b) in R space.

ODXAS and Structure

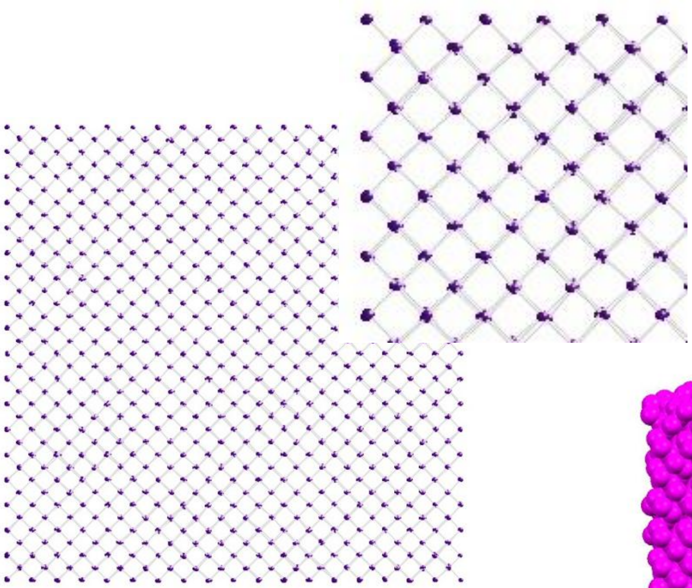


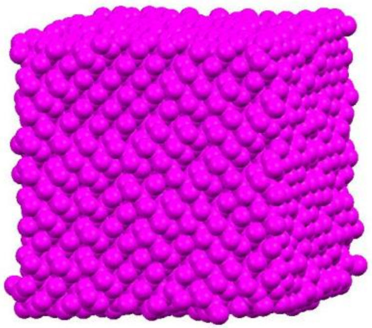
Structure: EXAFS and ODXAS

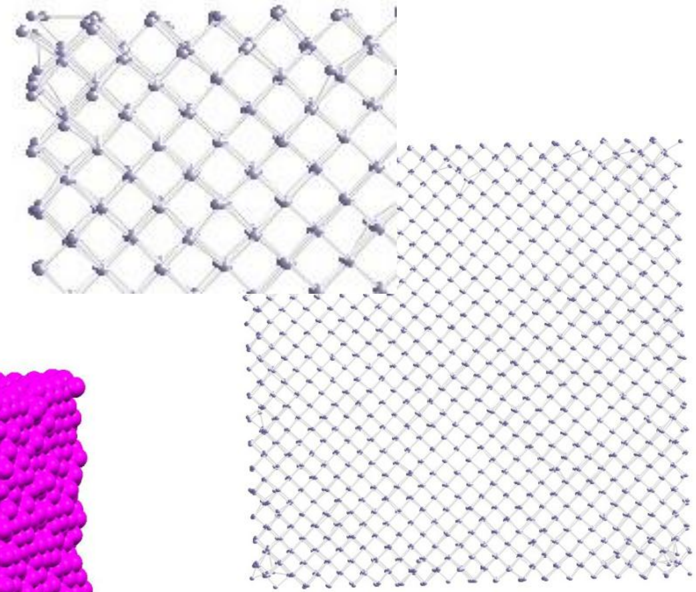
- R = 2.44(1) Å - consistent with the corresponding value for the diamond structure of *c*-Ge
- Debye-Waller factor (mean square relative displacements of atoms) of 0.0044(15) Å^2 (0.0027(2) Å^2 for *c*-Ge at this temperature).
- The coordination number was found to be reduced (2(0.7) against 4 in *c*-Ge).

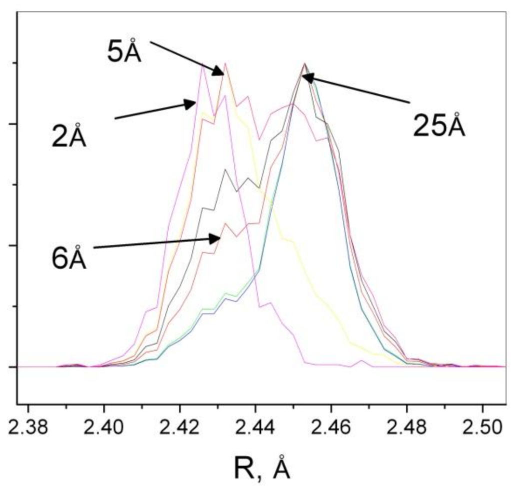


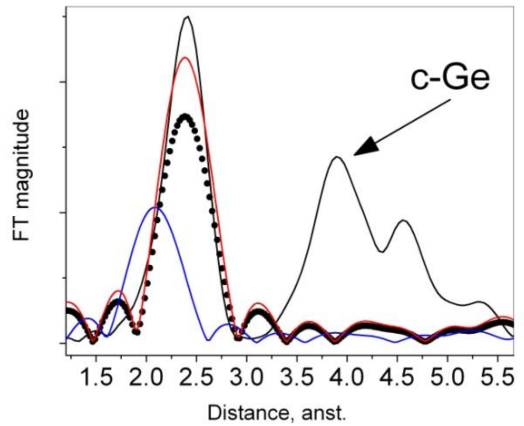
Structure: EXAFS and MD











Conclusion

•Comparison of OD-EXAFS, EXAFS and Raman shows that various sub-structures can be responsible for light emission.

• PL in Ge nanocrystals synthesised by various routes can be of different origin depending on the surface termination.

•We show that for a given nano-particle set OD-EXAFS can show sub-nanoparticle resolution.

Future work

- Surface/strain effects in PL and Raman.
- Improving photon yield and controlling peak wavelength.
- Blinking.
- In-vitro bio-stability and toxicity
- Magnetic semiconductor nanoparticles