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:

$$d = \frac{\lambda}{2NA}$$

Solutions - super-resolution: fluorescent super-resolution

SSIM, STED, PALM, STORM
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

- QPALM
- SOFI
- RainSTORM
- DirectSTORM
- DeconSTORM
- Com-STORM
# Cell imaging → Algorithm comparison

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>Description</th>
<th>Resolution</th>
<th>Data test (Image size)</th>
<th>Data test (Time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QPALM</td>
<td>ImageJ plugin</td>
<td>40nm</td>
<td>64<em>64</em>500</td>
<td>1 minute</td>
</tr>
<tr>
<td>SOFI</td>
<td>Matlab</td>
<td>20nm</td>
<td>64<em>64</em>500</td>
<td>1.5 minutes</td>
</tr>
<tr>
<td>Rain-STORM</td>
<td>Matlab</td>
<td>Pixel size</td>
<td>64<em>64</em>500</td>
<td>1.5 minutes</td>
</tr>
<tr>
<td>Direct-STORM</td>
<td>C</td>
<td>20nm</td>
<td>64<em>64</em>500</td>
<td>7 minutes</td>
</tr>
<tr>
<td>Decon-STORM</td>
<td>Matlab</td>
<td>&lt;50nm</td>
<td>64<em>64</em>500</td>
<td>20 minutes</td>
</tr>
<tr>
<td>Compress-STORM</td>
<td>Matlab</td>
<td>&lt;40nm</td>
<td>64<em>64</em>500</td>
<td>&gt;3 hours</td>
</tr>
</tbody>
</table>
Cell imaging

Fluorophores: why use Qdots

Dyes

- Improved optical characteristics
- Blinking
- Optically stable
- Biocompatibility

Qdots

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

- Morphological super-resolution imaging
- Cell signal imaging

CdSe

nc-Si
Si vs Ge

300 K

$E_x = 1.12 \text{ eV}$

$E_f = 2.0 \text{ eV}$

$E_g = 1.2 \text{ eV}$

$E_{ph} = 0.044 \text{ eV}$

$E_{c+} = 3.4 \text{ eV}$

$E_{c-} = 4.2 \text{ eV}$

300 K

$E_x = 0.66 \text{ eV}$

$E_f = 1.2 \text{ eV}$

$E_{ph} = 0.8 \text{ eV}$

$E_{c+} = 3.22 \text{ eV}$

$\Delta E = 0.85 \text{ eV}$

$E_{so} = 0.29 \text{ eV}$
Sample Preparation

(a) Stain Etching

HF: H₃PO₄: H₂O₂

(a) Ge nanocrystals: H-terminated
t=3h

(b) LP-PLA

Nd:Yag Laser

λ = 355 nm
E = 108 mJ

Quartz cuvette which contains Ge powder in liquid hexane
t=7h

Ge nanocrystals: Oxide-terminated

(c) Sol-gel synthesis

Step 1: Preparation of Gel (GeO₂SiO₂ Gel)
t=48h

- TEOG and TEOS is used as precursor
- Ethanol, HCl solution

Step 2: Heating Treatment in air GeO₂SiO₂
t=48h

- It is dried via heating treatment and converted into powder.

Step 3: Heating Treatment in H₂Ar gas medium t=3h

Ge NCs embedded in Silica are obtained after this process.
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

![Graphs showing Raman and Photoluminescence spectra.](image-url)
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:

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

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.

$$|C(0,q)|^2 = e^{-\frac{q^2r^2L^2}{4}}$$
## Size analysis results

<table>
<thead>
<tr>
<th>Method</th>
<th>Technique</th>
<th>Transmission Electron Microscopy (nm)</th>
<th>Raman Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Stain Etching</td>
<td></td>
<td>10 ± 4</td>
<td>6.9</td>
</tr>
<tr>
<td>(b) LP-PLA</td>
<td></td>
<td>41 ± 22</td>
<td>6.2</td>
</tr>
<tr>
<td>(c) Sol-Gel Method</td>
<td></td>
<td>10 ± 6</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Structure of nanoGe

1. Electron production
   Electrons are generated in the same way as in a television tube. Subsequently, they are pre-accelerated by electric fields in a Linear Accelerator.

2. Acceleration
   In a Booster Ring the electrons are further accelerated with the aid of powerful magnets (20,000 times greater than the magnetic field of the Earth) and electric fields, until they reach velocities greater than 99.999% of the speed of light.

3. Storage
   The electrons are then injected into a Storage Ring, where they are maintained in a circular orbit by strong magnetic fields. Velocity is kept constant by compensating for the energy lost as light emission with electric fields from a radio-frequency source.

4. Beam-lines
   Synchrotron Light is propagated through a Beam-line, placed tangentially to the ring. There are two types of beam-line, depending on whether Insertion Devices or Bending Magnets are used for light production.

5. Light condition
   In an optical "hutch" one selects certain wavelengths, i.e., a small portion of the entire electromagnetic spectrum, by means of a monochromator. These photons are transported and focused onto the sample by, for example, bent X-ray mirrors.

Data reduction and analysis
   In the central "hutch" the experimental setup and data collection is under computer control. Data are extracted, reduced, processed and prepared for analysis and/or storage.
FIG. 1. A schematic diagram of the excitation-luminescence cycles. Three different excitations—from a 1s state (absorption coefficient \( \mu_1 \)) to a continuum state, a 1s state (\( \mu_2 \)) to a bound state, and a 2s (\( \mu_3 \)) to a continuum state—give rise to a single luminescence with the respective luminescence yields \( \eta_1 \), \( \eta_2 \), and \( \eta_3 \). 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.
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

FT Magnitude

Ge-O
Ge-Ge

Interface
Surface
Core

R, Å

sol-gel, O-terminated
etched, H-terminated
etched, O-terminated
• $R = 2.44(1) \text{ Å}$ - 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) Å² (0.0027(2) Å² 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