Nanostructured Ge – physics and bio-applications

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Acknowledgments

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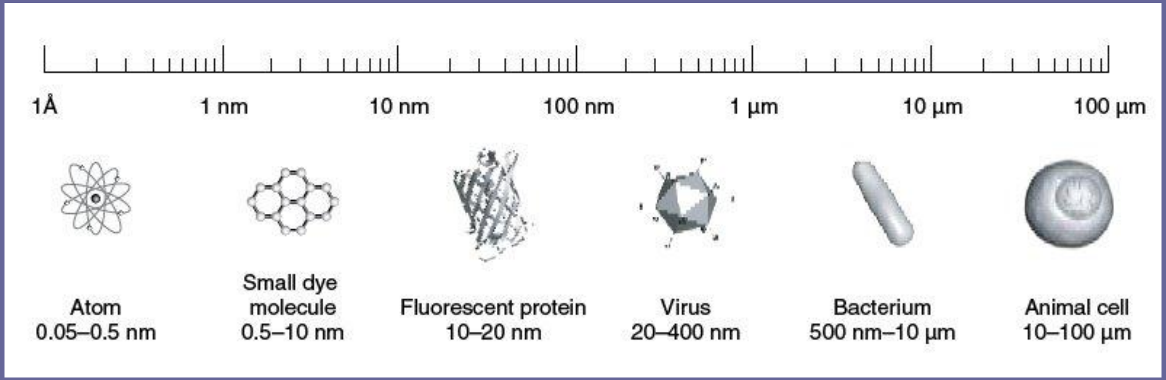
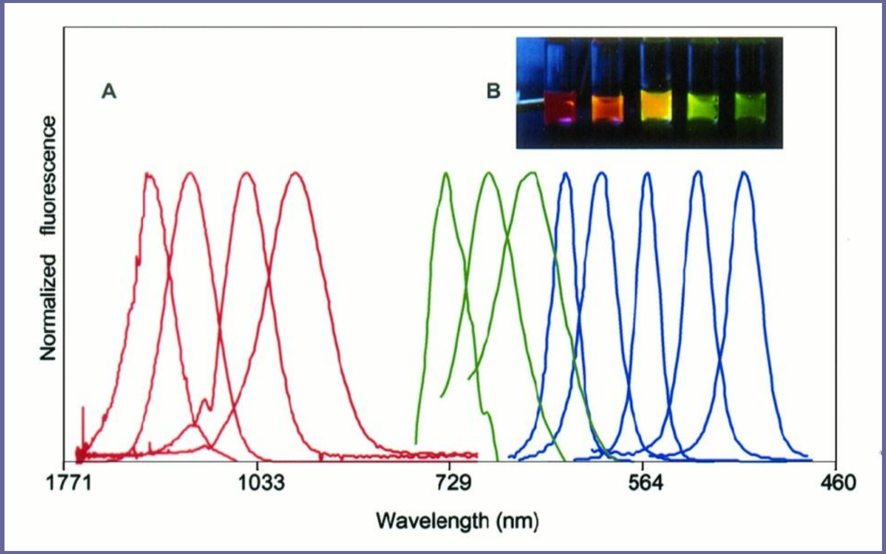
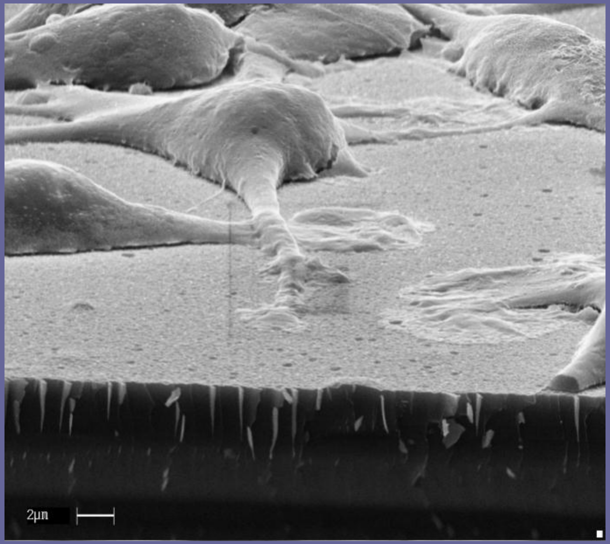
Motivation

Nanos in cell research:

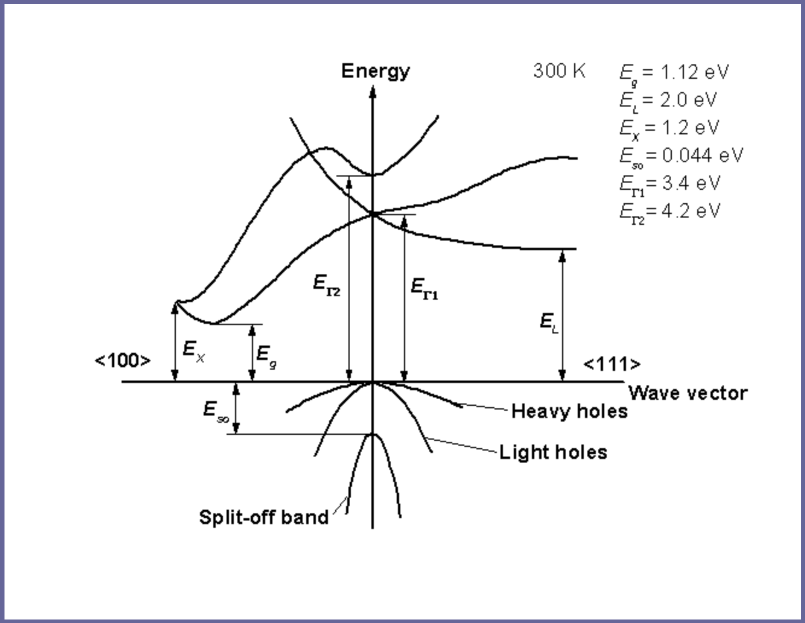
- Morphological imaging
- Passive substrate
- Active material

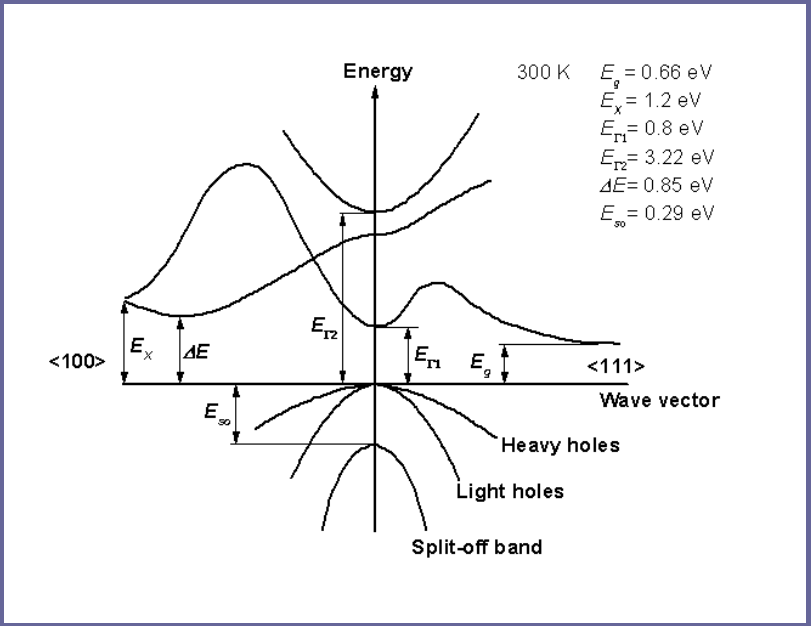






Si vs Ge


Energy
300 K
E_g = 1.12 eV
E_L = 2.0 eV
E_X = 1.2 eV
E_{so} = 0.044 eV
$E_{\Gamma1}$ = 3.4 eV
$E_{\Gamma2}$ = 4.2 eV
$E_{\Gamma2}$
$E_{\Gamma1}$
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
$E_{\Gamma1}$ = 0.8 eV
$E_{\Gamma2}$ = 3.22 eV
ΔE = 0.85 eV
E_{so} = 0.29 eV
$E_{\Gamma2}$
E_X
ΔE
$E_{\Gamma1}$
E_g
<100>
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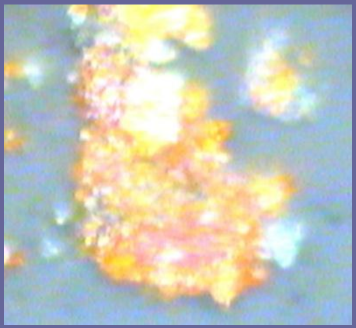
Wave vector
E_{so}
Heavy holes
Light holes
Split-off band

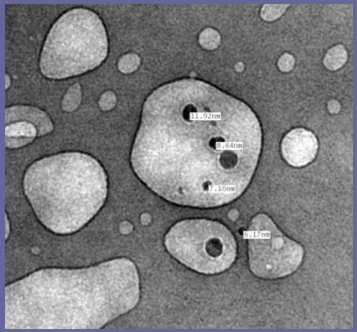
Preparation

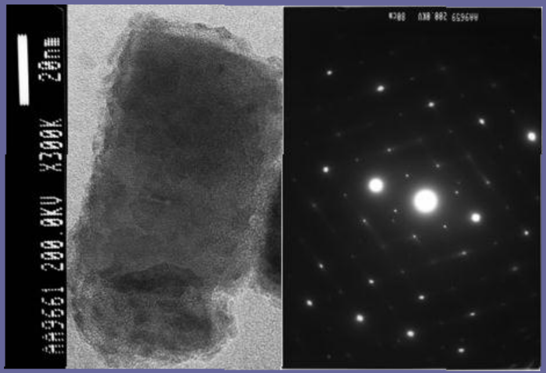
- Etching (HF+NHO3).
- Hole injection is essential for effective etching

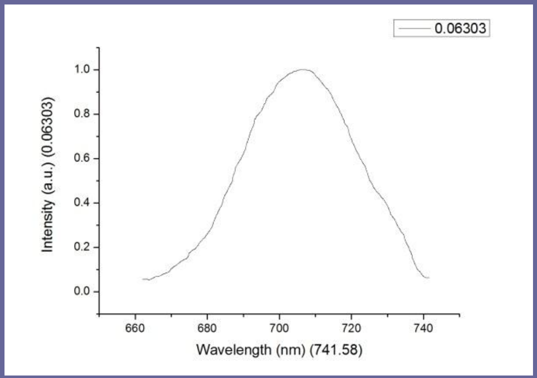
Holes can be injected ether electrically (anodisation) or via altering the chemical composition of etching solution and/or of the surface

Hole injection switches on etching activity



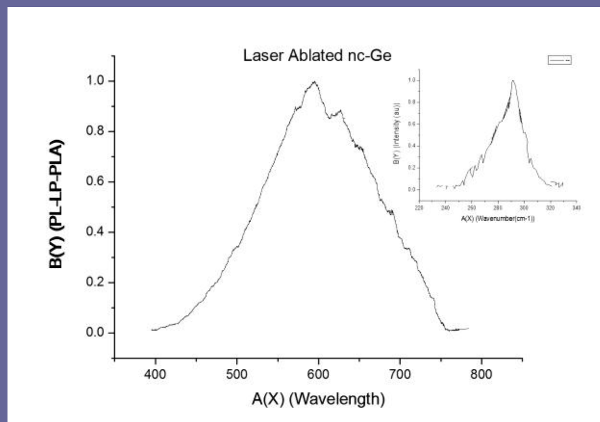


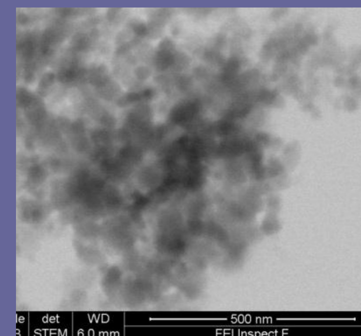




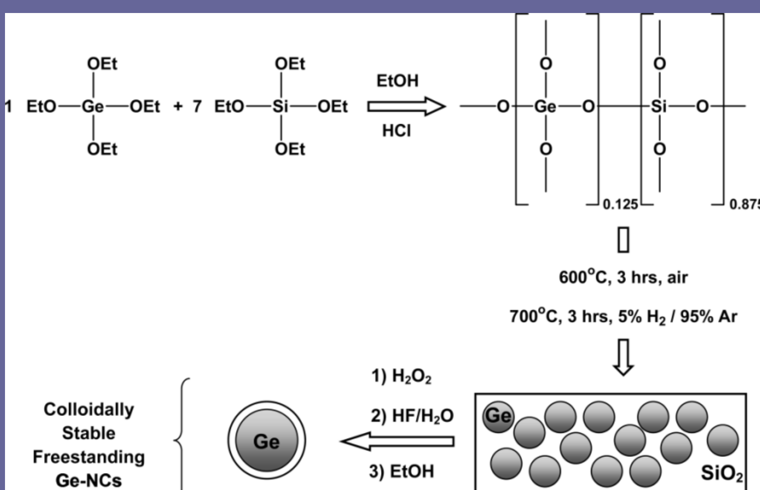
Preparation

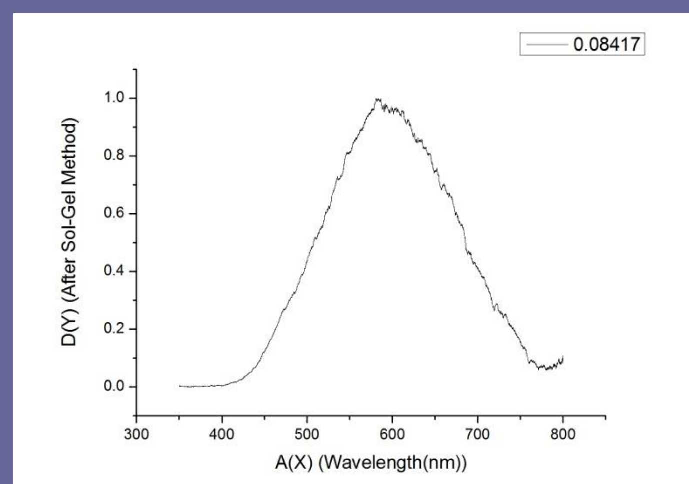
- Laser ablation (nanoGe and nanoSi)





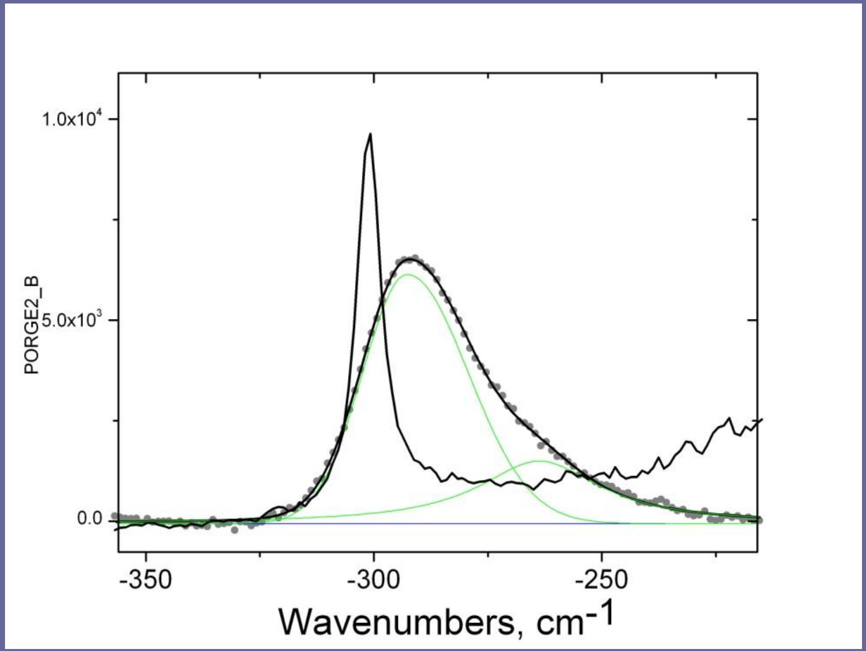
- Sol-gel synthesis (nanoGe: SiO2 capped nano-GeTetraethoxyorthogermanate and tetraethoxyorthosilicate)

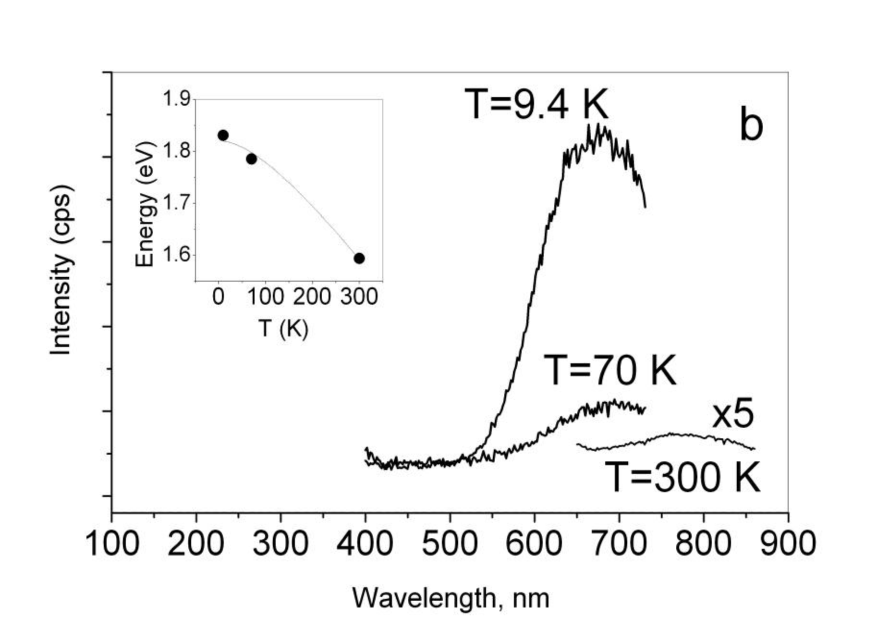




Characterisation

Raman
Photoluminescence
TEM/SEM
X-ray absorption





Quantum confinement

Weak confinement

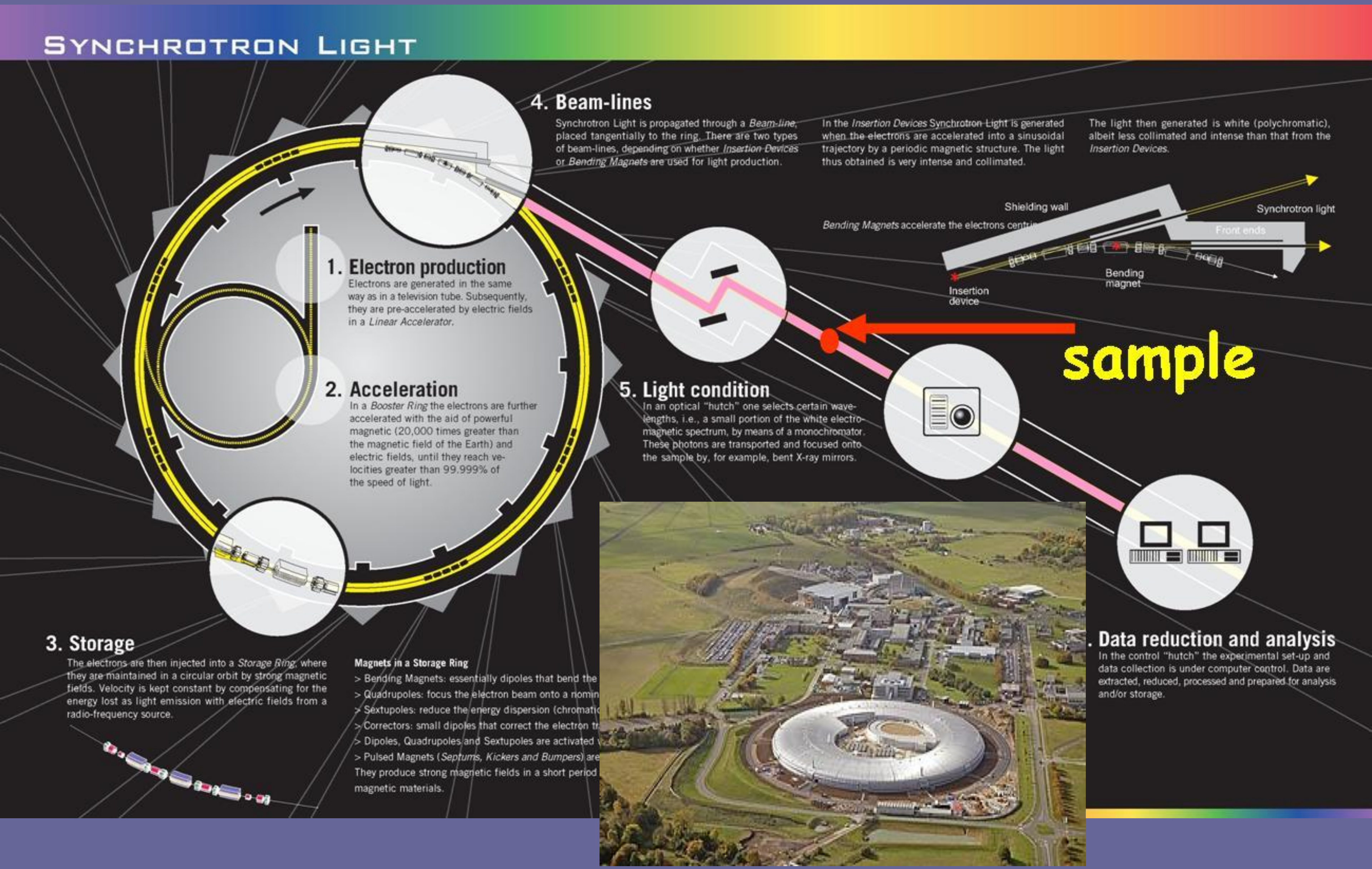
$$H = -\frac{\hbar^2}{2m_e^*}\nabla_e^2 - \frac{\hbar^2}{2m_h^*}\nabla_h^2 - \frac{e^2}{\varepsilon|\mathbf{r}_e - \mathbf{r}_h|}$$

Strong confinement

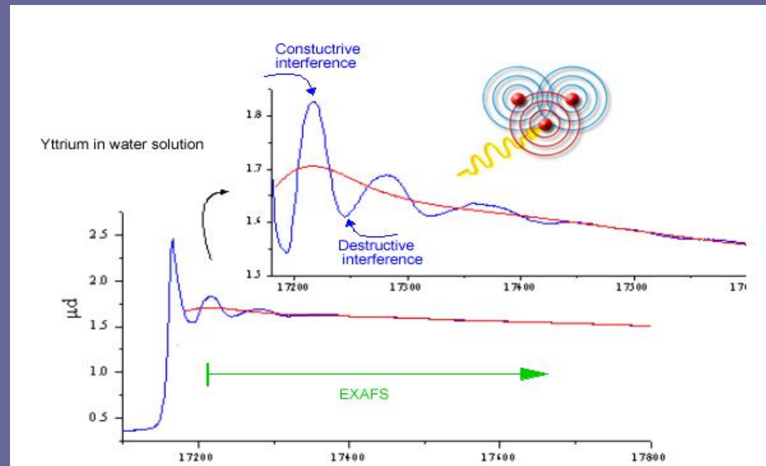
$$H = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\varepsilon|\mathbf{r}_e - \mathbf{r}_h|} + U(r)$$

$$E = E_g + \frac{\pi^2\hbar^2}{2\mu a^2} - 1.786\frac{e^2}{8\pi\varepsilon\varepsilon_0 a}$$

Structure of nanoGe



EXAFS



Debye-Waller term

$\sigma^2 = \sigma_{stat}^2 + \sigma_{vib}^2$

$\sigma < 0.10$ Å

n_X = # of X atoms in shell

amplitude function

phase function

$$\chi = \sum_{shells} \frac{n_X \cdot S_0^2 \cdot f_X(k)\, e^{-2k^2\sigma^2}}{k \cdot r^2} \sin\left(2kr + \alpha_{MX}(k)\right)$$

amplitude reduction factor

r = (average) MX distance

Atomic structure and PL

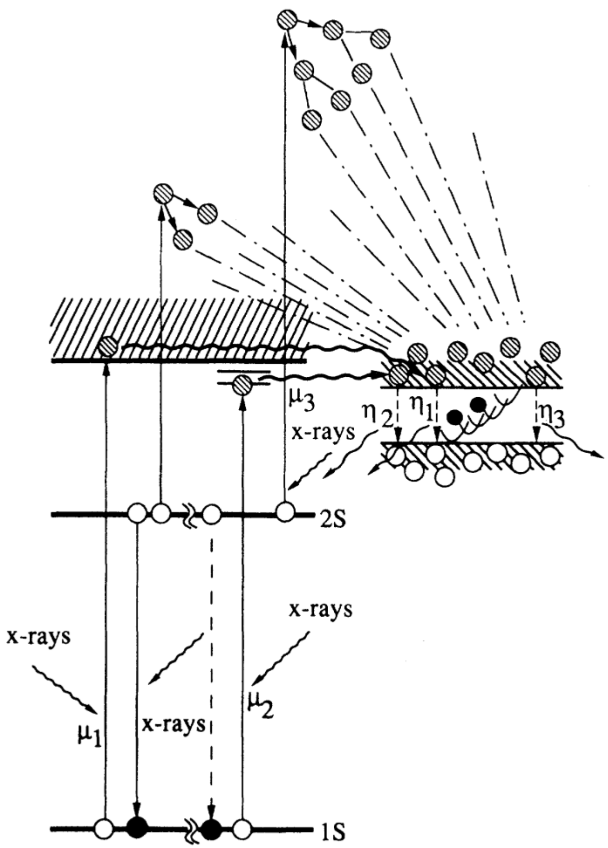
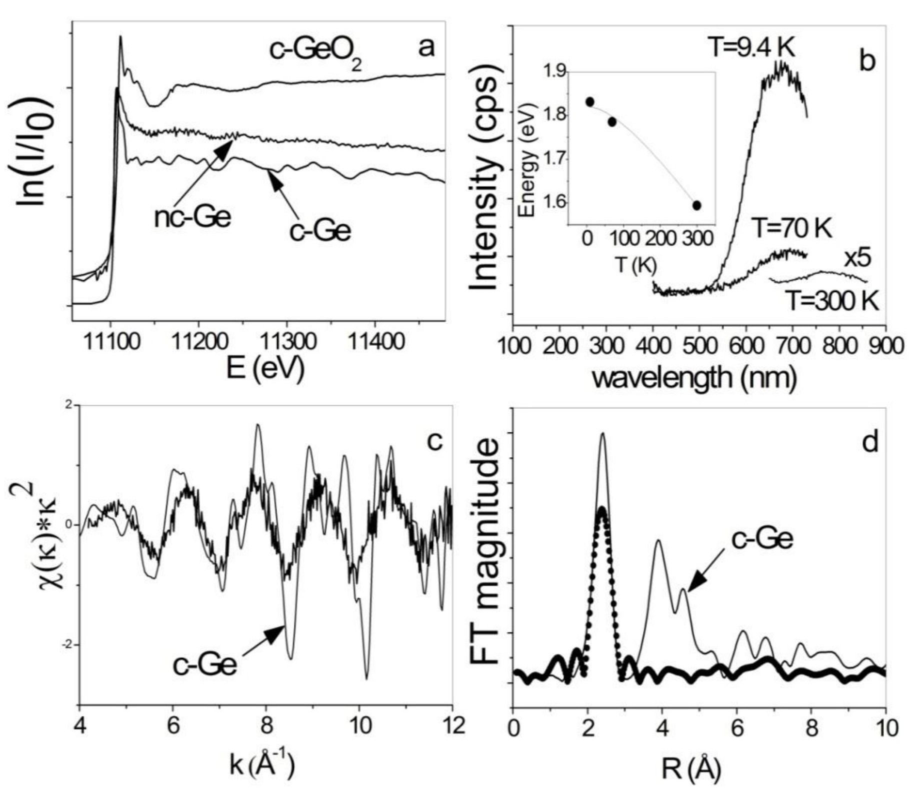
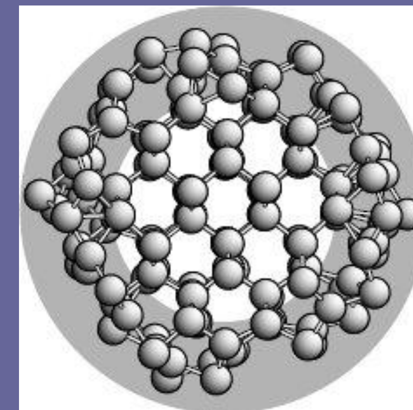


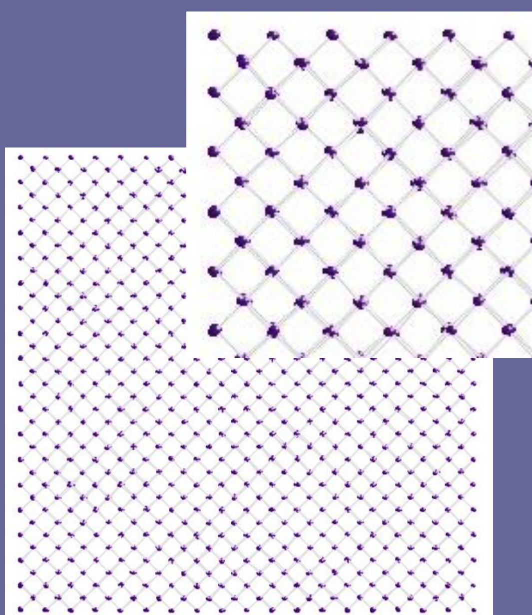
FIG. 1. A schematic diagram of the excitation-luminescence cycles. Three different excitations—from a 1s state (absorption coefficient μ_1) to a continuum state, a 1s state (μ_2) to a bound state, and a 2s (μ_3) to a continuum state—give rise to a single luminescence with the respective luminescence 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.

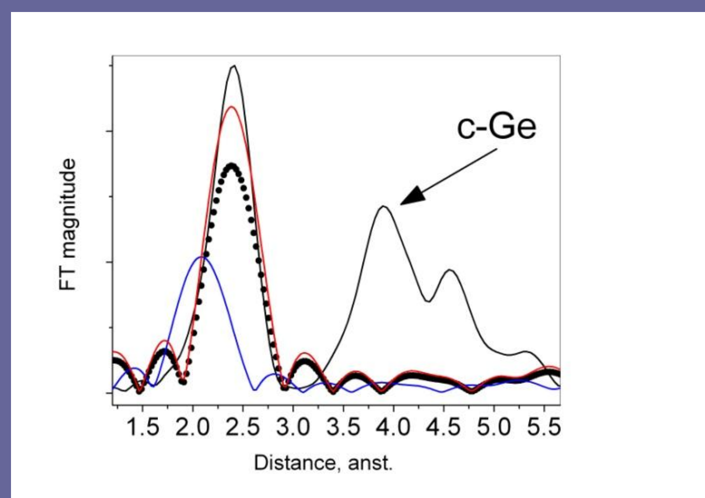


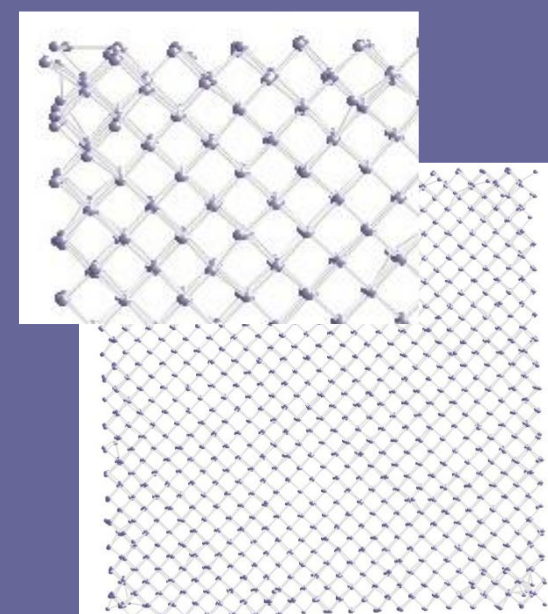
Structure: EXAFS and MD

•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).

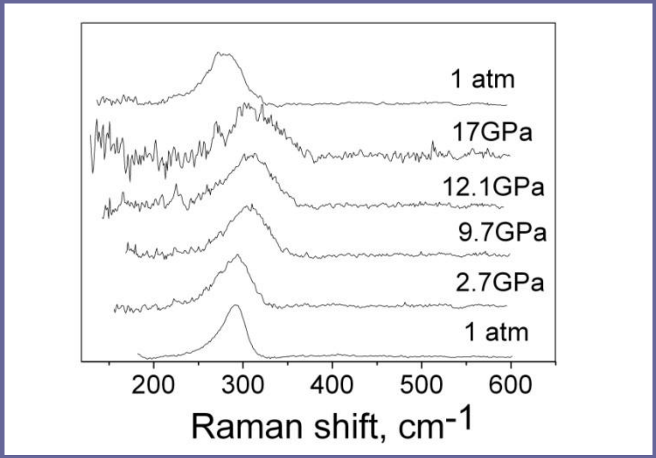


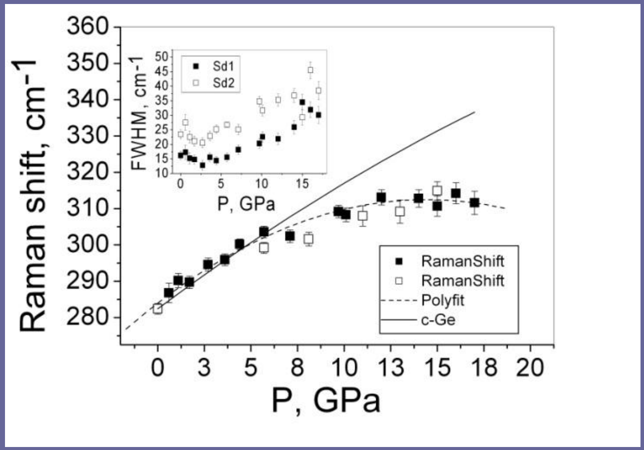


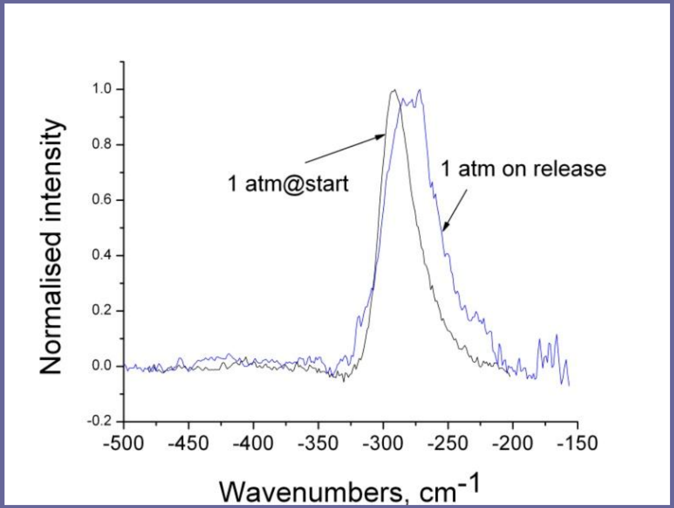




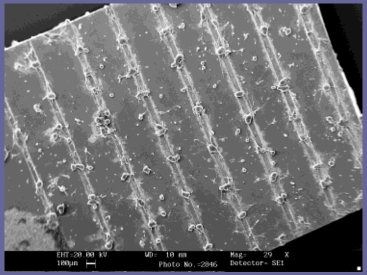
HP Raman

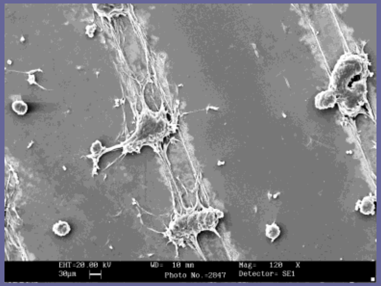

1 atm
17GPa
12.1GPa
9.7GPa
2.7GPa
1 atm
200
300
400
500
600
Raman shift, cm-1

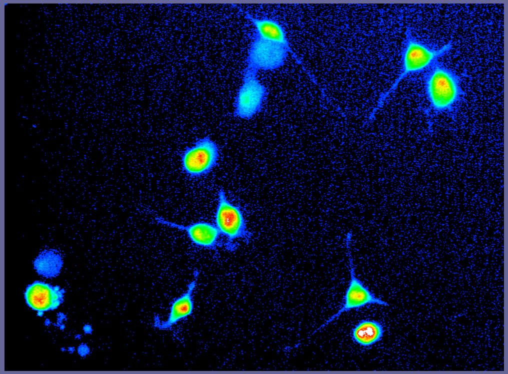

Raman shift, cm-1
P, GPa
FWHM, cm-1
Sd1
Sd2
RamanShift
RamanShift
Polyfit
c-Ge

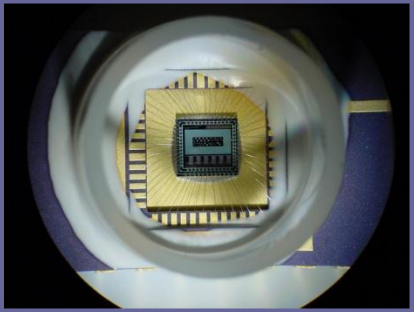

Normalised intensity
Wavenumbers, cm-1
1 atm@start
1 atm on release

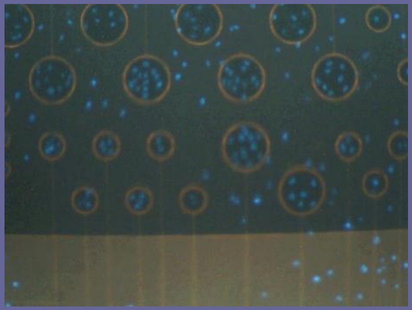
Nanos in Cell Research

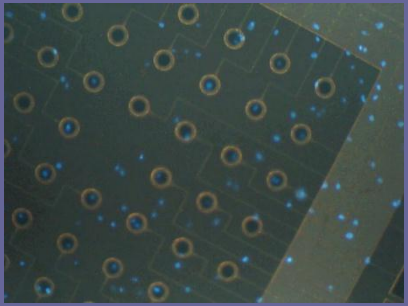


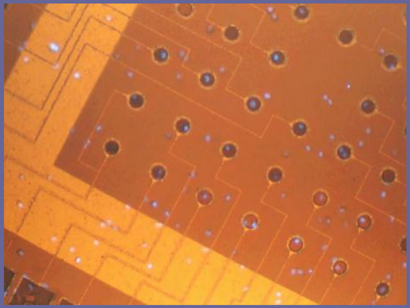




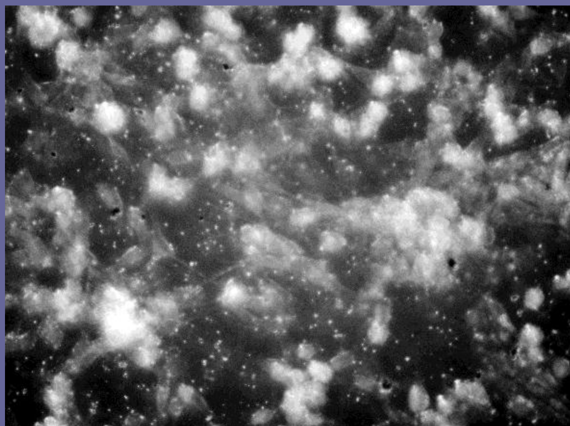


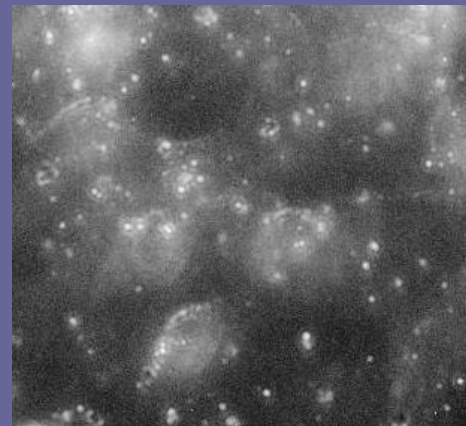


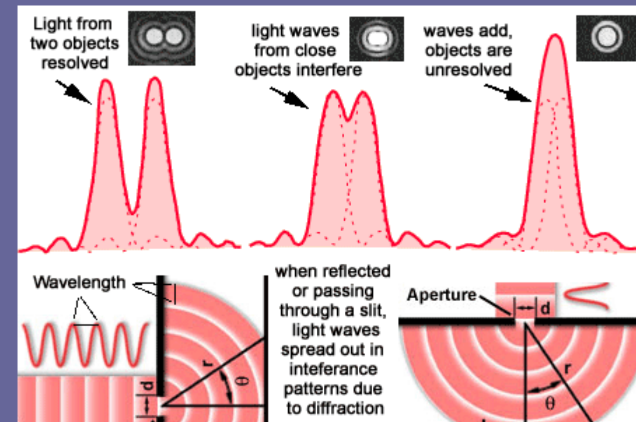


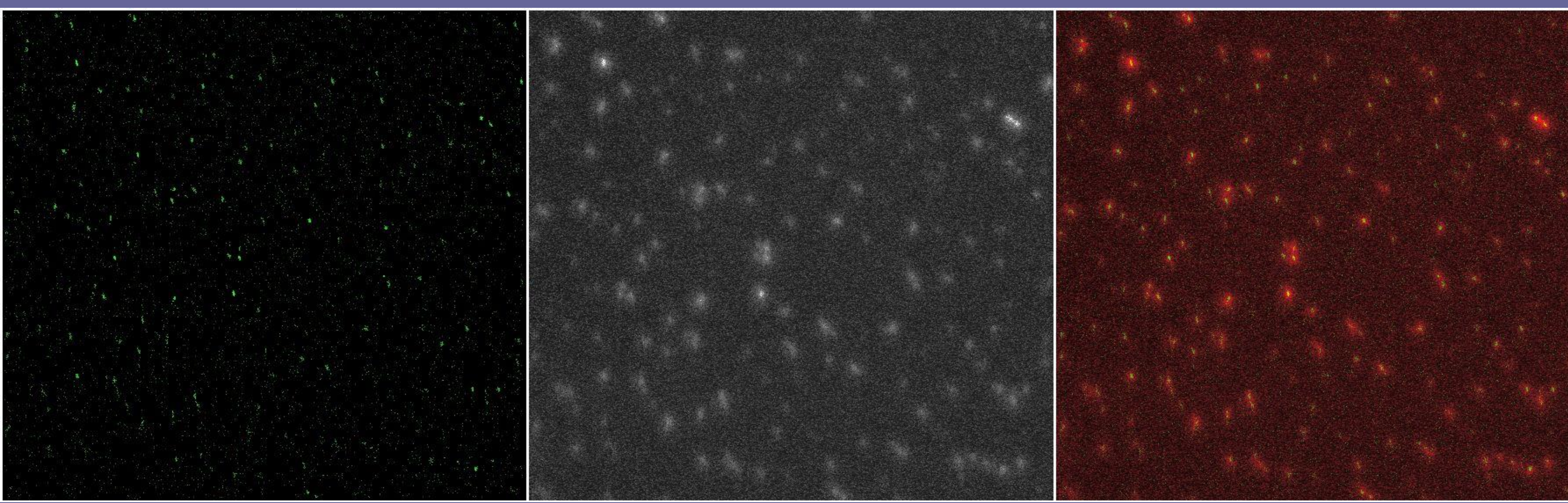


Imaging with nanoSi









Conclusion

- Strong visible luminescence
- Strong nonlinear T-dependent PL – requires detailed band-gap calculations
- Strong nonlinear pressure response – requires detailed atomistic description
- Presence of the topological disorder distinctly different from thermodynamically meta-stable amorphous state

Future work

- Surface effects in PL and Raman
- Resonance effects in excitation
- Blinking
- Magnetic semiconductor nanoparticles