Nanostructured Ge – physics and bio-applications

Andrei V. Sapelkin
Center for Condensed Matter and Materials Physics, School of Physics and Astronomy

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People:
Dr. K. Trachenko, CCMMP, QMUL, UK
Dr. J. Dennis, CCMMP, QMUL, UK
Mr. W. Little, CCMMP, QMUL, UK
Mr. A. Karatutlu, CCMMP, QMUL, UK
Mr. D. Bolmatov, CCMMP, QMUL, UK
Mr. Mingying Song, CCMMP, QMUL, UK
Dr. Ann Wheeler, Blizard Institute, QMUL, UK
Motivation

Nanos in cell research:
- Morphological imaging
- Passive substrate
- Active material
Si vs Ge

300 K

$E_g = 1.12 \text{ eV}$
$E_{1s} = 2.0 \text{ eV}$
$E_{12} = 1.2 \text{ eV}$
$E_{14} = 0.044 \text{ eV}$
$E_{10} = 3.4 \text{ eV}$
$E_{1z} = 4.2 \text{ eV}$

300 K

$E_g = 0.08 \text{ eV}$
$E_{1s} = 1.2 \text{ eV}$
$E_{12} = 0.8 \text{ eV}$
$E_{14} = 3.22 \text{ eV}$
$\Delta E = 0.85 \text{ eV}$
$E_{10} = 0.29 \text{ eV}$
Preparation

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

Holes can be injected either 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

\[ H = -\frac{\hbar^2}{2m_e^*} \nabla_e^2 - \frac{\hbar^2}{2m_h^*} \nabla_h^2 - \frac{e^2}{\varepsilon |r_e - r_h|} \]

Strong confinement

\[ H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{\varepsilon |r_e - r_h|} + U(r) \]

\[ E = E_g + \frac{\pi^2 \hbar^2}{2\mu a^2} - 1.786 \frac{e^2}{8\pi \varepsilon_0 a} \]
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 corresponding 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-lines: depending on whether insertion devices or Bending Magnets are used for light production.

   In the insertion devices Synchrotron Light is generated when the electrons are accelerated into a sinusoidal trajectory by a periodic magnetic structure. The light thus obtained is very intense and collimated.

   The light than generated is white (polychromatic), albeit less collimated and intense than that from the Insertion Devices.

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

3. Data reduction and analysis
   In the control "hutch" the experimental set-up and data collection is under computer control. Data are extracted, reduced, processed and prepared for analysis and/or storage.
EXAFS

\[ \chi = \sum_{\text{shells}} n_X \cdot S_0^2 \cdot \frac{f_X(k)}{k \cdot r^2} \cdot e^{-2k^2\sigma^2} \cdot \sin(2kr + \alpha_{MX}(k)) \]

\[ \sigma^2 = \sigma_{\text{stat}}^2 + \sigma_{\text{vib}}^2 \]

- \( n_X \) = \# of \( X \) atoms in shell
- amplitude function
- Debye-Waller term
- \( \sigma < 0.10 \) Å
- phase function
- \( r \) = (average) MX distance
- amplitude reduction factor
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.
• $R = 2.44(1)$ 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

[Graphs and data plots related to HP Raman spectroscopy are present, showing Raman shift over pressure and wavenumbers over pressure and normalized intensity.]
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