Origin of the photoluminescence in Si nanocrystals

S. Godefroo and V. V. Moshchalkov
INPAC-Institute for Nanoscale Physics and Chemistry, Pulsed Field Group, K.U.Leuven,
Celestijnenlaan 200 D, B-3001 Leuven, Belgium

M. Hayne
Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom

M. Jivanescu and A. Stesmans
INPAC-Institute for Nanoscale Physics and Chemistry, Semiconductor Physics, K.U.Leuven,
Celestijnenlaan 200 D, B-3001 Leuven, Belgium

V. Talalaev and M. Zacharias
Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

Outline

Introduction
- Sample Characterisation
- PL process

Theory
- Quantum Confinement
- Defects

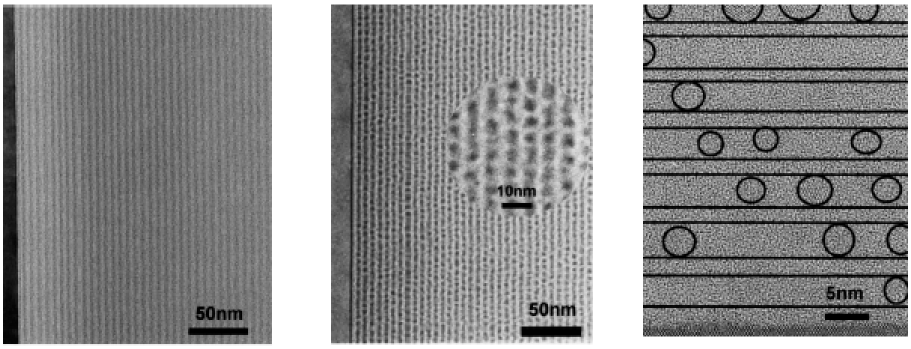
Experiments
- Influence of UV Irradiation on Defects
- Hydrogen Passivation
- Energy Shift in Magnetic Fields

Conclusions

Sample Characterisation

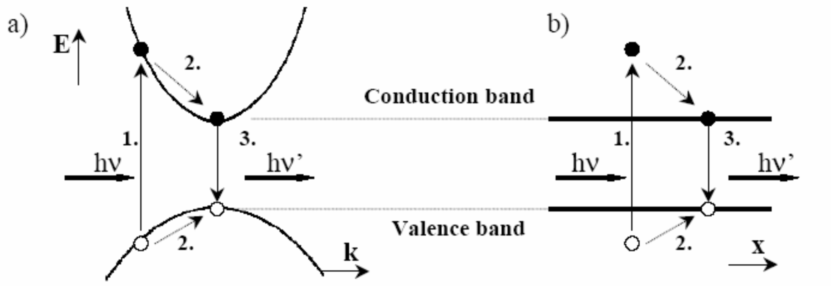
Si nanocrystals in SiO_2

- SiO/SiO_2 superlattice
- annealing @ 1100°C under N_2 atmosphere
    - ⇒ phase separation: $2SiO \rightarrow Si + SiO_2$
- independent control of nc size and denisty
- 45 periods of SiO (2 nm)/ SiO_2 (4 nm), estimated size of Si nc's: 4 nm



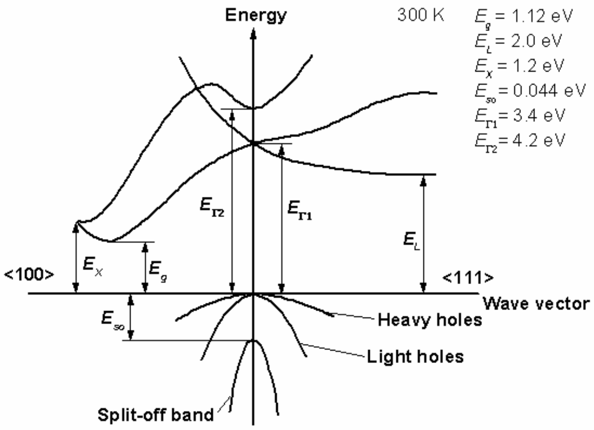
M. Zacharias et al. APL 80 (2002) 661

Photoluminescence Process



1. Excitation
    - Incoming photon creates excited e^- in CB and hole in VB
    - $E_{photon} \geq E_g$
2. Relaxation
    - e^- relaxes to minimum CB, hole to maximum VB
    - non-radiative scattering by phonons
3. Recombination
    - e^- and hole recombine
    - photon is emitted

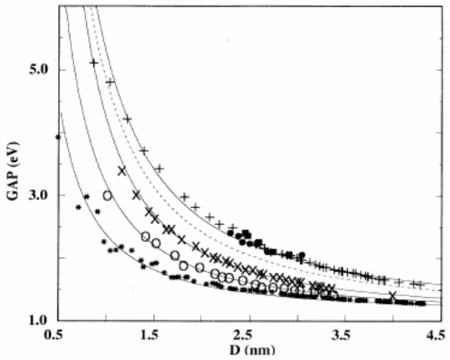
Quantum Confinement



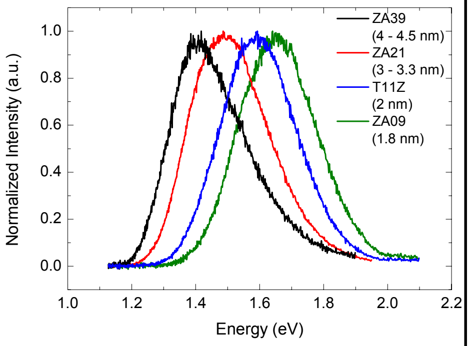
- Si: indirect band gap semiconductor → poor light emitter
- Discovery of room T, visible PL from porous Si in 1990 by Canham *et al*.
  origin of PL: Quantum size effects in small crystallites

Quantum Confinement

- QC: 1) increase band gap of crystallites compared to bulk Si
  → light emission in visible range
  2) breakdown of the k-conservation rule
  → direct optical transitions (no phonons)
- MAIN IDEA: Blue shift energy with decreasing size of Si nc's



C. Delerue et al. PRB 48 (1993) 11024



Defects

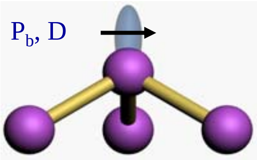
- P_b defects: - three valent Si atom back bonded to 3 Si atoms
  - occurs at Si/SiO_2 interface
  - no angle dependence: stems from Si nc/SiO_2 interface

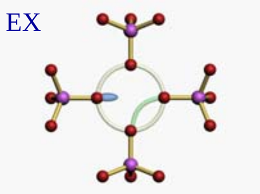
- D line: same defect as P_b but in disordered parts of Si

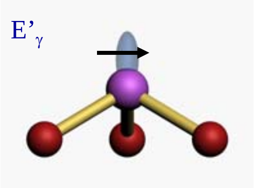
- EX center: delocalized electron shared by Si atoms bordering a vacancy in SiO_2

- E'_γ defect: oxygen vacancy commonly observed in a-SiO_2 bulk and thin films

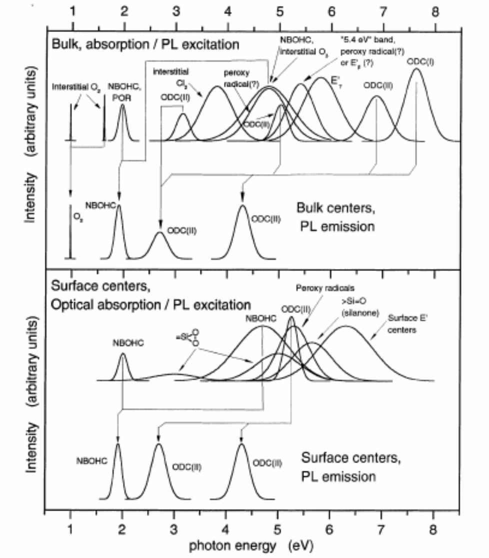
- NBOHC: created together with E' when $O_3 \equiv Si\text{-}O\text{-}Si \equiv O_3$ dissociates in $O_3 \equiv Si\bullet$ and $\bullet O\text{-}Si \equiv O_3$







Defects



L. Skuja et al. J. Non-Cryst. Sol. 239 (1998) 16

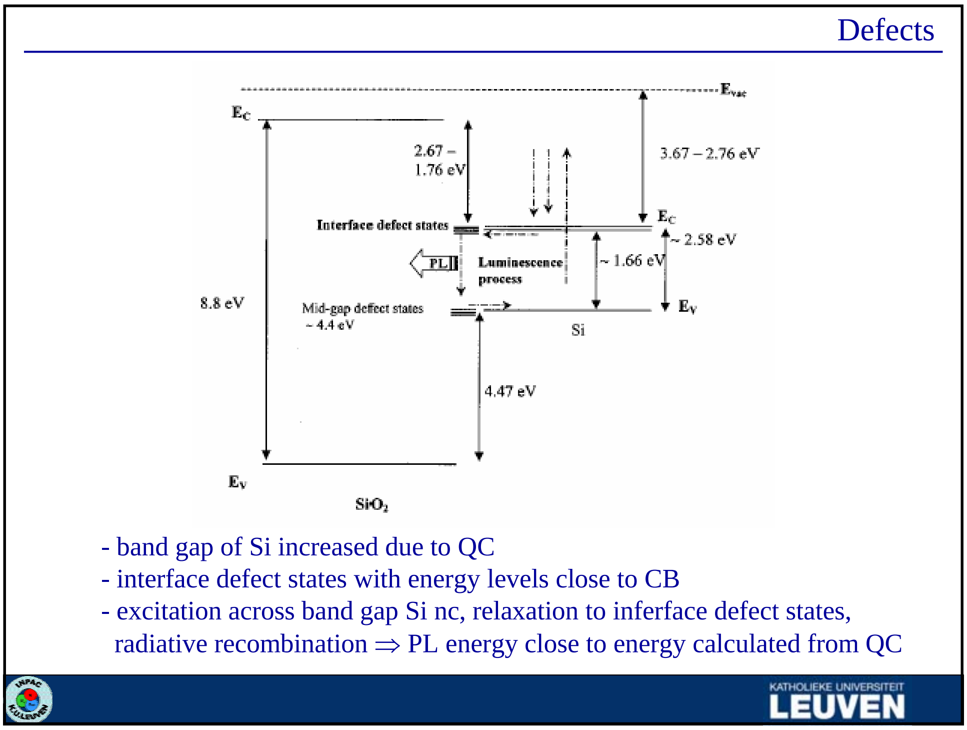
- E': no known PL bands

- NBOHC: PL band at 1.85 – 1.95 eV

- P_b: - non-radiative recombination centers
  - one P_b center at Si nc surface kills PL in 1.4 – 2.2 eV range

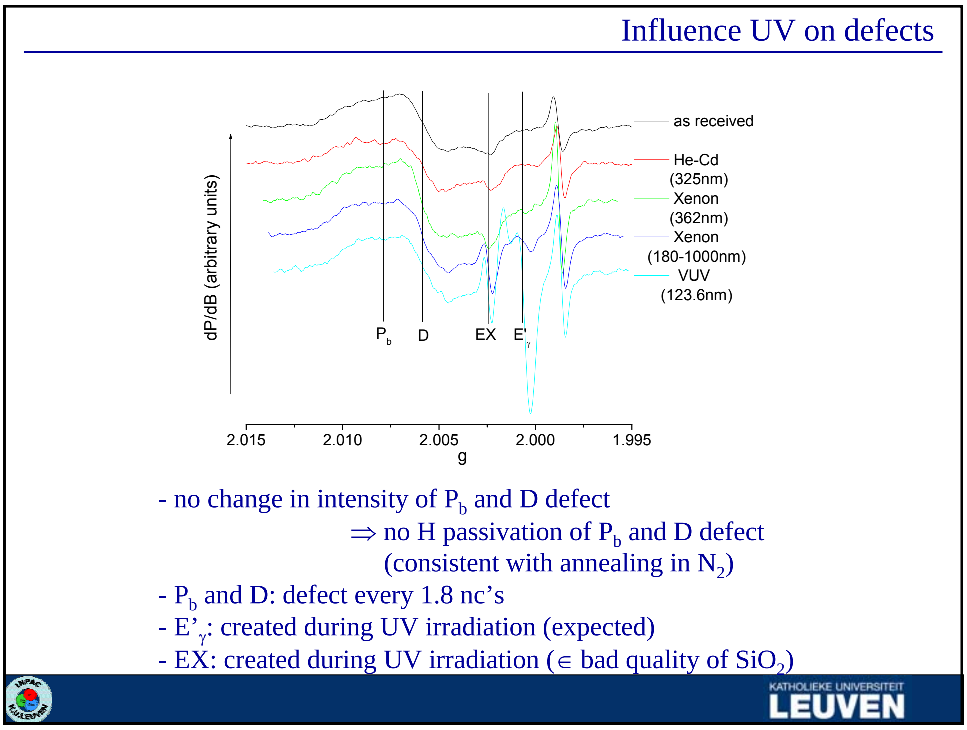
- D: - no known PL bands
  - one D center kills PL

- EX: no known PL bands



Defects

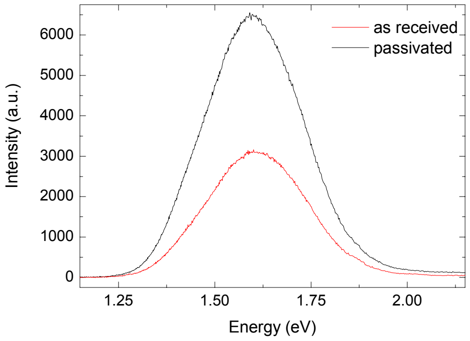
- band gap of Si increased due to QC
- interface defect states with energy levels close to CB
- excitation across band gap Si nc, relaxation to inferface defect states, radiative recombination ⇒ PL energy close to energy calculated from QC



Influence UV on defects

- no change in intensity of P_b and D defect
  ⇒ no H passivation of P_b and D defect (consistent with annealing in N_2)
- P_b and D: defect every 1.8 nc's
- E'_γ: created during UV irradiation (expected)
- EX: created during UV irradiation (∈ bad quality of SiO_2)

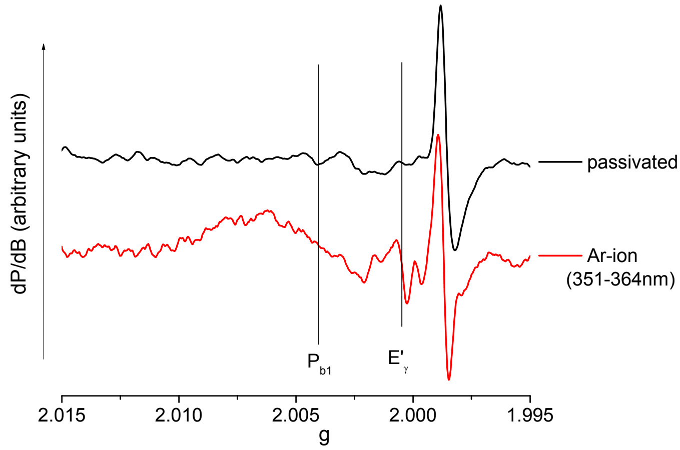
Hydrogen Passivation



After H passivation

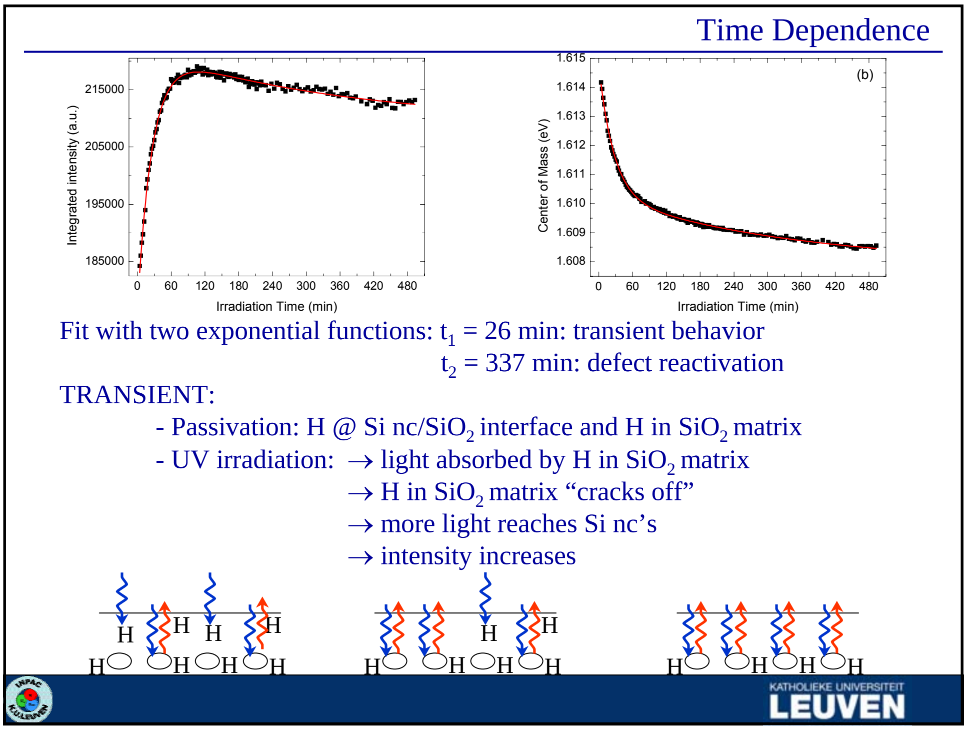
- defects (detectable with ESR) have disappeared
- PL signal is still there
  - → intensity increased (factor 2.1)
    consistent with 1 defect every 1.8 nc’s
  - → small red shift (10 meV)
  - → no change in line width

Time Dependence



- P_b and E'_γ reactivated by UV irradiation
- Intensity factor 6 smaller than for as received sample

⇒ INFLUENCE ON PL?

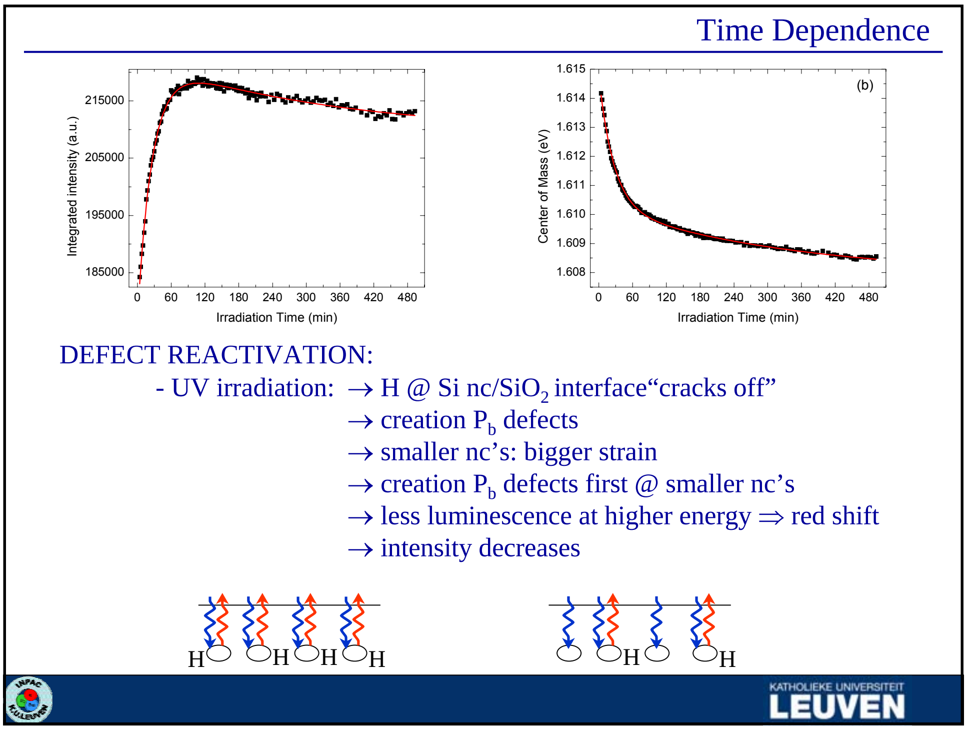


Time Dependence

Fit with two exponential functions: t_1 = 26 min: transient behavior
t_2 = 337 min: defect reactivation

TRANSIENT:

- Passivation: H @ Si nc/SiO_2 interface and H in SiO_2 matrix
- UV irradiation: → light absorbed by H in SiO_2 matrix
  → H in SiO_2 matrix “cracks off”
  → more light reaches Si nc’s
  → intensity increases

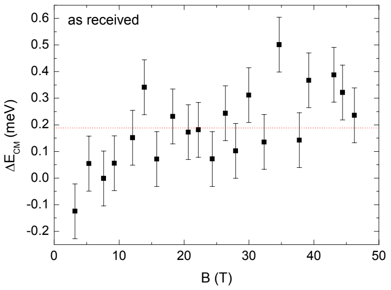


Time Dependence

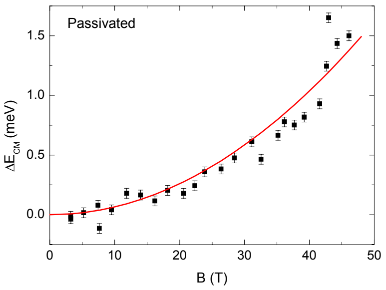
DEFECT REACTIVATION:

- UV irradiation: → H @ Si nc/SiO_2 interface“cracks off”
  → creation P_b defects
  → smaller nc’s: bigger strain
  → creation P_b defects first @ smaller nc’s
  → less luminescence at higher energy ⇒ red shift
  → intensity decreases

Energy Shift in Magnetic Field



- No shift in magnetic field
- Consistent with PL originating from defect states



$$\Delta E = \frac{e^2 < \rho^2 > B^2}{8\mu}$$

Assume $\mu = 0.20\ m_0$

- Diameter = 4.85 ± 0.10 nm
- Compared to estimated size of 4 nm
- Si nc borders are not well defined
- Wave functions of e^- and h^+ can spill out of nc

PROVES QC AS ORIGIN OF PL!

Conclusions

- PL in as received sample is originating from radiative recombination at interface defect states with PL energy close to the one calculated for QC

- PL in passivated sample is originating from QC