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Raman and SHG spectroscopy of ligand-stabilized Si nanocrystals

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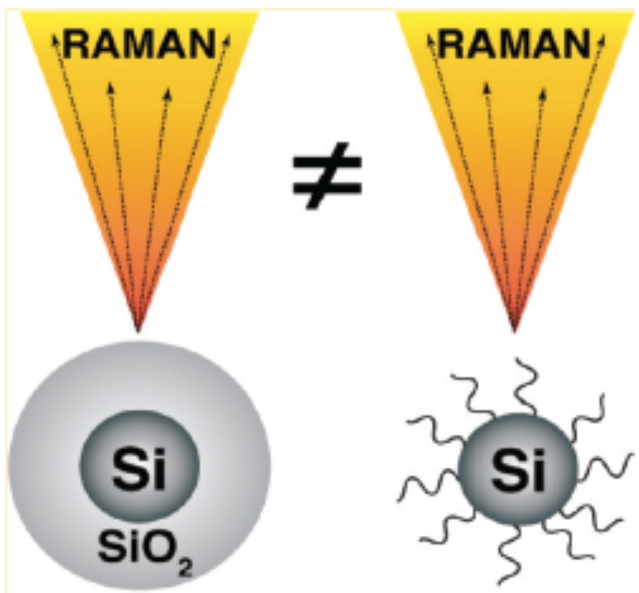
Most previous spectroscopy:

- Si NCs embedded in host matrix
- physical implantation methods
- NC size challenging to measure & widely dispersed (± 50%)
- NC interface complicated by:
  - stress
  - unusual bond structures
- spectra challenging to model theoretically

Our previous SHG/Raman/PLE/SE work:
Wei, *Phys. Rev. B* **84**, 165316 (2011)
JVST B **29**, 04D112 (2011)



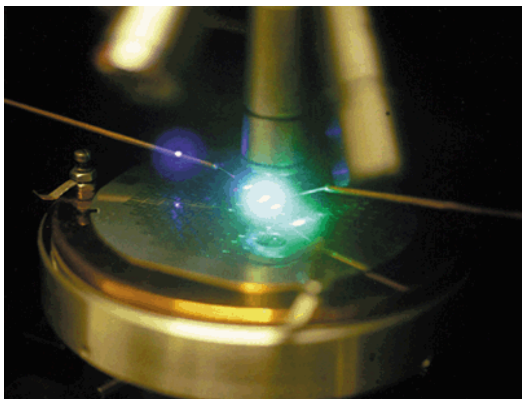
This work:

- **free-standing AND embedded Si NCs from common benchtop chemical synthesis**
- **accurate size measurement** (TEM, XS); **~monodisperse** (± 15%) **wide controlled size range** (3 - 100 nm)
- **stress/oxide-free Si NCs**
- **spectra more amenable to 1st principles theoretical analysis,** e.g. quantum confinement, interface effects distinguishable

Hessel *et al*., *J. Chem. Phys. Lett*. **3**, 1089 (2012)

Si nanocrystals have properties & applications different from those of bulk Si

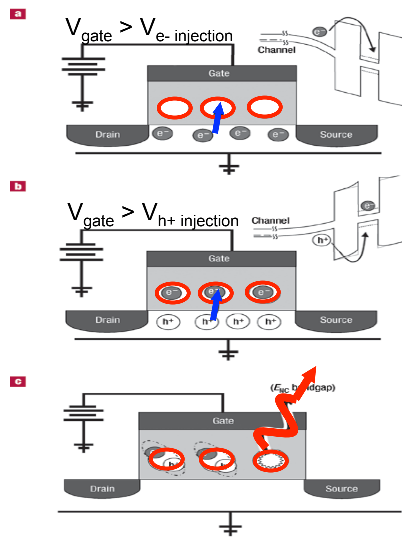
Si lasers?



Observation of optical gain in Si nanocrystals embedded in SiO_2

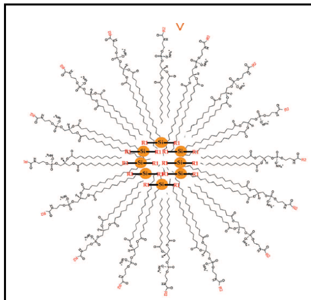
Pavesi et al., Nature 408, 440 (2000)

Field-effect LEDs

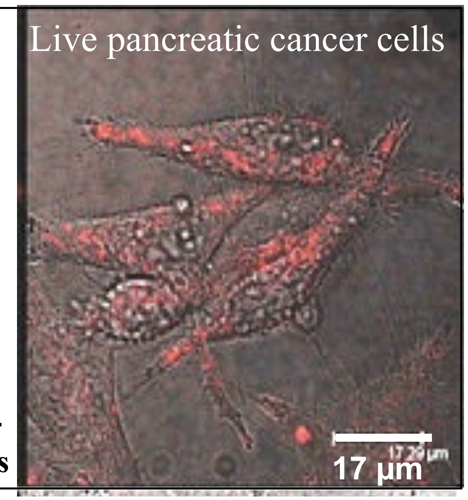


Walters *et al*, *Nature Mat.* **4**,143 (2005).

In vivo bio-sensing



amine-terminated micelle-encapsulated Si NC, a **non-toxic** alternative to CdSe NCs



Erogbogbo et al, ACS Nano.2, 873 (2008)

These interesting properties originate from a combination of quantum confinement and Si NC/SiO_2 interfaces.

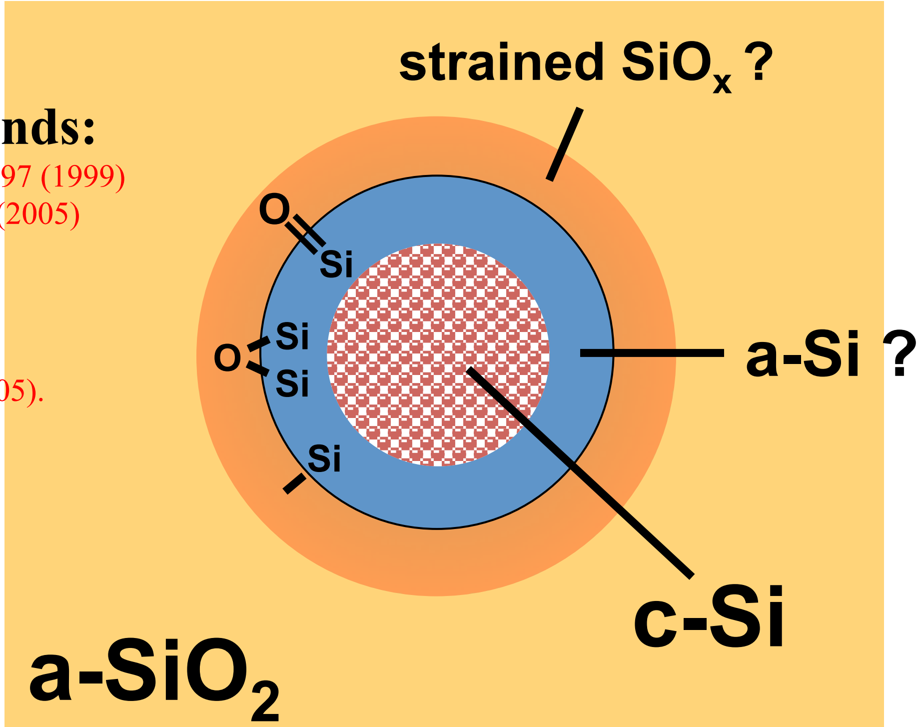
Their complex nano-interfaces make oxide-embedded Si NCs challenging to model & characterize

Transition layer(s):
Daldosso *et al.*, Phys. Rev. B **68**, (2003)

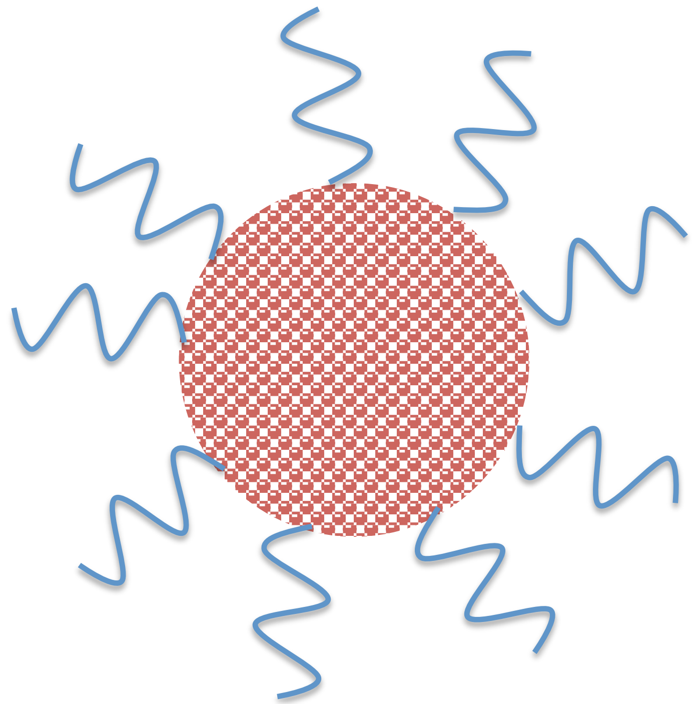
Radiative double bonds:
Wolkin *et al.*, Phys. Rev. Lett. **82**, 197 (1999)
Luppi & Ossicini, Phys. Rev. B **71** (2005)

Bridge bonds:
Sa'ar et al., Nano Lett. **5**, 2443 (2005).

Undercoordinated Si atoms, dangling bonds
Khoo, *PRL* **105**, 115504 (2010)



Free-standing ligand-stabilized NCs are much simpler

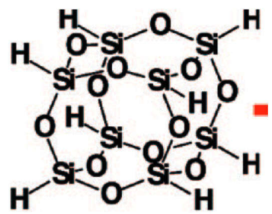


- Their spectra are more easily related to first principles theory
- Free-standing and oxide-embedded NCs can be synthesized from a common synthetic procedure

Benchtop chemical synthesis yields copious mono-disperse Si NCs of controlled size w/ or w/o oxide

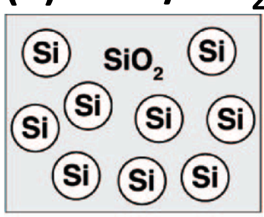
commercial "flowable oxide"

(1) Hydrogen silsesquioxane (HSQ: $H_8Si_8O_{12}$)



1100 - 1400 C
4% H_2/96% N_2
Δ
(1 hour)

(2) nc-Si/SiO_2



2 < d_{NC} < 100 nm

SAMPLE SERIES #1

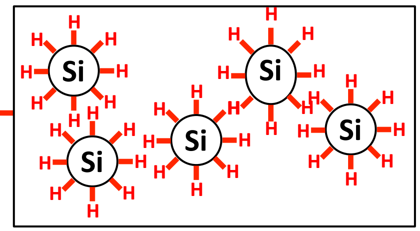
Etch oxide in 6:1 HF/HCl

eliminates background sub-nm a-Si clusters

macro-scopic yields

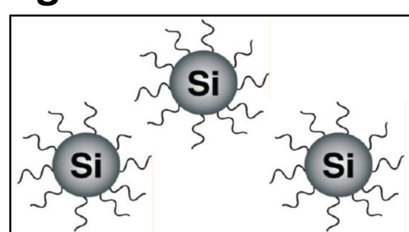
Hessel, *Chem. Mater.* **18**, 6139 (2006)
Gupta, *Adv. Funct. Mater.* **19**, 696 (2009)

(3) H-terminated oxide-free Si NCs



thermal hydrosilylation in 4:1 dodecene/ octadecene

(4) ligand-stabilized Si NCs

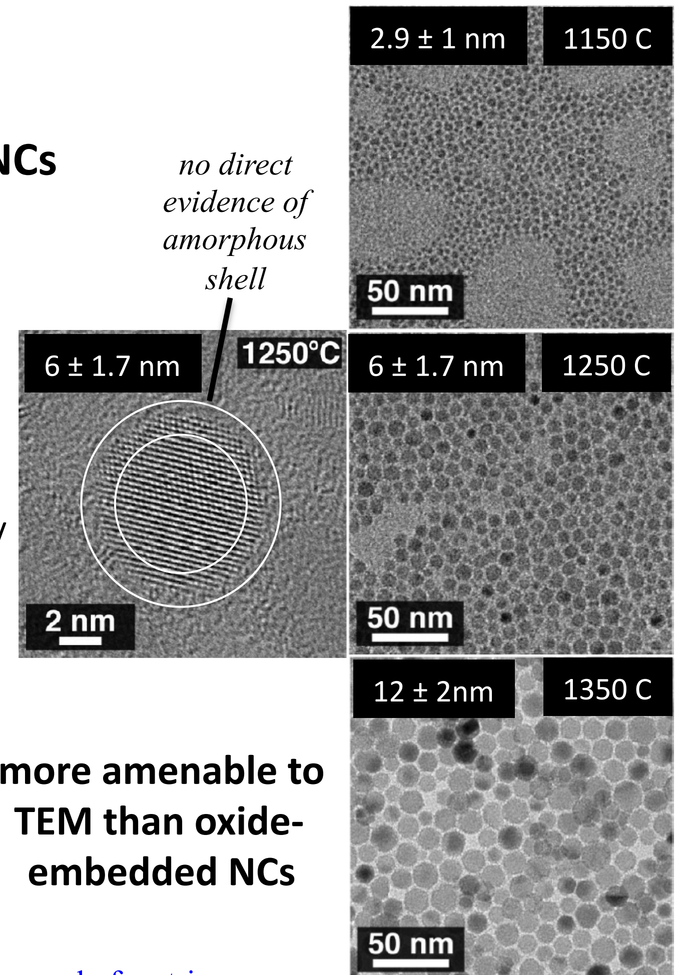


more amenable to TEM than oxide-embedded NCs

SAMPLE SERIES #2

Removal of matrix:
- eliminates surface strain
- sharpens q. confinement BC

no direct evidence of amorphous shell



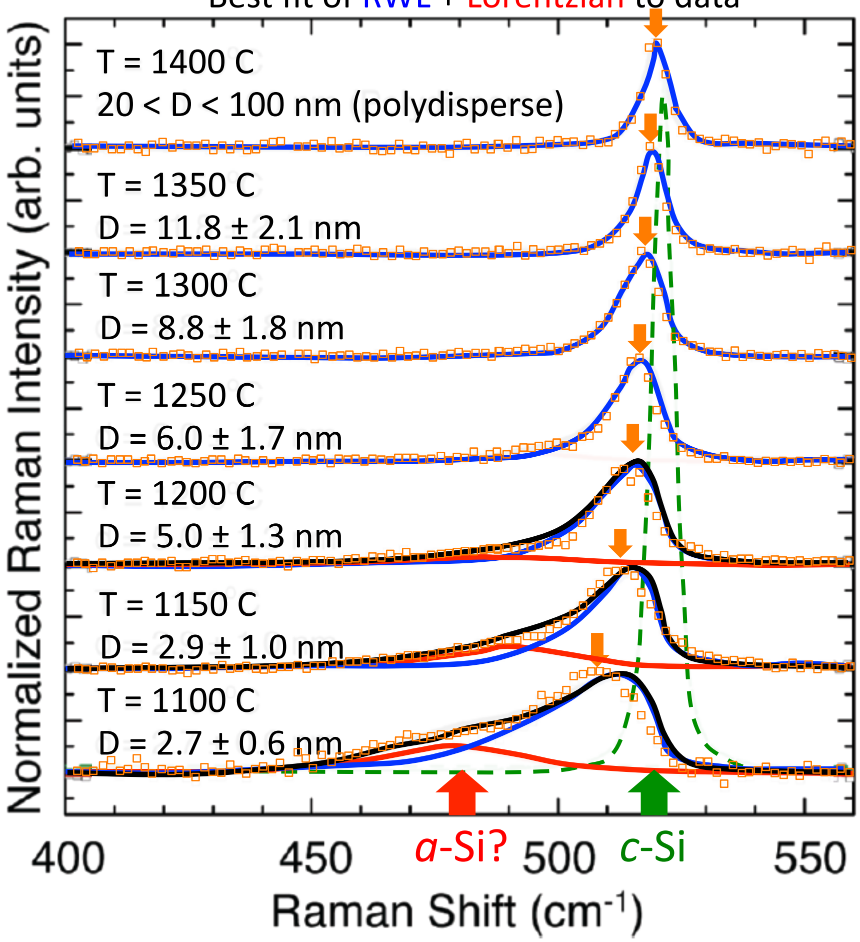
size, shape distributions readily characterized & minimized

Chemically synthesized Si NCs are model materials for fundamental spectroscopy

Raman spectra of free-standing ligand-stabilized Si NCs redshift & broaden monotonically with decreasing size D

- ReniShaw inVia microscope, backscatter geometry
- 514.5 nm Ar laser excitation at 0.02 mW/μm^2 (heating negligible)

Free-standing Si NC Raman data
Bulk c-Si reference spectrum (521 cm^{-1})
RWL model (w. arbitrary shift)
Lorentzian fit to low energy peak
Best fit of RWL + Lorentzian to data



Phonon Confinement Models

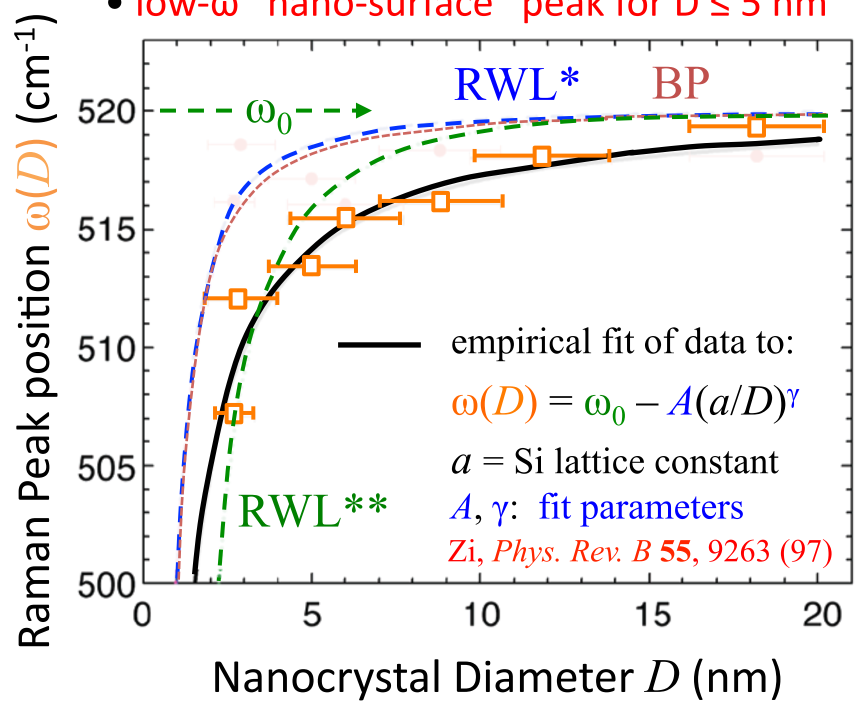
RWL: Richter, Wang, Ley, *Solid State Commun*. **39**, 625 (1981)
* Paillard, *J. Appl. Phys*. **86**, 1921 (1999)
** Faraci, *J. Appl. Phys*. **109**, 07311 (2011)

** 3D confinement weighting function

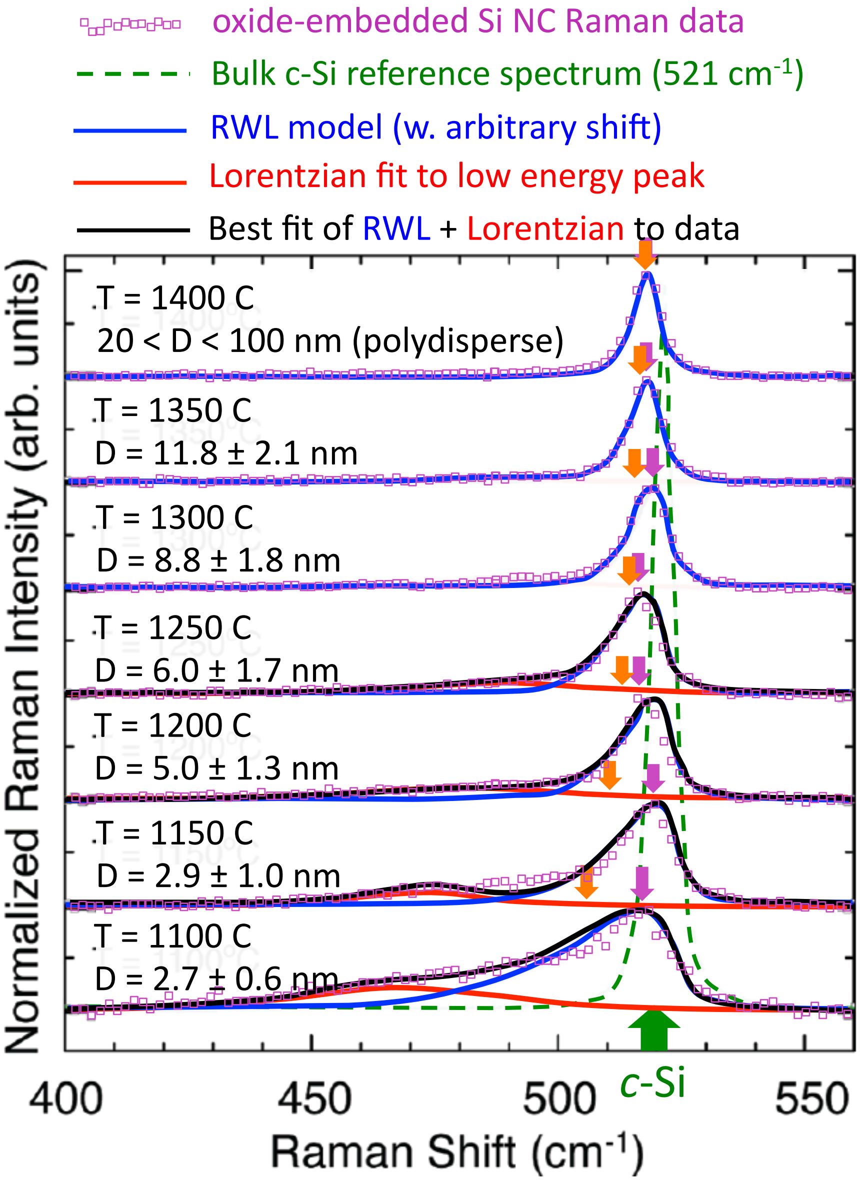
$$I(\omega) = B\int_0^{2\pi/a} \frac{|C(\vec{q})|^2\, d\vec{q}}{[\omega - \omega(\vec{q})]^2 + (\Gamma/2)^2}$$

* 3D phonon dispersion relation

- latest RWL models explain shifts fairly well…
  … and Raman line shapes very well
- low-ω "nano-surface" peak for D ≤ 5 nm

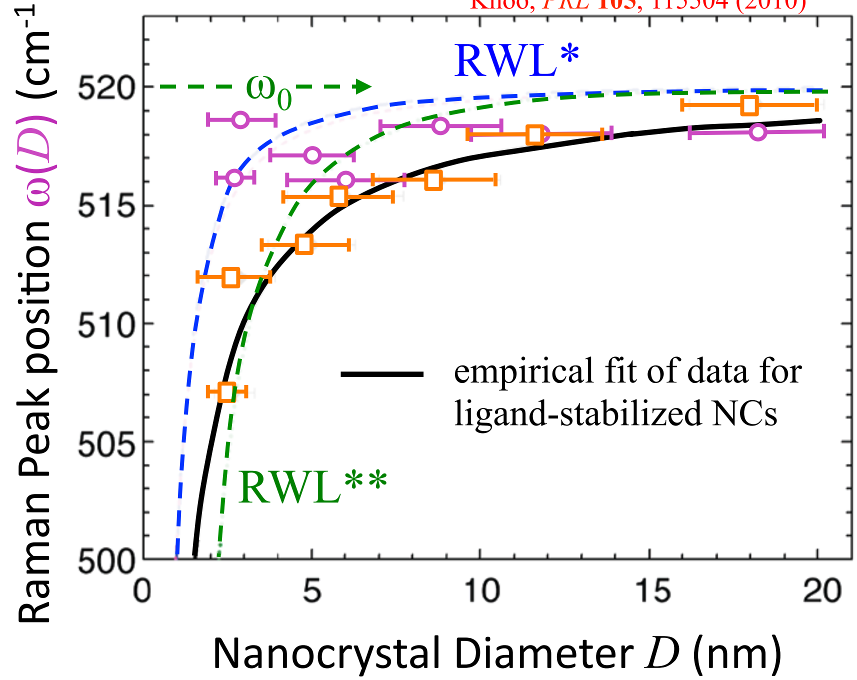


Comparative Raman spectra of free-standing & oxide-embedded NCs isolate the influence of oxide-induced strain



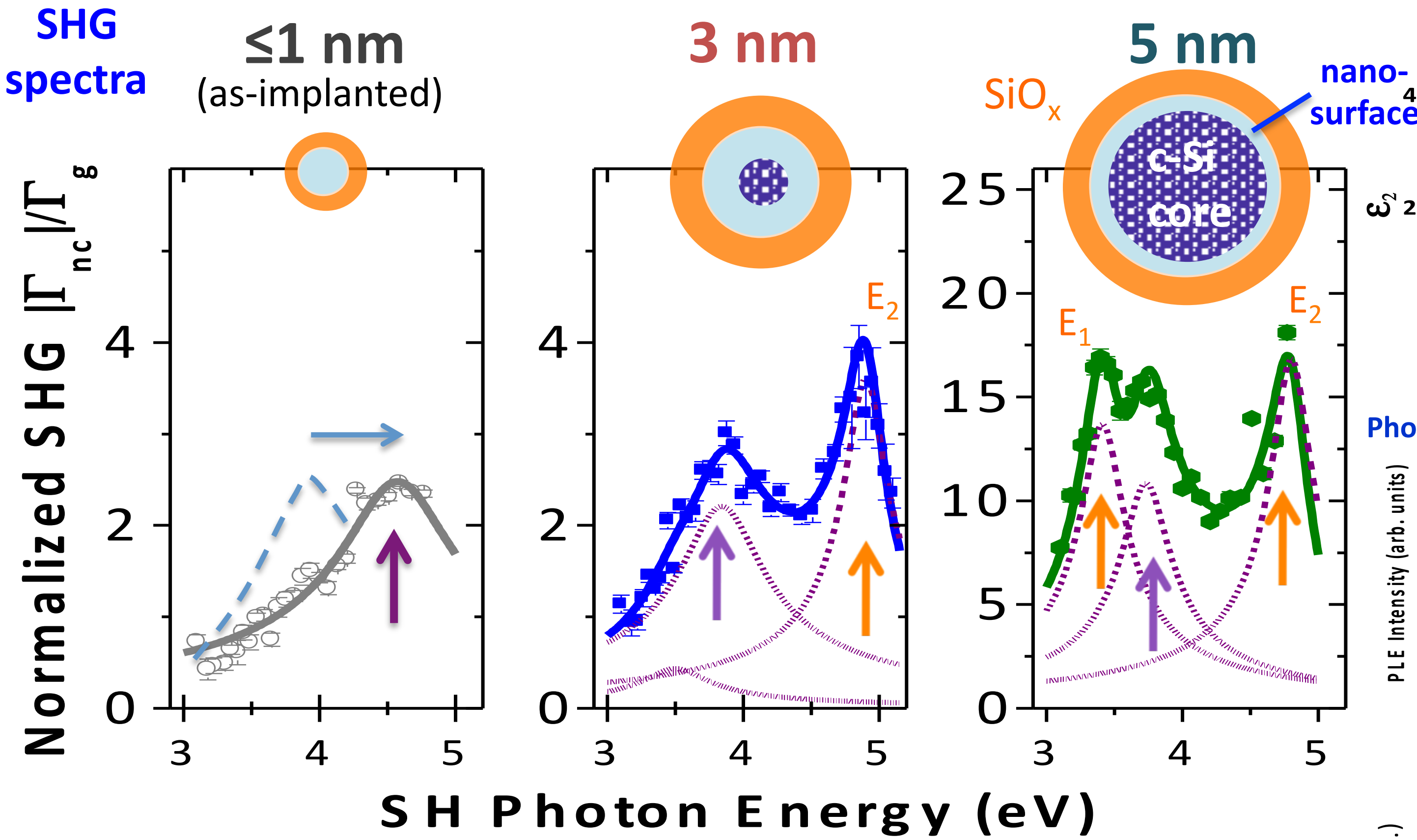
- oxide-induced strain **upshifts** Raman peaks compared to those of free-standing NCs
- the peak shifts **non-monotonically**, **unpredictably** with decreasing NC size
- shifts **accidentally** agree better with RWL* model; line shapes still well explained
- low ω peak nearly same as for free-standing NCs
  - ☹ oxide-strain-induced a-Si shell?
  - ☹ background a-Si clusters embedded in oxide matrix?
  - ☺ undercoordinated surface atoms w. short bond lengths!

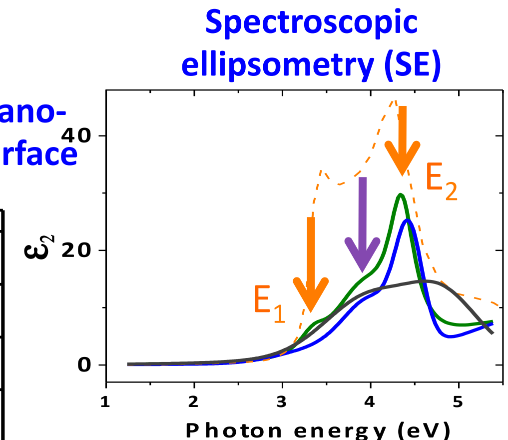
Khoo, *PRL* **105**, 115504 (2010)

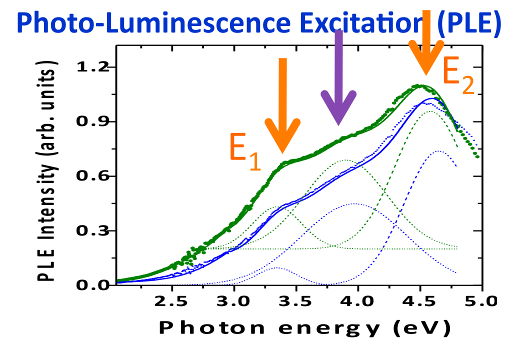


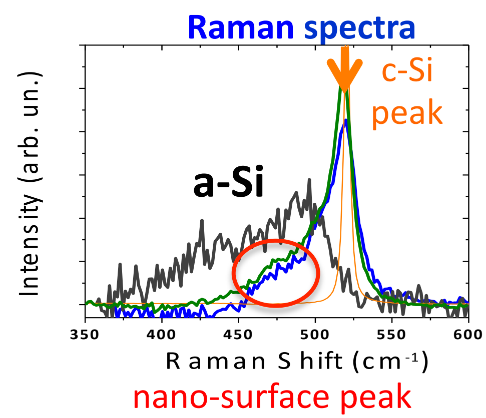
Previous SHG/SE/PLE spectra of oxide-embedded Si NCs revealed "intermediate" resonance correlated w. nano-surface Raman peak

Wei, MCD, *Phys. Rev. B* **84**, 165316 (2011)









Intermediate peak analogous to SHG spectral feature observed at **planar** Si/SiO_2:

G. Erley, W. Daum, Phys. Rev. B 58, R1734 (1998)

S. Bergfeld *et al*, Phys. Rev. Lett. 93,097402 (2004)

We are exploring this same correlation for free-standing, ligand-stabilized Si NCs

SUMMARY

- Ligand-stabilized Si NCs provide model, mono-disperse material for fundamental spectroscopic studies, free of complications from oxide
- Ligand-stabilized Si NCs show size-dependent Raman peak shifts that advanced phonon confinement models explain well, and promise to further refine Raman theory of nano-scale materials
- Benchtop chemical synthesis provides comparative samples of free-standing and oxide-embedded NCs, enabling isolation of spectroscopic influence of oxide-induced strain.

For further details:
C. M. Hessel *et al*., *J. Chem. Phys. Lett*. **3**, 1089 (2012)

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