Second Harmonic Spectroscopy Study of Silicon Nanocrystals Embedded in SiO₂

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

“Si lasers start to take shape”

Observation of optical gain in Si nanocrystals embedded in SiO₂

Those interesting properties originate at Si NC/SiO₂ interfaces
SHG has a reputation for being interface-specific
Interface and bulk contributions to SHG from planar surfaces are never separated with full rigor.

Empirical separation of surface & bulk contribution is usually based on:

1. Azimuthal anisotropy
2. Spectroscopy study
3. Interface modification

Similar bulk/interface ambiguity in SHG from Si NCs must be distinguished empirically


From symmetry alone,

$$\vec{P}^b(\vec{r}) = \gamma \nabla E^2 + \delta' \vec{E} \cdot \nabla \vec{E}$$

$$\vec{P}^s(\vec{r}) = \chi^s_{ijk}(a,b,f)F_jF_k,$$

assuming $l << r_{NC} << \lambda$

$$\vec{P}^{NL} = \Delta' \vec{E} \cdot \nabla \vec{E}$$

$$\Delta' = n_{NC}\left[\gamma_e(\delta',\gamma,a,b,f) - \gamma_m(\delta',\gamma,a,b,f) - \gamma_q(a,b,f)/6\right]$$
The samples are prepared by Si Ion implantation into SiO$_2$

1. Multi-energy implant (35-500 keV) yields uniform NC density
2. Samples annealed @ 1100 C / 1 hr in Ar + H$_2$ to precipitate NC formation

C. W. White et al., NIM B 141, 228 (1998) - ORNL

TEM Images

Si ions

Glass substrate

Raman Spectra

Photoluminescence excitation spectra

5 nm Si NCs
3 nm Si NCs
As-Implanted c-Si
Spectroscopic ellipsometry (SE) shows modified c-Si $E_1$ and $E_2$ critical points in the Si NCs

$E_1$ and $E_2$ critical points in the Si NCs:
• Bulk CPs $E_1$ and $E_2$ preserved, with $E_2$ dominating the spectra and $E_1$ greatly suppressed
• Appearance of peak around 3.9 eV

5 nm and 3 nm Si NCs:
• No bulk CPs $E_1$ and $E_2$
• Similar but blue-shifted shape to a-Si

As-Implanted:
• SE spectra provide a comparison for SHG spectroscopy
• Measured $\varepsilon_{1,2}$ determine the Fresnel factors used in SHG analysis
Cross-Polarized 2-Beam-SHG (XP2-SHG) enhances the signal from Si NCs by enhancing the field gradient

$$\vec{P}_{\text{eff}} = \Delta \vec{E} \cdot \nabla \vec{E}$$

**Single-beam SHG**

$$\vec{E} \cdot \nabla \vec{E} \sim \frac{E^2}{w_0}$$

**XP2-SHG**

$$\vec{E} \cdot \nabla \vec{E} \sim \frac{E_1 E_2}{\lambda} \sin \alpha$$

**Intensity Enhancement**

$$\sim \left( \frac{w_0}{\lambda} \sin \alpha \right)^2$$

XP2-SHG Measurement Setup

from 800 to 520 nm
SHG spectra show strong interface resonance and modified c-Si critical points in the Si NCs.

Quadrupolar SHG appears to be selectively sensitive to nano-interface structure (in close analogy to dipolar SHG of planar interfaces).
Conclusion

- SHG, complemented with SE, PLE and Raman, has been applied to study Si NCs to help elucidate the unique structure of the NCs.
- The unique sensitivity of SHG spectral structure and amplitude suggest SHG is uniquely sensitive to nano-interfacial structure.

**Future directions:**
1. Pump-probe XP2-SHG for dynamics study
2. Free-standing Si NCs

**Acknowledgements**

**Research group**
Robert Ehlert, Ming Lei, Loucas Loumakos, Adrienne Prem, Aaron Roberts

**Funding**
National Science Foundation
Grant DMR-0706227
Robert Welch Foundation
Grant F-1038