Raman Spectroscopy of Silicon Quantum Dots

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Abstract

Silicon quantum dots are synthesized and studied extensively by the REMRSEC, but they have not thus far had a fast and reliable way to characterize them. In this work, Raman spectroscopy is employed to study dots in varying types of samples, with special attention paid to the effects excessive laser power density can have on amorphous silicon.

Background

Raman Spectroscopy

- The vast majority (99.99999%) of scattered light is scattered elastically (Rayleigh scattering)
- Some is scattered inelastically, losing or gaining energy to vibrational states in the scattering medium (Raman scattering)
- We can collect Raman light and use these energy shifts to learn about the structure of materials
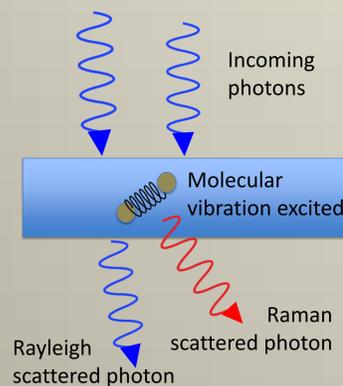
Silicon Quantum Dots

- Silicon quantum dots (QD's) are nanocrystals small enough to exhibit quantum confinement
- They have the potential to create third-generation photovoltaic devices
- Characterizing them with TEM, XRD is time-consuming and can be unreliable
- Raman could be a valuable tool to allow us to determine characteristics such as dot size and crystalline fraction

Previous Work

- Quantum confinement effects in Raman peaks (broadening from breaking of optical phonon mode degeneracy, redshift due to momentum conservation breakdown) was first explained about 30 years ago via the phonon confinement model[a]
- Since then, a bond polarization model has also been proposed[b]
- Earlier this year, Raman measurements on oxide-embedded and ligand-stabilized Si QD's were performed successfully[c]; this work aims to emulate their analysis

Experimental Setup

- The argon-ion laser excitation line at 514.5nm was used in a backscattering geometry
- The laser was focused through a 45x objective into a spot of area 0.73μm²
- Wavenumber shifts were calibrated using the mercury green line
- A rotary filter adjustable from optical density 0 up to 2 was inserted into the beam path to modulate the power density to desired levels
- Particular parameters (power density, exposure time, any background subtraction or other analysis) are noted with their respective plots

Results

Determination of Crystalline Fraction

- Films in these experiments were Si QD's embedded in an amorphous silicon (a-Si) matrix
- Following established analysis[d], 3 Gaussian peaks were fitted representing crystalline (c-Si), hexagonal (h-Si), and a-Si phases
- The approximate crystalline fraction was determined from the ratio of the sum of the c-Si and h-Si peak areas to the total integrated intensity
- These data were all obtained from 40-minute exposures at a power density of ~.068mW/μm²
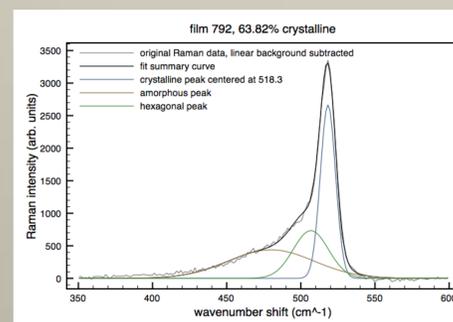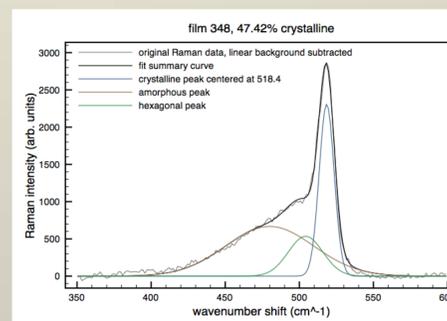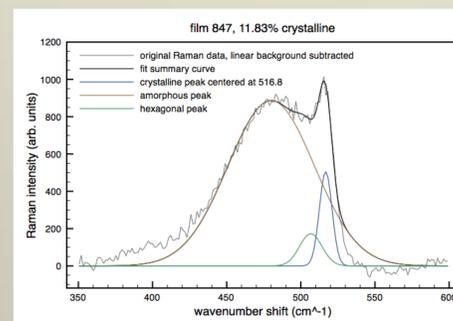
Crystallite Size

- Based on Hessel's[c] data, average sizes can be estimated:

| Film	c-Si peak location (cm^{-1})	Approx. avg. size (nm)
847	516.8	9.5
348	518.4	17.6
792	518.3	17.5

Results from loose QD powders

- These samples were piles of powder originally deposited on silicon, and were viewed between two thin wafers of alumina (Al_2O_3), which is Raman-inactive in the relevant region
- Data at right were obtained from a 1-hour exposure at a power density of .015mW/μm²
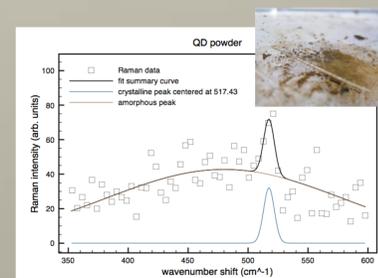

Results from QD films

- This sample was a film of quantum dots deposited on silicon
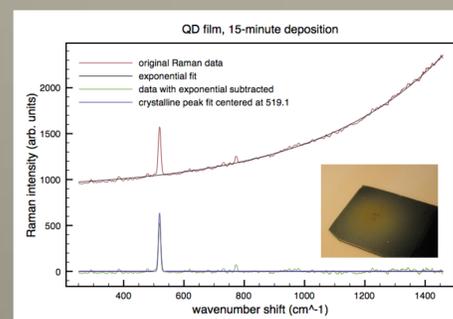
- In this treatment, the dots are highly fluorescent, even at low power density, so an exponential was fitted to the background and subtracted
- Note that no amorphous peak is observed – these dots appear to be highly crystalline; however, it is possible that the c-Si substrate affects this measurement

Heating Effects

- Excessive laser power density incident on QD's can burn them (see right) or cause amorphous silicon to crystallize (see below)
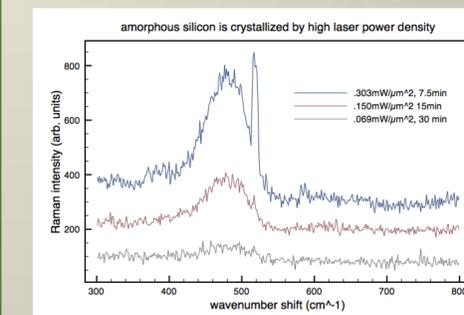
Bottom of a chunk of QD's charred by laser

- We aimed to stay well below threshold cited by similar work[c] of 1mW/μm²

Conclusions

- Raman measurements were successfully performed on silicon quantum dots as loose particles, in mixed-phase films, and in pure films
- Measurements were obtained at power densities low enough not to modify the samples by causing amorphous silicon to crystallize or the dots to oxidize
- From these spectra, crystalline fraction and dot size were estimated

Future Work

- Spectra, particularly from loose powder, should be exposed at similar power density for much longer times to reduce noise and improve curve fits
- Exponential fit to luminescence should be compared to PL measurements from other sources
- Size estimations should be compared to measurements from other sources

Acknowledgements

References

a) Richter, H. et al. The One Phonon Raman Spectrum in Microcrystalline Silicon. *Solid State Comm.* 39, 625-629. 1981.
b) Zi, J. et al. Comparison of Models for Raman spectra of Si nanocrystals. *Phys. Rev. B* 55, 9263-9266. 1997
c) Hessel, C. et al. Raman Spectroscopy of Oxide-Embedded and Ligand-Stabilized Silicon Nanocrystals. *J. Phys. Chem. Lett.* 2012, 3, 1089-1093
d) Houben, L. et al. Structural Properties of microcrystalline silicon in the transition from highly crystalline to amorphous growth. *Phil. Mag. A*, 77:6, 1447-1460. 1998