Abstract

Light-emitting Si nanocrystals (NCs) embedded in amorphous SiO$_2$ have attracted attention for their potential application in Si photonics. The structure of the elusive NC/SiO$_2$ interfaces and their role in luminescence, however, remain unsolved problems. Optical spectroscopy can probe the energy spectrum of the bulk and interface states of the nanocrystals and help elucidate the unique bonding structures at the interfaces. In this poster, we report the second-harmonic generation (SHG) spectroscopy in a 2-beam, cross-polarized geometry in order to elicit spectral structure unique to the nano-interfaces of 1 μm-thick layer of Si NCs of 3 and 5 nm in diameters.

Sample Preparation and Characterization

Samples were prepared by implanting multi-energy (35-500 kV) Si ions into fused silica to yield a uniform silicon density profile, then annealed in Ar and Ar+H$_2$ mixture to precipitate NC formation. The formation of spherical NCs with two different average diameters—3nm and 5nm—were confirmed by the TEM images. Photoluminescence (PL) shows annealing in Ar+H$_2$ mixture (the blue curve) enhances luminescence (compared to annealing in Ar—the red curve). The normalized PL and photoluminescence excitation (PLE) spectra (the blue curve represents the 3nm NCs and the olive one represents the 5nm) reveal the size effect on the PL of these NCs.

Spectroscopic Ellipsometry & Raman Spectra

The dielectric functions of the Si NCs are extracted by fitting the SE spectra based on Bruggeman effective media approximation using Gauss-Lorentz oscillator model. A strong influence of size effect on the dielectric functions is shown, with the E$_1$ CP resonance becoming weaker and tending to disappear while E$_2$ dominating the spectra and blue-shifting with decreasing size.

The Raman spectra of the annealed NCs show a sharp peak around 520 cm$^{-1}$, characteristic of c-Si, and a broad asymmetric shoulder on the lower energy side, extending through the 450 cm$^{-1}$ resonance characteristic of a-Si, suggesting a nanocrystalline core-amorphous shell structure of the NCs.

Cross-Polarized Two-beam SHG (XP2-SHG)

- XP2-SHG signal enhancement
- XP2-SHG z-scan measurement
- XP2-SHG setup

XP2-SHG Spectra

- SHG spectra show broad resonance between bulk Si E$_1$ and E$_2$ CPs
- SHG spectra of Si NC interband transitions can be modeled by resonant functions

The SHG spectra are modeled and reproduced as a coherent superposition of CP-like resonances with excitonic line shape. The phase and amplitude spectra are Kramer-Kronig consistent. The fitting results reveal resonances around 3.50 eV, 3.73 eV and 4.89 eV (for 3nm NCs) or around 3.41 eV, 3.73 eV and 4.86 eV (for 5nm NCs). The resonances around 3.8 eV correspond closely to SHG resonances observed at planar Si/SiO$_2$, and are attributed to transition of atoms at the interfaces between the NCs and the matrix with unique bond structures.

Conclusion

- SHG spectroscopy, complemented by conventional spectroscopic studies, has been applied to reveal the interface and electronic structures of Si NCs embedded in amorphous SiO$_2$
- SHG spectra differ markedly from their SE and PLE spectra: PLE are dominated by E$_1$ and E$_2$ CP resonances; SHG spectrum is nearly featureless for 3nm NCs but develops pronounced resonances at 3.46 eV and 3.86 eV for 5nm NCs
- The resonances of SHG spectra between E1 and E2 CPs can be attributed to the interface bonding structures, similar to the SHG responses at the planar Si/SiO$_2$ interfaces, suggesting the model with an intermediate transition layer of variable compositions between the Si NC core and the amorphous SiO$_2$ matrix, with further support from Raman spectra.

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