White-light-emitting silicon nanocrystal generated by pulsed laser ablation in supercritical fluid

- Investigation of spectral components as a function of excitation wavelengths and aging time -

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White-light-emitting silicon nanocrystals (Si-NCs) ranging from the near UV to the near IR region were fabricated by pulsed laser ablation (PLA) of a bulk silicon crystal in a supercritical fluid. The broad photoluminescence (PL) spectra, white light continuum, were investigated by measuring time evolution against aging in the atmosphere or oxygen ambience. The results show that the PL intensity of the higher-energy component increases, whereas that of the lower-energy component decreases as aging time increases (Figure 1). According to rate constants of PL-intensity enhancement, the increase in the PL intensity was ascribed to the oxidation of the Si-NCs. This enhancement became significant when the sample was generated at the thermodynamic state showing a critical anomaly of supercritical CO_2. Figure 2 shows rapid cooling of the hot Si-NC in supercritical CO_2 immediately after PLA produces many defects (dangling bonds), and then capped by the oxidation to form radiative centers. As a result, a luminescent Si-NC in the blue-green wavelength region is produced. This process is described in Figure 3. Based on PL spectral measurements at five excitation wavelengths, the lower- and higher-energy PL components were assigned to electronic structures arising from the quantum confinement effect of the Si-NC and the electron-hole recombination at the radiative centers at the surface of the Si-NC, respectively.

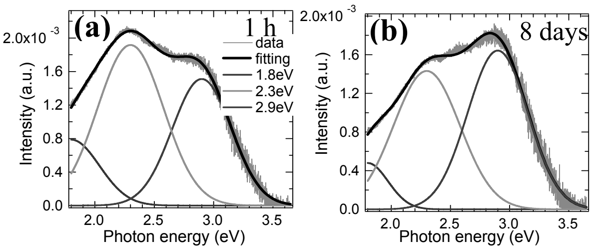

Figure 1. Photoluminescence spectra at the excitation wavelength of 325 nm. The spectra are decomposed by best-fitted Gaussian functions peaked at 1.8 eV (red PL), 2.3 eV (green PL), and 2.9 eV (blue PL) . The time evolution of aging in air displayed at (a) 1 h (b) 8 days.

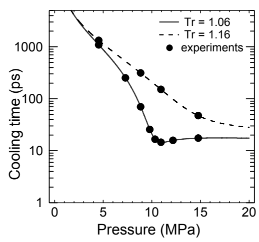

Figure 2. Cooling time of hot Si-NCs was calculated from heat capacities and thermal conductivity immediately after laser ablation. Rapid cooling is observed at $T_r = 1.06$.

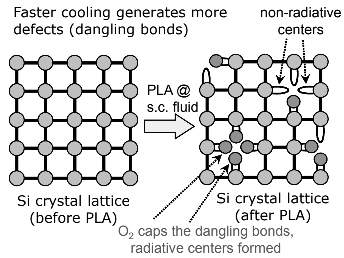

Figure 3. Schematic diagram of lattice of Si-NC before and after rapid cooling in a supercritical fluid. The rapid cooling produces the defect-rich Si-NC consisting of many dangling bonds that are oxidized by the aging. Otherwise, the capping of the dangling bonds reduces the radiative centers.