学位論文要旨

Nanoparticles Generated by Pulsed Laser Ablation in High- pressure Fluid:
Static and Dynamic Spectroscopic Measurements

（高圧流体中でのパルスレーザーアブレーションによるナノ粒子生成：静的・動的分光測定）

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1. General introduction

The gold (Au) nanoparticles has been widely utilized for surface-enhanced Raman scattering, cancer therapy, X-ray agent, and photovoltaics. The silicon (Si) nanoparticles has also been applied innovatively in LEDs, lasers, nontoxicity indicators within the human body. Nanoparticles could be produced by pulsed laser ablation (PLA) in gas and liquid phase. PLA in supercritical phase enables us generating nanoparticles with different chemical physical properties simply and efficiently.

2. In situ multipurpose time-resolved spectrometer and the dynamics of gold nanoparticle generation in supercritical fluid

We obtained chemical physical informations of nanoparticles by *in situ* measurements, i.e. samples without taken out of the sample cell, which giving direct understand to the generation processes and enhancing the functionality of nanoparticles. These *in situ* measurements could be difficult before, because of the severe experimental conditions at high temperature and high pressure, especially in a thermodynamic sensitive supercritical fluid.

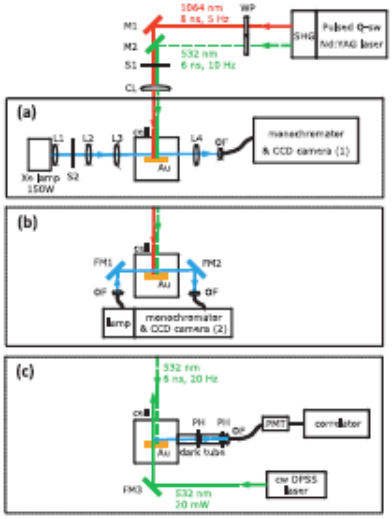

Figure 1. Schematic of optical configurations of the three spectrometers. (a) Transient absorption spectrometer, (b) absorption spectrometer for long delay times, and (c) DLS spectrometer.

We developed a multipurpose time-resolved spectrometer, which could be used for: (i) transient absorption spectrum measurements to investigate the dynamics of nanoparticle generation from ns to ms after PLA, (ii) absorption spectrum measurements to observe the time evolution of nanoparticles for delay times from seconds to hours after PLA, and (iii) dynamic light scattering (DLS) measurements to track nanoparticles with sizes from 10 nm to 10 μm generated from seconds to hours after PLA. (Fig. 1) This apparatus consists of a new-designed high-pressure optical cell for *in situ* time-resolved spectroscopic experiments at temperatures up to 400 K and pressures up to 30 MPa with fluctuations within ±0.1% h^{-1}. (Fig. 2)

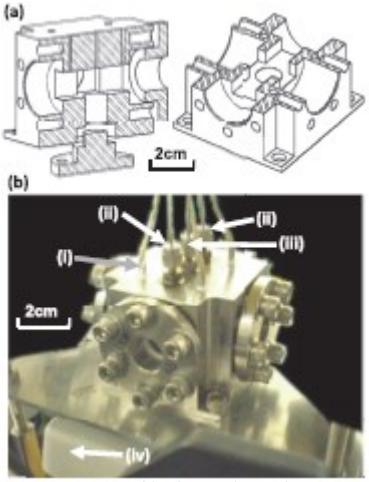

Figure 2. (a) Side-view and top-view cross sections of high-pressure optical cell. (b) Photograph of high-pressure optical cell: (i) cartridge heaters, (ii) fluid inlet–outlet ports, (iii) thermocouple, (iv) magnetic stirrer.

We demonstrated: (i) the plasmon resonance band spectra of

Au nanoparticles within 200 ns indicated the fragmentation of large nanoparticles occurs within 10 μs after PLA, (ii) very small Au nanoparticles generation caused the interband transition's absence and the plasmon band's shrink, (iii) the formation of Au nanonetworks induced the size distribution changed significantly within 10 min after PLA.

3. Spectroscopic time evolution of the white-light-emission from silicon nanocrystal and the investigation of its mechanism

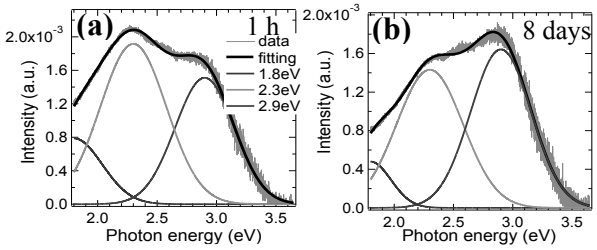

Figure 3. Photoluminescence spectra at the excitation wavelength of 325 nm. The spectra are decomposed by best-fitted Gaussian functions peaked at 1.8 eV (red PL), 2.3 eV (green PL), and 2.9 eV (blue PL) . The time evolution of aging in air displayed at (a) 1 h (b) 8 days.

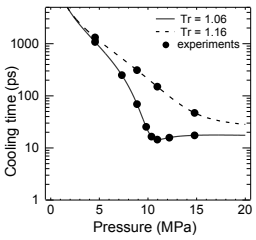

Figure 4. Cooling time of hot Si-NCs was calculated from heat capacities and thermal conductivity immediately after laser ablation. Rapid cooling is observed at $T_r = 1.06$.

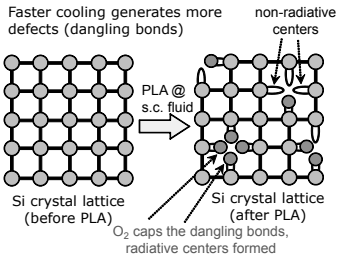

Figure 5. Schematic diagram of lattice of Si-NC before and after rapid cooling in a supercritical fluid. The rapid cooling produces the defect-rich Si-NC consisting of many dangling bonds that are oxidized by the aging. Otherwise, the capping of the dangling bonds reduces the radiative centers.

We fabricated white-light-emitting silicon nanocrystals (Si-NCs) ranging from near UV to red region by PLA in supercritical CO_2, which has been lacked of the details for the luminescence mechanism and the luminescence alteration as a function of aging time. That is: (i) is there any existence of light-emitting color limitation for the Si-NCs? (ii) how the fabrication environment affects the luminescence and the morphology of the products? (iii) what is the white-light luminescence mechanism?

We investigated the broadband continuum white-light photoluminescence (PL) spectra by measuring the time evolution against aging in the atmosphere or oxygen ambience, by tuning the excitation energy, and also by utilizing the thermal properties of supercritical fluid.

The results show that: (i) the PL intensity of the higher-energy component increases whereas the lower-energy component decreases as aging time increases, which is ascribed to the oxidation of the Si-NCs. (Fig. 3) (ii) rapid cooling of the hot Si-NC produces a luminescent Si-NC in the blue-green wavelength region, showing a thermodynamic critical anomaly of supercritical CO_2. (Fig. 4) (iii) the lower- and higher-energy PL components are 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 crystal surface, respectively. (Fig. 5)

【公表論文】

1） Shaoyu Wei and Ken-ichi Saitow, *Rev. Sci. Instrum.* **83**(2012), 073110-1‐073110-8.

2） Shaoyu Wei, Tomoharu Yamamura, Daisuke Kajiya, and Ken-ichi Saitow, *J. Phys. Chem. C* **116**(2012), 3928‐3934.