学位論文要旨

Synthesis of Si Quantum Dots and Development of Hybrid Light-Emitting Diode

シリコン量子ドットの作製及びハイブリッド発光ダイオードの開発

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Introduction Nanostructured Si exhibits unique electronic structure and optical properties due to quantum confinement effect and surface structure. Si nanomaterials hold great promise in application of optoelectronic device, photovoltaic and in-vivo bio-imaging, by taking advantages of its nature abundance, nontoxicity and biodegradability. Since the first report on room-temperature photoluminescence (PL) from porous Si, theoretical and experimental studies on luminescent Si nanoparticles (NPs) have been numerously conducted. Preparation of Si NPs can be achieved by bottom-up or top-down approaches. The bottom-up approaches consist of pulsed laser ablation, mechanochemical ball milling, and electrochemical etching, while the top-down approaches focus on the plasma pyrolysis of silane, thermal pyrolysis of hydrogen silsesquioxane, and the solution-based chemical etching of tetrachloride silane, etc. Hybrid light-emitting diode (LED) that consists of inorganic light-emitting quantum dots (QDs) and organic carrier transport materials has attracted much attention in next-generation solid-state lighting technology and display technology, because high color purity and luminescence can be achieved due to the narrow width of QD emission and high PL quantum yield (QY). In addition, a solution-based process can be applied for large area deposition during device fabrication. Electroluminescence (EL) from Si QD based hybrid LED have been observed in red region, however, emission in green and blue regions has not been reported so far. In this thesis, luminescent Si NPs were prepared via both bottom-up and top-down approaches. The world first blue light-emitting Si QDs based hybrid LED was also developed.

Chapter 2 Synthesis of Si NPs by pulsed laser ablation in liquid was conducted in six different organic solvents. A significant solvent dependence in particle size, PL and QY of synthesized Si NPs was demonstrated. It revealed that NP size and QY were well correlated by carbon atom ratio in organic solvent, as shown in Figure 1. Synthesized Si NPs exhibit common blue PL which origins from the recombination of hole and electron in the quantum confined band structure of ultra-small Si core. In addition, enhancement of QY was also observed from Si NPs aged in 1-octyne. The mechanism was studied by analyzing the radiative and non-radiative recombination process, as well as surface chemical

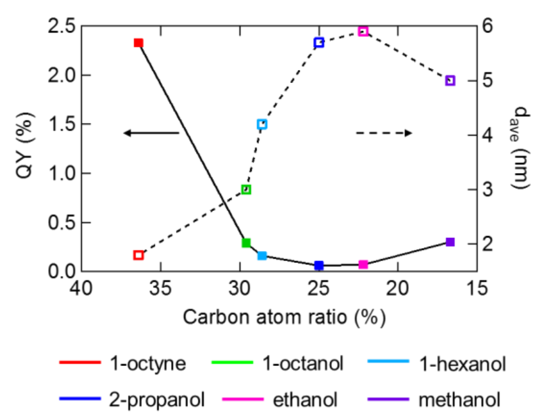


Figure 1. QY and size of Si NPs as a function of carbon atom ratio in organic solvent.

components, as a functional of aging period. The enhanced QY is due to the progressive passivation of alkyl chain on Si dangling bonds during aging.

Chapter 3 By utilizing blue light-emitting Si QDs synthesized via pulsed laser ablation in 1-octyne (Figure 2a), a hybrid LED (Figure 2b) with structure of ITO/PEDOT:PSS/poly-TPD/Si QDs/Alq_3/Al was fabricated. The developed hybrid LED perform high current and optical power densities, which are 280-times and 350-times higher than previously reported data. Efficient emission from Si QDs occupies 77.8 % of entire EL spectra of hybrid LED (see Figure 2c). This is the world first reported blue Si QD based hybrid LED. The superior performance of this device is attributed to the Si QDs prepared by the pulsed laser ablation synthesis, the effective carrier migration throughout the LED and carrier recombination in the Si QD layer, as well as to dark spots-free film morphology, those of which result from careful optimization of the layered structure.

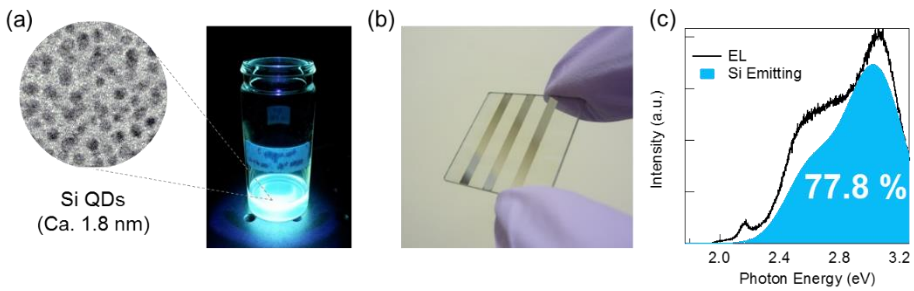
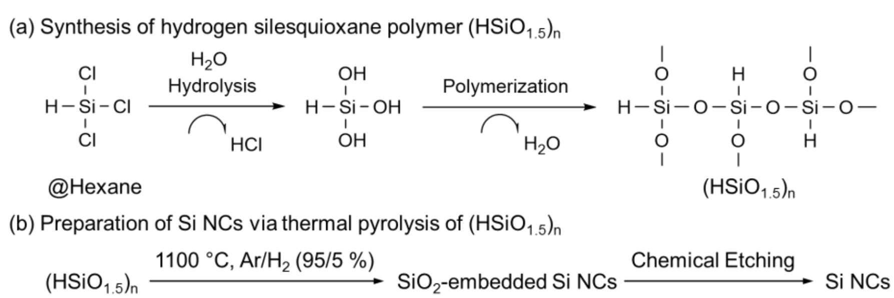


Figure 2. (a) Si QDs synthesized by pulsed laser ablation in 1-octyne; (b) fabricated Si QD based hybrid LED; (c) EL spectra of hybrid LED with 77.8 % efficient emission from Si QD.

Chapter 4 Luminescent Si nanocrystals (NCs) was prepared via thermal pyrolysis of $(HSiO_{1.5})_n$ polymers and a new size-controlling method was developed. $(HSiO_{1.5})_n$ polymers were synthesized by reaction between $HSiCl_3$ and water in hexane, whose reaction is illustrated as Scheme 1a. Si NCs were prepared by thermal pyrolysis of $(HSiO_{1.5})_n$ polymers under 1100 °C followed with chemical etching, as Scheme 1b shown. Here, $(HSiO_{1.5})_n$ with different network-to-cage structure were selectively synthesized by altering the reaction conditions, such as the reaction speed between $HSiCl_3$ and water, and the amount of hexane. Small or large Si NCs were generated by thermal pyrolysis $(HSiO_{1.5})_n$ polymers with high or low network-to-cage ratio, respectively. The synthesized Si NCs show different PL wavelength in visible region.



Scheme 1. (a) Synthesis of $(HSiO_{1.5})_n$; (b) preparation of Si NCs via thermal pyrolysis.