Synthesis and Characterization of Oxide-Embedded and Surface-Passivated Silicon Nanocrystals

NNIN Grad Program

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Introduction:

Silicon nanocrystals (SiNCs) emit light, a nanoscale phenomenon that is being explored for new biomedical and optoelectronic applications. Quantum confinement effects govern the light emission properties for silicon, and various colors of light can be obtained by changing the crystal size [1]. However, the size at which quantum confinement effects subside to bulk electronic properties is still unclear. Here, our goal was to elucidate the size at which quantum confinement effects vanish in Si nanocrystals by measuring the photoluminescence properties of SiNCs with diameters greater than the Bohr exciton radius (5 nm), the size at which quantum confinement effects are proposed to emerge.

Experimental Procedures:

Bulk oxide-embedded SiNCs were synthesized using hydrogen silsesquioxane (HSQ) as a precursor. Solvent (methyl isobutyl ketone) was evaporated from HSQ stock solution to obtain solid white HSQ, which was subsequently processed at 1100-1400°C for one hour in a 7% H_2 / 93% N_2 atmosphere. All samples were heated at 18°C / min in a furnace. The products were ground with a mortar and a pestle and then characterized by x-ray diffraction (XRD) and photoluminescence (PL).

Thin film oxide-embedded SiNCs were also fabricated in order to compare the PL intensities. HSQ stock solution was spin-coated on quartz substrates and readily heated in the furnace under the same processing condition as mentioned above. Photoluminescence was measured for these thin film samples.

SiNCs were etched from the oxide matrix and passivated with dodecene by thermal hydrosilylation to produce hydrophobic colloidal nanocrystals. First, the ground oxide-embedded composites were shaken with 3 mm glass beads for 10 hours to reduce their grain size. The shaken particles were etched with hydrofluoric acid (HF) for 3.5 hours to remove oxide matrix surrounding the SiNCs. These nanocrystals were washed and extracted by centrifugation with ethanol and chloroform and their surfaces were subsequently passivated with dodecene by thermal hydrolylation. Finally, SiNCs were washed and extracted by centrifugation with ethanol and methanol, and readily dispersed in chloroform. The products were observed by a transmission electron microscope (TEM) and characterized by PL and photoluminescence excitation (PLE).

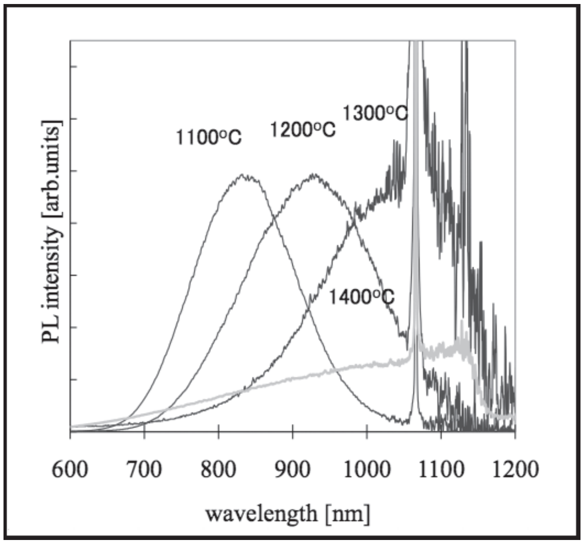

Figure 1: PL of bulk HSQ processed at 1100-1400°C.

Results and Conclusions:

Figure 1 is the PL results of oxide-embedded composites processed at various temperatures. The PL emission red-shifted from 850 nm to approximately 1100 nm as processing temperature was increased from 1100°C to 1300°C. The PL intensity dropped significantly for HSQ processed at 1400°C and an accurate peak wavelength could not be obtained due to spectral range limitations. XRD studies on HSQ processed at these temperatures show the SiNCs from HSQ processed at 1300 and 1400°C are 7.5 and 13.4 nm, respectively [2]. Luminescence from these samples demonstrates that SiNCs emit light at sizes much larger than is predicted by traditional quantum confinement theory. This also shows light emission at bulk silicon bandgap (1.1 eV, 1100 nm).

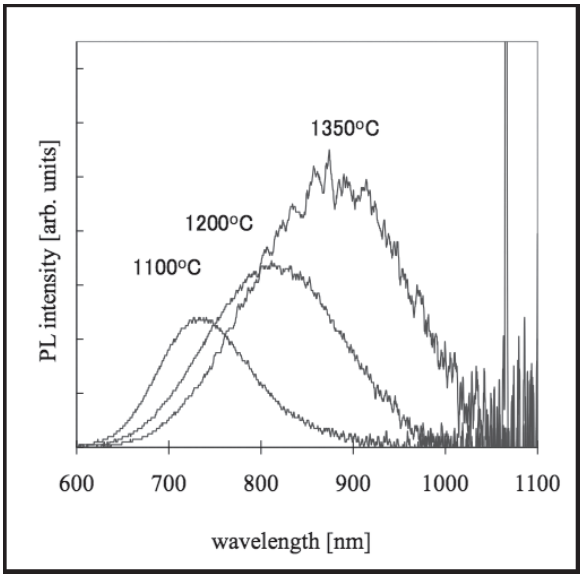

Figure 2: PL of thin film HSQ processed at 1100-1350°C.

Figure 2 shows the PL emission of thin film HSQ samples red shifts and increases in intensity with higher process temperatures. The former trend can be explained by typical quantum confinement effects, but the latter trend is opposite to our prediction. It is because we believe that quantum confinement effects diminish in larger nanocrystals. We think that these unexpected results were due to nonuniformity of the films. We note that only few luminescent spots could be obtained from some film samples, and that the PL intensities were different depending on the spots. Therefore, preparation of uniform samples and more accurate investigation are needed. The PL emission intensity from freestanding SiNCs was very strong, and easily observed under a hand held UV light (lambda = 366 nm). Figure 3 shows the PL red-shifts with higher process temperatures. An unknown peak in the PL spectrum from the 1300°C sample seems to be coming from oxide residue. The PLE results indicate that peak excitation wavelengths were similar (Figure 4). In order to determine optical property of surface-passivated SiNCs, further measurements including absorption spectroscopy are needed.

In conclusion, various sizes of SiNCs were synthesized and characterized in bulk, thin film, and freestanding morphologies. Luminescence from SiNCs larger than Bohr exciton radius (5 nm) was observed, a phenomenon that is the most interesting result in this study. Emission red shifts with larger nanocrystals were observed from all the three morphologies, indicating quantum confinement effects govern optical property of SiNCs.

Future Works:

- XRD measurement using the exact same bulk samples which were used for PL spectroscopy.
- Fabrication of and uniform thin-film samples in order to visualize the diminishing quantum confinement effects with increasing the crystal size.
- Process at higher temperature (1500-1700°C) to obtain larger SiNCs.
- Longer process at the critical temperature which gives the crystal size with weakened luminescence.
- Time resolved and low temperature PL.

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References:

[1] Zhizhong Yuan, et al., Proceedings of the IEEE, Vol. 97, No. 7, pp. 1250-1268, 2009. [2] Colin M. Hessel, et al., J. Phys. Chem. C, Vol. 111, Vo. 19, pp. 6956-6961, 2007.

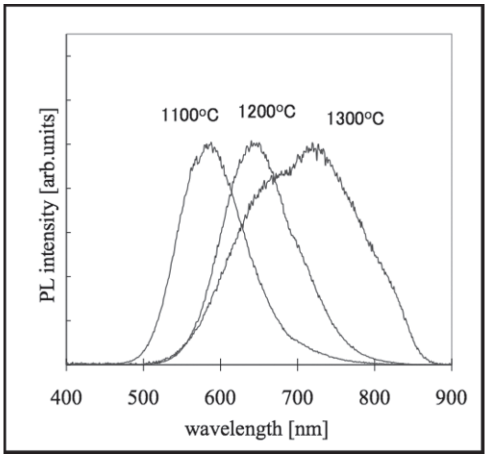

Figure 3: PL of surface-passivated SiNCs processed at 1100-1300°C.

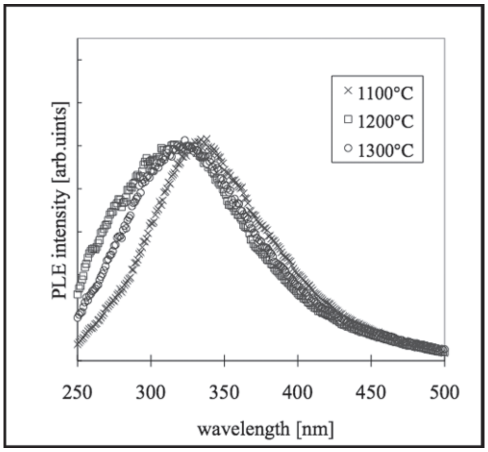

Figure 4: PLE of surface-passivated SiNCs processed at 1100-1300°C.