

I. Deliverable Report on Demonstration of 1-5 nm Quantum Dot Fabrication and Deposition of Blanket Layer on Silicon

Task ID 425.019

Task Title Low Environmental Impact Processing of Sub-50 nm Interconnect Structures

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II. Summary

There are several challenges in implementing optical interconnects at the reduced geometries of ICs. Quantum dots (QDs) or nanocrystals (NCs) with dimensions less than 5 nm are compatible with reduced geometries if methods can be developed to integrate these materials with Si CMOS. QDs containing ZnSe with and without Cd doping were fabricated using a simple batch synthesis process. ZnSe is a wide-gap material, allowing the bandgap to be tuned by introduction of other metal ions. Based on UV-vis spectra, TEM, and AFM, the QDs contained sharp band edges (low defects), were crystalline, and varied in size from 1-5 nm, which could be controlled by reaction process time. QD layers were deposited on Si substrates by drying liquid solutions creating electrostatically bound layers. Covalent attachment is an important next step in the integration of these nanoparticles. QDs fabricated in this way could reduce the cost of interconnects and other structures incorporating these nanoparticles.

III. Technical Results and Data

Experimental

Quantum dots were made in solution using the following procedure. The chemicals were used as purchased from Sigma-Aldrich. All reactions were carried out in ultra pure de-ionized (DI) water, open to air. Hydrazine (N₂H₄, 35 wt. % in H₂O) [Safety notice: hydrazine may be explosive and should be handled carefully] was introduced to keep the reaction in a reducing atmosphere, enabling highly oxygen-sensitive sodium hydroselenide (NaHSe) to react with Zn-thiol complexes forming QDs. Sodium hydroselenide (NaHSe) was prepared by mixing sodium borohydride (NaBH₄, reagent grade, ≥98.5%) and selenium (Se, 99.99%) powder in DI water. A dark red solution was obtained after the Se powder was completely reduced by NaBH₄. A typical synthetic procedure for ZnSe QDs follows: 1 mmol of Zn(NO₃)₂ (reagent grade, 98%), a calculated amount of a thiol molecule, and 2 mL of N₂H₄ were dissolved in 100 mL of DI water in a three-neck flask. The thiol molecules used were 3-mercaptopropionic acid (MPA) (≥98%), thioglycolic acid (TGA) (≥99%), and L-glutathione (GSH) (≥98%). Two milliliters of as-prepared NaHSe solution were added to the flask with vigorous stirring. The pH value of the mixed solution was tuned to 11 with the addition of 1M NaOH. The molar ratio of Zn:thiol:Se was 1:1.3:0.5. During refluxing of the reaction mixture in air, the red color gradually faded, resulting in a homogeneous, colorless solution, which subsequently turned light blue as the ZnSe QDs grew. Aliquots were removed from the reaction vessel at regular intervals, rapidly cooled to room temperature, and stored at 4 °C in the dark.

A typical synthetic procedure for Zn_xCd_{1-x}Se QDs follows: Cd-thiol complexes were prepared in a three-neck flask by mixing 1 mmol of Cd(NO₃)₂ (reagent grade, 99%) with a calculated amount of a thiol-bearing molecule dissolved in 50 mL of DI water. The molar ratio of Cd:thiol was 1:1.3. A Cd-thiol solution was added during refluxing of a Zn-thiol-Se solution, which was prepared as described. The Cd:Zn ratio was varied from 0.1:1 to 2:1. The solution turned light yellow as Zn_xCd_{1-x}Se QDs grew. Aliquots were removed from the reaction vessel at regular time intervals, rapidly cooled to room temperature, and stored at 4 °C in the dark.

Aliquots were diluted with DI water for characterization without any size sorting. UV-vis absorption spectra of QD samples in aqueous solution were obtained using an Agilent 8453 UV-vis spectrometer. Room temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using a PTI fluorescence spectrometer (814 photomultiplier detection system and LPS-220B power supply). The PL quantum yield was obtained by comparison with a standard (2-aminopyridine (≥99%) in 0.1 M H₂SO₄, QY = 60%) for samples of both ZnSe QDs (emission in the UVA range) and Zn_xCd_{1-x}Se QDs (emission in the blue range) following a procedure reported in the literature.²¹ High-resolution TEM (HRTEM) was performed on a conventional Hitachi H8100 electron microscope operating at 200 kV. Samples for HRTEM were prepared by putting a few drops of a solution containing QDs on an amorphous carbon substrate supported on a copper grid and allowing the solvent to evaporate at room temperature. AFM was performed using a Veeco MultiMode III.

Results

The temporal evolution of ZnSe QDs capped with three different ligands is shown by the UV-vis absorption spectra in Figure 1. When the ligand was MPA, small ZnSe QDs formed after 10 min with a distinct absorption peak at 315 nm that shifted continuously to 321 nm after 20 min and to 337 nm after 30 min (Figure 1a). The absorption peak attenuated sharply for longer growth times, becoming a shoulder at approximately 360 nm. When TGA and GSH were used as capping ligands, similar results were obtained where a distinct absorption peak shifted to longer wavelengths and attenuated with increasing growth time (Figures 1b and 1c). The peaks at short wavelengths in the absorption spectra suggest homogeneous nucleation of small crystallites that grew by an Ostwald ripening process, forming larger crystals at the expense of smaller ones. The relatively pronounced absorption peaks show that at early stages the size distribution of ZnSe QDs was nearly monodispersed, with growth stopping in the “focusing of size distribution” regime. At later stages the absorption shoulders drifted toward longer wavelengths and the absorption peaks were no longer distinct or disappeared entirely, showing that the quality of the QDs degraded. The highest quality QDs were obtained after 30 min of growth, suggesting that there was little thermodynamic driving force for growth and a particularly stable crystal structure was obtained.

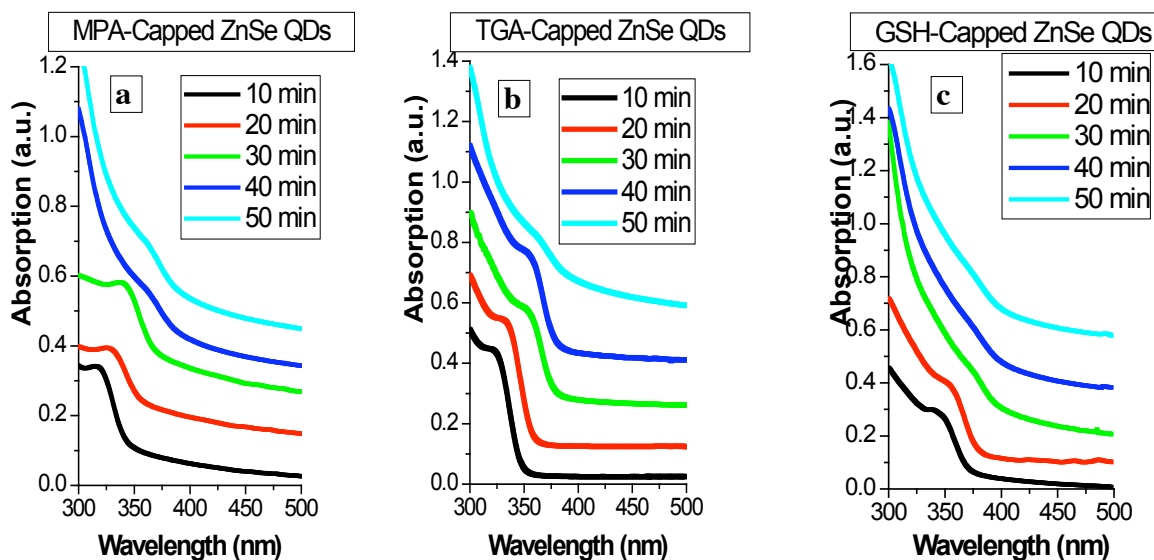


Figure 1: UV-vis absorption spectra of (a) MPA-capped, (b) TGA-capped, and (c) GSH-capped ZnSe quantum dots.

Figure 2 shows high-resolution TEM (HRTEM) images of TGA-capped ZnSe QDs with near bandgap emission at 372 nm and TGA-capped $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs samples with near bandgap emission at 425 nm. The HRTEM confirmed that the size distribution of the as-synthesized TGA-capped ZnSe QDs and the TGA-capped $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs were nearly monodispersed with average diameters of 2.5 and 3.0 nm, respectively. This is consistent with the correlation between the size and band gap of QDs calculated from UV-Vis absorption peaks. The insets of Figures 5a and b are magnified TEM images of single ZnSe and $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs, showing the existence of distinct lattice planes and confirming the crystallinity of QDs synthesized in water.

A solution containing QDs capped with TGA were exposed to a Si surface and dried using ultrapure nitrogen. The AFM results in Figure 3 indicate that the QDs were approximately uniformly distributed over the surface with an average size of 3.8 nm, which corroborates the TEM results. Both single QDs and clusters of many QDs could be identified. These QDs are not covalently bonded to the surface but rather

electrostatically bound, since the carboxylate group ($-\text{COO}^-$) at the end of a TGA ligand is negatively charged at a pH near 8 of the QD solution and is attracted to the positively-charged Si atoms in the thin oxide covering the substrate.

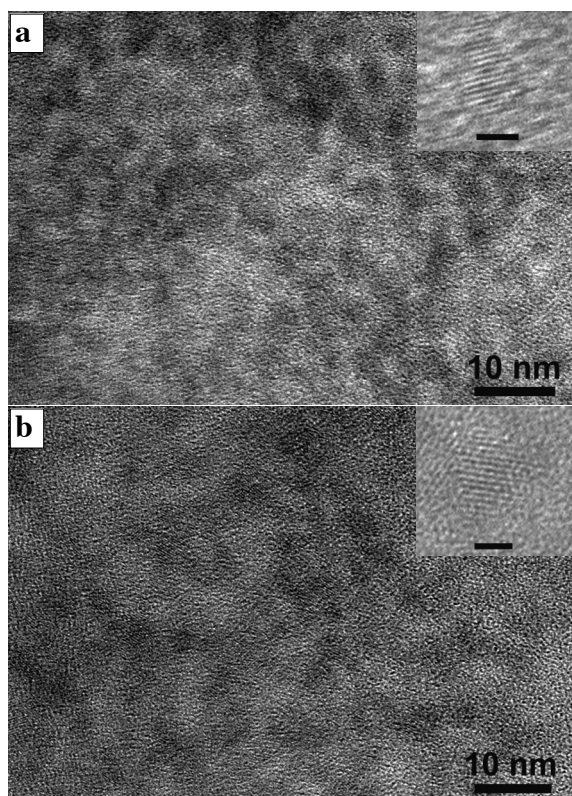


Figure 2: High-resolution TEM images of TGA-capped ZnSe with near bandgap emission peak at 372 nm (a) and TGA-capped $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QD samples with near bandgap emission peak at 425 nm (b). Inset (a) and (b) are the magnification TEM images of corresponding single ZnSe and $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QD, and their scale bars are 2 nm.

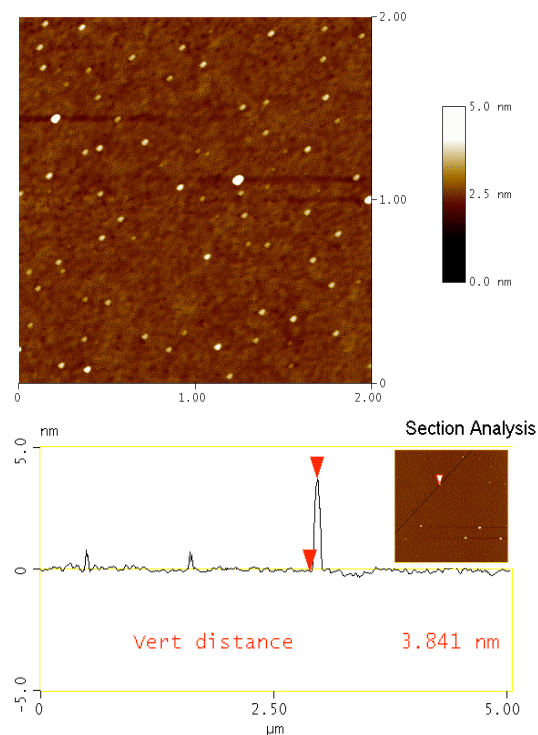


Figure 3: (top) AFM topography image of TGA-capped quantum dots with maximum emission at 590 nm on hydrophilic silicon wafer substrate; (bottom) Height profile of AFM line scan in the image shown in the inset. Red arrows define dimensions of one typical quantum dot with a diameter close to 3.8 nm.

IV. Conclusions

QDs containing ZnSe with and without Cd doping were fabricated using a simple batch process. The photoluminescence of the QDs could be tuned by size selecting QDs based on reaction time. The size of a QD was proportional to reaction time. The QDs were crystalline and varied in size from 1-5 nm as shown by TEM and AFM of QDs deposited on Si substrates.

V. Supplementary Materials Available

Z. Deng, F. L. Lie, S. Shen, I. Ghosh, M. Mansuripur, A. J. Muscat, "A Simple Open-to-Air Water-Based Route to Ligand-Selective Synthesis of ZnSe and $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ Quantum Dots with Finely Tunable UVA to Blue Photoluminescence," submitted to Journal of Physical Chemistry, 2008.