CHAPTER 3

Synthesis of Quantum Dots

3.1 CHARACTERISTICS OF QDs

The quantum dot is a form of nanocrystals, or a monodisperse crystalline metal or semiconductor particle whose diameter is adjustable on the nanoscale. QDs are of particular interest from a device standpoint as the electron and photon behaviour in the materials differ greatly from that of bulk materials. When deposited in an ordered manner and formed into a solid, collective traits may arise that are also distinctive. As an individual particle, the performance of a QD may be tuned through variations in size and shape, leading to changes in electron hole generation and recombination dynamics, tunnelling behaviour, and energy transfer. As in bulk semiconductors, population inversion can be achieved with a sufficient excitation rate and energy, which results in an emission coefficient greater than the absorption coefficient leading to net optical gain.

Furthermore, the three dimensional confinement of electron-hole pairs (exciton wave function) leads to discretized energy levels and delta-function-like distribution of the density of states. Under excitation, the emission of QDs is spectrally much sharper than their bulk material counterparts, which results in a sharp gain spectrum and therefore high gain, low loss, and high quantum efficiency (Fig. 3.1) [45]. The spectral response of QDs can be easily tuned by particle size and composition. These unique properties make QDs ideal materials for optoelectronic applications.

Conventional QD photonic devices utilize self- organization at the interface of strained epitaxial grown III–V or II–VI semiconductor layers to create pyramidal QD nanostructures due to lattice mismatch. The fabrication is often done through Metal-Organic Chemical Vapour Deposition (MOCVD). The Stranski–Krastanov process is the basis for manufacture of the first QD lasers, which have been theoretically and experimentally demonstrated with improved gain characteristics and reduced lasing current thresholds compared to quantum well and quantum film structures. Although high-quality optoelectronic devices have been obtained using the self-organization method, the process itself is often not compatible with silicon CMOS fabrication.

Another process to fabricate QDs is through chemical synthesis, or solution-based processes. The resulting QDs are in colloidal form and have been widely used as fluorescent tags in biomedicine. The colloidal QDs can then be subsequently deposited on a variety of substrates including silicon and mixed with different materials using various methods to be described later, resulting in rapid expansion in applications such as whispering gallery lasers, sensors, organic LEDs, and solar cells. In the colloidal case, where individual nanoparticles are fabricated in a solution suspension, the composition materials often fall in the semiconductor category such as II–VI and III–V. The process often involves controlled injection of reagents into the solvent to nucleate and grow the compound of interest. Recently, synthesis of group IV semiconductor QDs has also been investigated. In the case of CdSe nanocrystals, dimethyl cadmium, and organ phosphine selenide combine to form a core QD structure. A shell layer, such as ZnS, may be subsequently added by solution growth to suppress surface oxidation and improve the fluorescence behaviour. The diameters of the core and shell thicknesses determine the energy levels in the QD, which affect the absorption spectrum and correspond to the emission wavelength of the photon generated after the excitation and recombination of an electron-hole pair [46].

The shell layer also allows further surface chemical treatment to enable specific reactions with surrounding media. By design, a shell material with a larger bandgap is commonly selected to enable better electron-hole pair confinement, whereas the surface is treated with stabilizers and can be conjugated with molecules for specialized binding activity, which is dependent on the application. Colloidal QDs offer high fabrication and integration flexibility. This article focuses on the fabrication, deposition, and photonic devices made of colloidal QDs.

3.1.1 Colloidal Synthesis

Colloidal semiconductor nanocrystals are synthesized from precursor compounds dissolved in solutions, much like traditional chemical processes. The synthesis of colloidal quantum dots is done by using precursors [47], organic surfactants [48], and solvents. Heating the solution at high temperature, the precursors decompose forming monomers which then nucleate and generate nanocrystals. The temperature during the synthetic process is a critical factor in determining optimal conditions for the nanocrystal growth. It must be high enough to allow for rearrangement and annealing of atoms during the synthesis process while being low enough to promote crystal growth. The concentration of monomers is another critical factor that has to be stringently controlled during nanocrystal growth. The growth process of nanocrystals can occur