Self-Assembled Quantum Dots: Physics and Photonics Applications

Jin Dong Song, Young Ju Park, Won Jun Choi, Ilki Han, Woonjo Cho, and Jungil Lee*

Nano Device Research Center, Korea Institute of Science and Technology, 39-1 Hwolgok Seongbuk, Seoul 136-791, Korea
*Corresponding author : jil@kist.re.kr, Fax: +82-2-958-5709, Tel: +82-2-958-5786

Abstract

It has been well known that self-assembled semi-conductor quantum dots (QDs) have potential applications in electronic and optoelectronic devices due to the unique zero-dimensional features of carrier wavefunctions. After reviewing brief history of semi-conductor nano-devices, the advantages of utilizing nano-structured semiconductor materials, in particular, III-V compound materials, in optoelectronic devices is discussed. It is presented that atomic layer molecular beam epitaxy (ALMBE), quantum dot patterning, different self-assembly methods for growing quantum dots, quantum dot laser diodes, superluminescent light emitting diodes and infrared photodetectors (QDIP’s) including quantum dot growth. Device processing techniques such as wavelength tuning utilizing impurity free vacancy disordering of self-assembled quantum dots is also discussed.

1. Introduction

For semiconductor materials, the era of nano started in 1960 when D. Khang succeeded in fabrication of Si metal-oxide-semiconductor field effect transistors (MOSFET’S) via thermal oxidation [1]. Six years later, with this device structure, F. Fang et al. observed the two-dimensional nature of the electron gas formed at the inversion layer of Si MOSFET’S for the first time [2]. Until then the low dimensional systems existed only in quantum mechanics textbooks. In 1980 quantum effect was discovered with Si MOSFET’S, which is also the most dominant semiconductor device in semiconductor integrated circuit industry nowadays. However application of Si in optoelectronic devices has been hindered due to the indirect bang gap property of this material until recently extensive research efforts showed possibilities in porous and nano crystal Si materials. Development of semiconductor optoelectronic devices has been performed on direct band gap compound semiconductors mainly, GaAs and InP-based III-V materials. The history of laser diodes development shows the impact of reducing the dimensionality of the active materials on the improvement of the device performances, from double heterostructures, quantum wells, superlattices, and finally to quantum dots (QD), much obliged to the invention of epitaxial growth technologies. [3-4].

2. Selective Formation of QDs

The spatial distribution of self-assemble QD(SAQD) is, in general, random and sometime one need to control the position of QD structures. In this study, two kinds of methods were employed: one is to use the electron beam patterned oxide mask layer, and another is the strained superlattice.

In particular, using the pre-patterned masked substrate, one can assemble the dots in a specific region. In this case the gallium oxide was used as a mask material which can provide a benefit for in-situ formation and removal processes of mask layer. Typical thickness of the oxide layers is approximately 30 nm. The oxide patterns were defined by electron beam lithography (JSM 6400 SEM, JEOL Co.) operating at 35 keV using a 4 % polymethyl-methacrylate (PMMA) positive resist. The beam line-dose and the beam probe current were 1.4 nC/cm and 6 pA, respectively. After development, the samples were etched in buffered oxide etch for 3-5 seconds. The epitaxial growth was performed on GaAs (100) substrates with the pre-patterned oxide layers in a molecular beam epitaxy (MBE; VG80H MK-II) as following procedures; After confirming deoxidation of the reference sample attached together with the lithographically prepared samples on the same Mo-block, a 20 nm GaAs buffer layer was deposited at 570°C before the In$_x$Ga$_{1-x}$As QD growth was started. The self-assembled In$_x$Ga$_{1-x}$As quantum dot formation was performed by the injection of In and Ga flux with a 25 % duty cycle under the As flux of which the beam equivalent pressure corresponds to 1x10$^{-5}$ torr. The growth rate for the self-assembled In$_{0.45}$Ga$_{0.55}$As QDs was 0.40 ML/sec. Typical Indium mole fractions for the growth of QDs were in the range of 0.30-0.43. Rapid cooling down to avoid any annealing
effects was one of the important growth parameters for the formation of the quantum structures reproducibly in this work.

We can see dots selectively formed in two dimensionally arrayed oxide mask layer with the opening widths of 0.1µm x 0.1 µm as shown in Fig. 1. The single QDs and the coalesced 3D islands consisted of two or three QDs were nicely positioned in the patterned regions [5]. Typical size of a single QD formed on the two-dimensionally patterned region is nearly the same as that on the non-patterned substrate.

![Fig. 1 Atomic force micro-scopy image of two-dimensional arrayed InGaAs QDs.](image)

As for another recipe for the positioning of self-assembled QDs, the InAs/GaAs superlattice (SL) was used as a controllable strain-relaxed layer. The controllable strain-relaxed system can provide more appropriate strained layer, compared with conventional bulky one, since it produces strain fields with higher uniformity, enabling more flexible control of alignment of QDs without the need of any complicated pre-processes.

The strained layers formed, consisting of a 1 InAs ML/4 GaAs ML SL, followed by a GaAs spacer layer that was 20 MLs thick. The GaAs spacer layer, which blocks carriers between the SL and QDs, is needed for enhancing optical and morphological properties [6]. In our experiment, the number of cycles of SL, n, was varied as 10, 15, 25, and 30. Finally, we deposited 2 MLs of InAs on a strained layer for the formation of QDs.

Figures 2(a) - (c) show AFM images of the sample surface for n=10, 15, and 30, respectively. As expected, the alignment of QDs occurred in the samples with n≥15, whereas the alignment of QDs in the sample of n=10 was not observed. The QDs in the sample of n=15 firstly aligned in the [110] direction. This result indicates we can precisely control the generation of misfit dislocations along which QDs can be formed selectively. It is interesting to note that the alignment of QDs along the [110] direction becomes dominant as shown in Fig. 2(b). In the case of n=30, as shown in Fig. 2(c), strong alignment of QDs were observed along two orthogonal directions, [110] and [110], across the entire region of the sample. The aligned QDs would be useful for the quantum devices such as Schottky wrap gate single electron transistor (SET) [7].

![Fig. 2 AFM images of aligned QDs (a) n=10, (b)n=15, and (c) n=30.](image)

3. Characteristics of ALE-grown InAs/GaAs QDs

InAs self-assembled QDs were formed on (100) GaAs substrate using alternate source supply of In and As which corresponds to the 3ML in thickness. Figure 3 shows the cross sectional TEM image of a QD. Typical height and width of QD were found to be 6.3 nm and 25 nm, respectively. Typical facet plane of a QD side-wall was {136} and the aspect ratio was 0.25(ratio of height/diameter), indicating a feasible geometrical shape of QD.

![QDs and Ga2O3](image)
Fig. 3 Cross sectional TEM image of a ALE-grown InAs/GaAs QD.

Figures 4(a) and (b) shows the optical properties of the ALE-grown QDs. Not only the ground state but also the excited states are obvious with a full width at half maximum of 28-30 meV in PL spectra as shown in Fig. 4(a). It should be noted that the temperature dependent FWHM of the PL spectra associated with the ground state energy level does not much varied[8]. This indicates that the strong confinement of carriers in the ALE-grown QDs comparing to that of conventional SAQDs which has an advantage for the fabrication of photonic devices such as laser diode and optical amplifier.

4. QD Laser Diodes

QD laser diodes are expected to show significant reductions in threshold current and temperature instability at high temperature (350K within 50-150K) along with the improvement in the dynamical and spectral characteristics. In this work, we report some characteristics of laser diodes using InGaAs/GaAs QDs in an In0.3Ga0.7As quantum well. The laser structure was grown by solid-source MBE on a <100> n+GaAs substrate using atomic layer epitaxy (ALE) method. The laser structure is shown in Fig. 5.

We adopted the quantum dot-in-a-well (DWELL) design by putting six pairs of InAs QDs into strained In0.3Ga0.7As quantum well because of the following advantages: 1) the well enhance the carrier capture by dots, 2) the well suppresses their thermionic emission at high temperature, and 3) the design increases the density of quantum dots to 7×10^{10} cm^{-2} over growth GaAs directly. The peak of PL is about 1.25 \mu m at room temperature. We fabricated the broad area laser diodes (BALDs) with an aperture size of 100\mu m and ridge waveguide laser diodes(RWLDs) with a aperture size of 5, 10, 15, 20, 25, and 30 \mu m to investigate the characteristics of the QDLDs. Figure 6(a) shows the L-I curve of BALDs with cavity length of 2mm at 15°C under the condition of pulse operations (1us/1ms). The slope efficiency is 10% and threshold current density is 1kA/cm^2. Figure 6(b) shows the dependence of electro-luminescence (EL) on the level of injection current. There are several states because of large quantum dot size (~47nm x ~10nm) and with an increasing injection current the emission peak shifts from the longer wavelength side to the shorter wavelength side due to the band filling effect[9].

The stronger emission at higher-order subbands directly reflects the larger degeneracy of eigenstates at them. Fig. 6(b) shows the lasing wavelength, which is different from PL peak (ground state transition)
because there is competition among transition between the possible states in QDs as shown EL data and then the omnipotent high order transition appears at the lasing. Fig. 7 shows the characteristic temperature, \( T_0 = 84K \).

![Graph](image1)

Fig. 6 (a) L-I curve and (b) EL characteristics of BALD.

![Graph](image2)

Fig. 7 Threshold current density of QD-LD as a function of temperature.

5. QD Infrared Photodetector

We also fabricated the QDIP structure using ALE-grown QDs. In particular, three periods of InGaAs QDs/GaAs with a doping concentration of \( 1 \times 10^{18} \text{ cm}^{-3} \) were employed. In order to reduce dark currents, single-sided 40 nm thick \( \text{Al}_{0.3}\text{Ga}_{0.7}\text{As} \) blocking layer was positioned under the top contact layer as shown in Fig. 8.

![Diagram](image3)

Fig. 8 QDIP structure

![Diagram](image4)

Fig. 9. Photocurrent as a function of bias voltage.
Figure 9 shows the photocurrent (PC) spectra taken at 10 K. The photoresponse was observed at 4-8 µm in wavelength. A sharp drop at 5.77 mm was appeared due to gas bsorption during measurement. The PC peaks at ~4-6.8 mm are due to the electron interband transitions from the ground state to the quasi-bound and continuum states whereas the PC peaks at ~7-8 mm are intraband transitions from the QD electron excited states. Also, it might be due to intraband transitions from the QD ground states to QD high-excited bound states. However, no photocurrent was observed at 80 K due to high doping level and dark currents. The structure and doping level need to be optimized further [10].

6. Intermixing - Wavelength Tuning

QD structures with delta-function like density of states is expected to have higher differential gain, lower threshold current density, and higher temperature stability in QD laser, than in quantum well lasers. However, relatively wide inhomogeneous broadening in PL spectrum of self assembled QD’s, due to compositional distribution and size distribution, negates the advantages of QD as an active medium of optical devices such as QD laser diodes and QD IR PD’s. Furthermore, the growing temperature of In(Ga)As/GaAs SAQDs is relatively lower than the normal growing temperature of InGaAs/GaAs material system, inducing defects in QD structures, which degrade the optical quality of the QD devices. Post-growth thermal processes such as rapid thermal annealing with dielectric capping layers can improve the optical property of QD’s and tune the wavelength of interest.

In this study, we have studied the effect of dielectric capping films such as SiO₂ and SiNₓ on the optical properties after thermal annealing of dielectric capped InGaAs/GaAs SAQD structure grown by MOCVD method in order to improve their optical quality. The InGaAs SAQD structure used in this study was grown by MOCVD method on semi-insulating GaAs substrate at 500°C by using TMG (trimethylgallium), TMI (trimethylindium), and AsH₃ as sources of Ga, In and As, respectively. The 840 nm thick GaAs buffer layer was grown at 650°C before the growth of In₀.₅Ga₀.₅As quantum dot and finally a 120 nm thick GaAs layer was grown.

Fig. 10 shows the AFM image of QDs. The density, the aspect ratio, and the lateral size of SAQD were 4x10¹⁰ cm⁻², 0.2, and about 30 nm, respectively, which was confirmed by AFM. Thermal annealing of samples was carried out at 700°C under N₂ gas ambient for the time range from 1 min to 4 min. After the thermal annealing, PL measurement has been carried at 18K for the characterization.

Figure 11 shows PL spectra before and after thermal annealing. The as-grown SAQD sample showed its PL peak at 1162 nm with FWHM value of 68.9 meV. There are red-shifts in the SiO₂ capped sample and SiNₓ capped sample after dielectric capping without annealing, which may be attributed to the strain near semiconductor-dielectric interface. As shown in Fig. 11, PL peaks of SAQDs were blue-shifted up to 157 meV as the annealing time increased from 1 min to 4 min. The increase of a blue-shift with annealing time is attributed to the intermixing of In and Ga atoms in SAQD structure. It has been well known that the thicker dielectric capping induces larger blue-shift when SiO₂ and SiNₓ film are used capping film. Therefore the blue-shift for SiNₓ-SiO₂ capped sample is larger than that for SiO₂ capped sample at the same annealing time[11].
As shown in Fig. 11, FWHM of PL spectrum was narrowed from 76 meV to 47 meV as the annealing time increased. The reduction of FWHM may be attributed to both the size and compositional changes in SAQDs. Note that the increase in integrated PL intensities for SiNx-SiO2 capped samples is larger than that for SiO2 capped samples. It has been well known that SiO2 capping layer induces larger defects near interface than SiNc capping layer. Furthermore, since thermal expansion coefficient of SiO2 is smaller than that of SiNx, the strain generated near interface during high temperature annealing process would be smaller for SiNx-SiO2 capped region than that for SiO2 capped region because the thermal expansion coefficients of SiO2 and SiNx are smaller than that of GaAs. These facts may result in the reduction of strain induced defect indiffusion and consequently result in larger increase in the integrated PL intensity for SiNx-SiO2 capped sample.

7. Quantum dot superluminescent diodes (QD-SLDs)

SLDs are light sources having characteristics of high optical output power and simultaneously broad spectral bandwidth. Key technique is to suppress Fabry-Perot lasing mode in the devices. They are very attractive for the applications to optical coherence tomography (OCT), fiber optical gyroscope, and wavelength division multiplex passive optical network [12-14].

![Fig. 12. Characteristics of an uncoated 2-mm-long QD SLD under the pulse mode: (a) Light power versus current characteristics for, (b) Emission spectra of a QD SLD at the various injection current levels. [15,16]](image)

SLD's were fabricated on the same InGaAs QD structures that were utilized for the LD's. An active region was clearly defined by a triangular SiO2 window. Metals for the p-ohmic contacts were evaporated in the form of 7° tilted triangular p-electrodes [17]. The taper angle is 3° with the center axis tilted by 7°. The length and the aperture of the fabricated QD SLD's are 2 mm and 100 µm, respectively. These types of SLD's are very useful to suppress Fabry-Perot spectral modulation because an unpumped absorbing region is formed at the end of the taper and there is negligible reflection at the other end of the taper due to the tilt by 7°.

Uncoated diodes are tested in the pulse mode. The pulse width and the repetition rate are 3 µs and 1 kHz, respectively. Figure 12 shows the L-I characteristics and the measured emission spectra at different injection currents of the QD SLD. From Figure 12 (a), an abrupt change in the slope (that is, turn-on of SLD) occurred around 4 ~ 5 A. The optical power linearly increases up to 0.9 W with a slope efficiency of 26%. It
should be noted that the output power starts to increase around 4 ~ 5 A. This turn-on current is slightly higher than that of QW SLD’s with a similar geometry [17]. The higher turn-on current is attributed to loss due to the low-temperature growth (about 510°C) of the QD structures. From Figure 12(b), the emission spectra are asymmetric and are shifted to the shorter wavelength region with increasing injection current. The asymmetric emission of QD SLD’s is believed to be closely related to the material gain spectra and is attributed to the contribution of excited QD states. The 3-dB bandwidth of the QD SLD’s is around 93 nm. This value of the 3-dB bandwidth is much higher than those of muti-quantum-well (MQW) SLD’s with normal QW’s and chirped QW’s [18]. The modulation depth was measured to be in the range of 3 ~ 6%. When it is considered that the 7° tilt angle of the p-electrode was optimized at a wavelength of 1.55 µm [17], it is reasonable that the reflectivity of QD SLD’s might be high at the emission wavelength of QD SLD’s around 1 µm. That was the reason the modulation depth was a little bit high. We believe that the modulation depth will be suppressed if the angle is optimized at a wavelength of 1 µm. These results imply that utilizing QD’s is very attractive for SLD’s with wider spectral bandwidths. When the QD size is controlled and the QD size at the each stack layer is variable (we name the structures chirped QD’s because they are quite similar to chirped QW’s), SLD’s with much wider spectral bandwidths over 93 nm, can be obtained.

8. Conclusions

We have reviewed the impact of nanotechnology on semiconductor optoelectronic devices. Certainly, QD structures promise new functionality and improved performance in these devices. However, to enter the nano-cosmos, we are facing challenges in design, growth, post-growth treatment of semiconductor low dimensional device structures. Some examples of such efforts from our laboratory are presented. The national or global alert to this new cosmos is providing a great opportunity for researchers around the world.

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