CHAPTER TWO

Formation and optical properties of InAs quantum dots with low densities and long emission wavelengths

2.1 Introduction

A quantum dot is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (pairs of conduction band electrons and valence band holes) in the three dimensions of space. A quantum dot is often referred to as an 'artificial atom', because it has discrete energy states for electrons, similarly to an atom (Fig. 2). The energy spectrum of a quantum dot can be engineered by controlling the geometrical size, shape, and the strength of the confinement potential. Since the proposal by Arakawa and Sakaki, many groups have attempted to fabricate quantum dots, mainly using photo or electron-beam (EB) lithography and epitaxial growth on mask-patterned substrate. However, the crystals fabricated by these processes suffered from process damages (interface degradation, contamination, *etc)*, resulting in optical property degradation. Break-through technology for fabricating quantum dots have occurred at 1985, which indicated the transition from 2D nucleation to the formation of 3D islands using InAs materials on GaAs substrate.

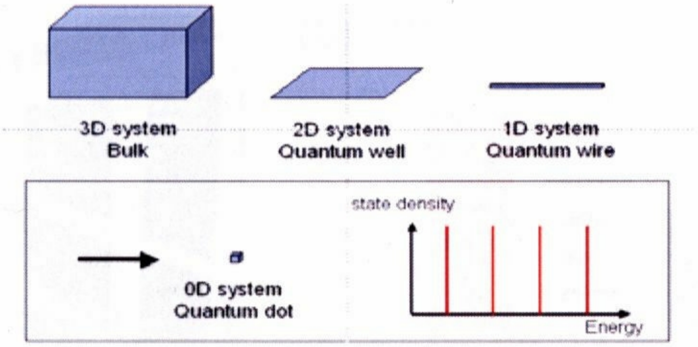


Fig.2-1 Schemes of bulk, quantum well, quantum wire and quantum dot.

This transition is called Stranski-Krastanow (SK) growth mode and quantum dots grown by SK mode are self-assembled quantum dots.These days, self-assembled quantum dots can be successfully grown by molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). Quantum dots (QDs) used in this study were fabricated by MOCVD because it has many advantages. The advantages of MOCVD are as follows:

(1) MOCVD has economical advantages over MBE technique, especially in terms of productivity of semiconductor optical or electronic devices. One growth run tales one or two hours with MOCVD, while MBE growth nees many hours of preparation

(2) The operating pressure of MOCVD(~76Torr) is much higher than that of MBE(~10^{-10}Torr) and thus it requires less effort to maintain the state of operating pressure in MOCVD than in MBE.

2.2 Formation of InAs quantum dots with low densities and long emission wavelengths

MOCVD system is shown in Fig.2-2(a). All samples were grown using trimethylindium (TMI), trimethylgallium (TMG), triethylgallium (TEG) as the group Ⅲ sources, and tertiallybutylarsine (TBA) as the group Ⅴ source. The total background pressure during the growth was 76 Torr. Growth procedure is shown in Fig.2-2(b).

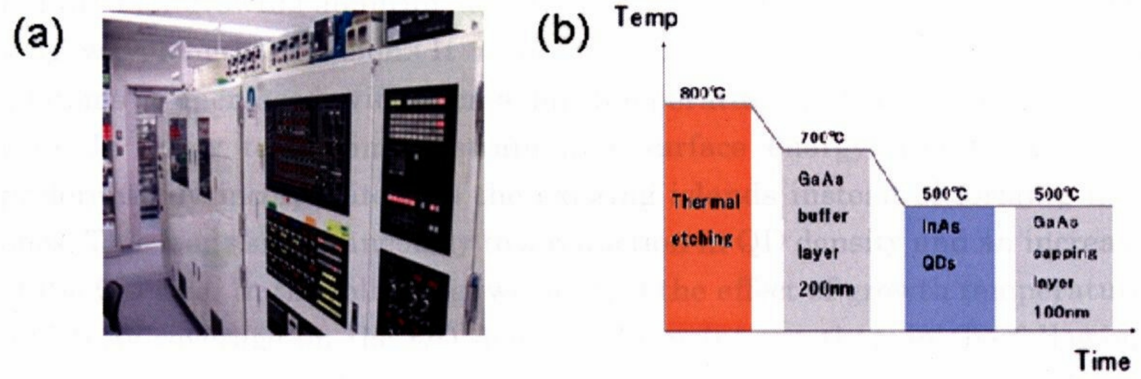


Fig.2-2 (a) Pictures of MOCVD system. (b) schematic diagram of the growth procedure.

After oxide desorption at 800°C, a 200 nm GaAs layer is deposited at 700°C using TMG and TBA. Substrate was then cooled down to 490-540°C and the growth of InAs QDs is done using TMI and TBA. Finally, InAs quantum dots are capped by 100nm GaAs, using TEG and TBA. In case of samples for AFM measurement, capping process is omitted.

In the growth of self-assembled InAs QDs, the QD size, i.e. height and diameter, QD shape, size distribution, composition, density and the related optical characteristics, depend on the growth conditions such as the growth temperature (GT), growth rate (GR) and InAs coverage (θ), i.e. growth time. In this study, we will focus on the QD density and size, via the QD height, and to a lesser extent, on the size distribution. Figure.2-3(a) shows the 1 × 1 μm^2 AFM image of the reference sample, previously used for the fabrication of QD lasers.[i] The QDs are grown with a nominal InAs coverage of 2.32 ML, at 500 °C with a growth rate of 0.011 $ML.s^{-1}$. This QD layer yields a density of ~1.5×10^{10} cm^{-2}, with average height of 9 nm. This QD density is appropriate to fabricate QD lasers, with reasonable values of modal gain, but is too high to fabricate single photon sources, or even allow the observation of single dot emission by μ-PL measurement. In order to grow quantum dots with low density suitable for observation of single dot emission and long emission wavelength, we investigated the QD growth conditions.

(a) Growth of low density and big size InAs QDs with high growth temperature

In general, a low growth rate and/or a high growth temperature are required for growing quantum dots with low density and big size, suitable for long wavelength emission. It is because the migration length of the In adatoms is increased with increasing temperature and decreasing growth rate. In order to minimize strain and surface energy, the In adatoms preferentially incorporate into the existing islands instead of forming new ones. This leads simultaneously to a reduction in QD density and an increase of the QD size. In the following, we studied the effect of growth temperature and InAs coverage on the QD density. We point out that, in the following studies, we maintained the InAs growth rate at 0.011 $ML.s^{-1}$. Indeed, a lower growth rate leads to a decrease of the QD density. However, it also leads to a broadening of the linewidth, as reported in Ref. 24, as well as an increase in the size of the coalesced dots, i.e. plastically-relaxed islands, which are detrimental for the QD emission efficiency. Since, as shown below, the effect of decreased InAs coverage has turned out to be very effective in achieving ultra-low density of 10^6-10^7 cm^{-2}, the effect of growth rate has not been studied. We point out also that, in all experiments, the V/III ratio was maintained to ~ 0.3.

In order to decrease the QD density, the growth temperature was increased. Figure.2-3(b) shows the AFM image of a InAs/GaAs QD layer grown with identical InAs coverage and growth rate as that shown in Fig.2-3(a), but at 520 °C. The density is equal to ~7.5×10^9 cm^{-2}, the size distribution remains unimodal, with average island height of ~11 nm. There is thus a significant effect of increasing growth temperature.

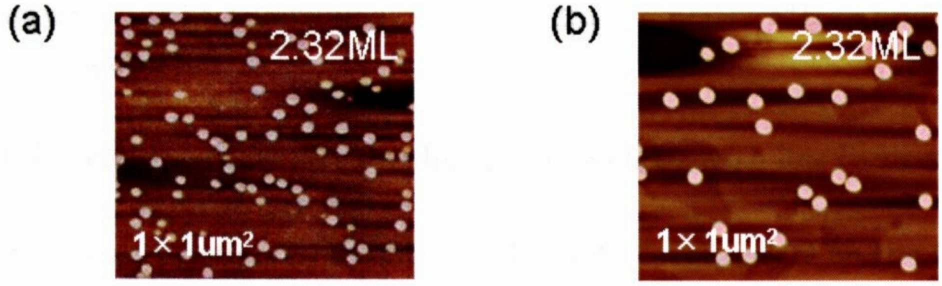


Fig.2-3 AFM images of self-assembled InAs quantum dots grown with *GR*=0.011 ML/s and θ=2.30 ML at different temperatures: (a) 500°C (b) 520°C

	(a) 500℃	(b) 520℃
Density	~10^{10}cm^{-2}	~10^{9}cm^{-2}
Height	9nm	11nm

Table.2-1 Average sizes and densities of self-assembled InAs quantum dots grown at different temperatures. (a) 500°C (b) 520°C

As shown in Fig.2-3, quantum dots which were grown at 520°C, have lower density and bigger dot size than quantum dots which were grown at 500°C. The specific size and density were analyzed by AFM, and are shown in Table.2-1. In the following, we chose to maintain the growth temperature at an intermediate value of 520 °C, mainly for two reasons. The first one is the fact that for capped QD samples, a quite low capping temperature of ~500

°C is required, in order to prevent significant In/Ga intermixing and induced emission blueshift. Thus, a growth interruption (GI) is required, and the higher is the QD growth temperature, the longer should be the growth interruption time, in order to decrease the wafer temperature. However for too long GI, we observed a decrease in PL intensity, probably due to diffusion of the In adatoms from the coherent islands towards the coalesced dots, and induced increase of the dislocation density. The second reason is that for too high growth temperature, the emission wavelength does not increase further, despite the slight increase in QD size. This is probably due to In evaporation and change in composition of the InAs QDs, with enhanced incorporation of Ga atoms. In order to maintain a high PL emission efficiency, we thus chose in the following to maintain the QD growth temperature at 520 °C. Hence the growth conditions of all QD presented in the following are grown with GR=0.011 ML.s^{-1} and GT=520 °C unless specified.

(b) Growth of low density and big size InAs QDs with low InAs coverage

Then, we investigate the effect of the InAs coverage (θ) on the QD density and size. Figure.2-4 shows the AFM images of InAs/GaAs QD layers grown with various InAs coverage which is varied between 1.95 and 2.1ML. And Fig.2-5 shows the QD density and island height dependence on the InAs coverage.

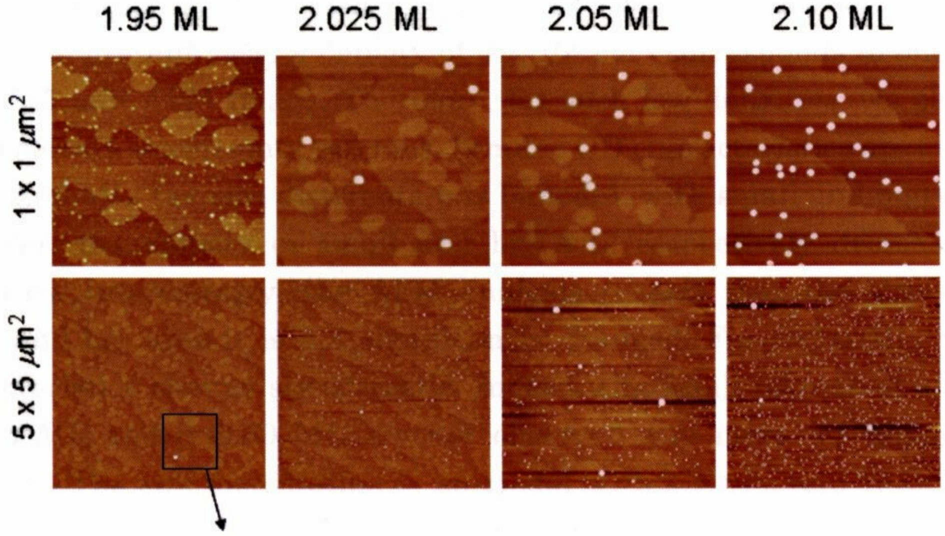


Fig.2-4 AFM images of InAs/GaAs QD layers grown with various InAs coverage

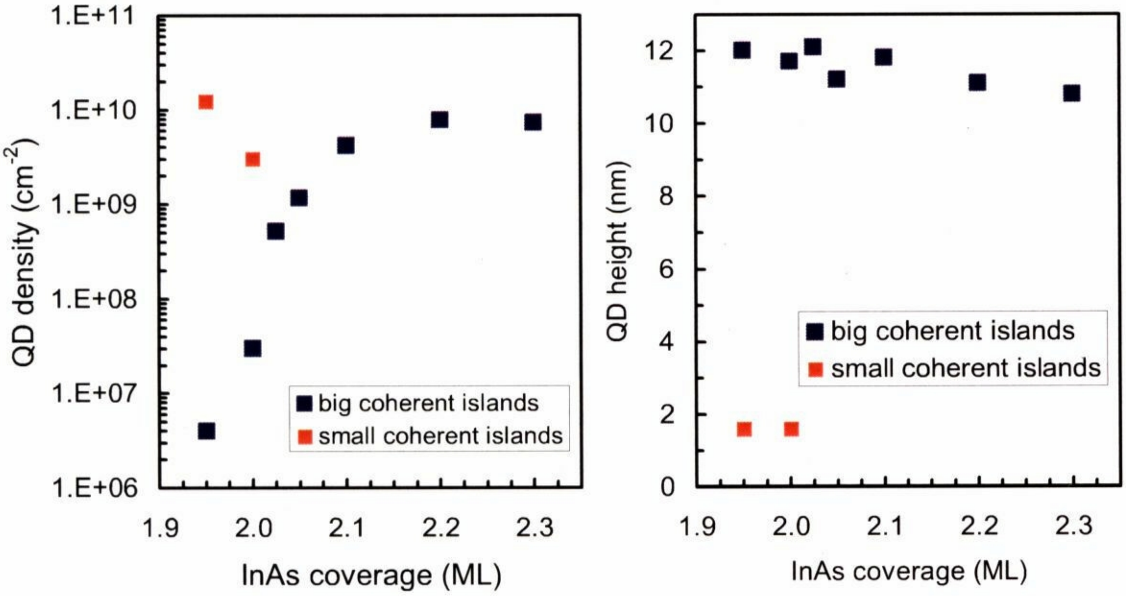


Fig.2-5 QD density and height dependence on InAs coverage

For θ=1.95 ML, the layer is composed of a bimodal distribution, with a high density of small-size islands of average height of ~1.5 nm and density of $\sim 1.3 \times 10^{10}$ cm^{-2}. These small three-dimensional islands are located both on top of the surface terraces and at the terraces steps. We observe also the presence of much bigger coherent islands with average height of 12 nm, as pointed by the arrows on the corresponding 5×5 μm^2 AFM image. The approximated density of these bigger islands is around 4×10^6 cm^{-2}. For such low densities, the density is extracted from 5×5 μm^2 AFM images, and in the present case, a density of 4×10^6 cm^{-2} corresponds to one island per 5×5 μm^2 AFM image. Therefore, for such low densities, we point out that a certain uncertainty remains. Similar QD characteristics are observed for θ=2.00 ML: the size distribution is bimodal, with small and bigger dots. However, the density of small and big dots respectively decreases and increases. Interestingly, the AFM analysis reveals that the size of both small and big islands is not significantly changed. For θ>2.0 ML, the QD characteristics change significantly. Indeed, the small islands observed at θ=1.95 ML and θ=2.00 ML are not observed any more for higher InAs coverage. The size distribution is unimodal with big coherent InAs islands with height in the range of 10-12 nm, as shown in Fig.2-5. We note also for θ>2.05 ML the onset of coalescence, with the appearance of giant dots with height up to 15 nm and diameter of up to 140 nm. Simultaneously, the density of the big coherent InAs islands increases gradually with increasing InAs coverage, from 4×10^6 cm^{-2} to 7.8×10^9 cm^{-2} for θ equal to 1.95 and 2.20 ML, respectively. For higher InAs coverage, the density is constant and even decreases for $\theta > 2.4$ ML, at the expense of an increase of the size and density of coalesced dot density (not shown here).

The achievement of such low densities for InAs coverage just above the InAs coverage for the two dimentional – three dimentional transition is not so surprising, the most striking feature is that the QD size is almost constant over the entire range of coverage, with height ranging between 11 and 12 nm. Besides, the lowest densities of InAs/GaAs QDs with high coherent size are extremely low, below 10^7 cm^{-2}. Such densities are significantly lower than those obtained, for instance, by Alloing *et al.*, who achieved QD layers with density of 2×10^8 cm^{-2} by MBE, with significantly lower InAs growth rate of 0.0012 ML.s^{-1}. As soon as there is formation of InAs islands, the latter reach a large size. This is possible because of the large diffusion length of the In adatoms, induced by the combination of low growth rate and high growth temperature. In the case of lower growth temperature, typically 500 °C, the size distribution is bimodal in the low coverage range. We note also the formation of giant coalesced dots, with height of ~40 nm, appearing for all the samples for $\theta > \sim 2.05$ ML.

2.3 Optical properties of InAs quantum dots with low densities and long emission wavelengths

To investigate the optical properties of low density quantum dots, a second QD sample was grown under the same conditions except that the dots were capped by 100 nm thick GaAs. Photoluminescence (PL) characteristics were measured at RT using liquid-nitrogen cooled InGaAs photodiode array, with the excitation of a semiconductor laser. The diameter of laser spot was about 50um. Figure.2-6 shows the macro PL spectra of low density (~10^8cm^{-2}) QD sample measured at different excited powers. The PL spectra exhibit two emission peaks at 1.37um and 1.28um, which corresponds to the ground state and the first excited state transition, respectively. Because of low QD density, the first excited state transition is dominant at high excited power (P=3mW). When we decreased the excited power, ground state transition became dominant.

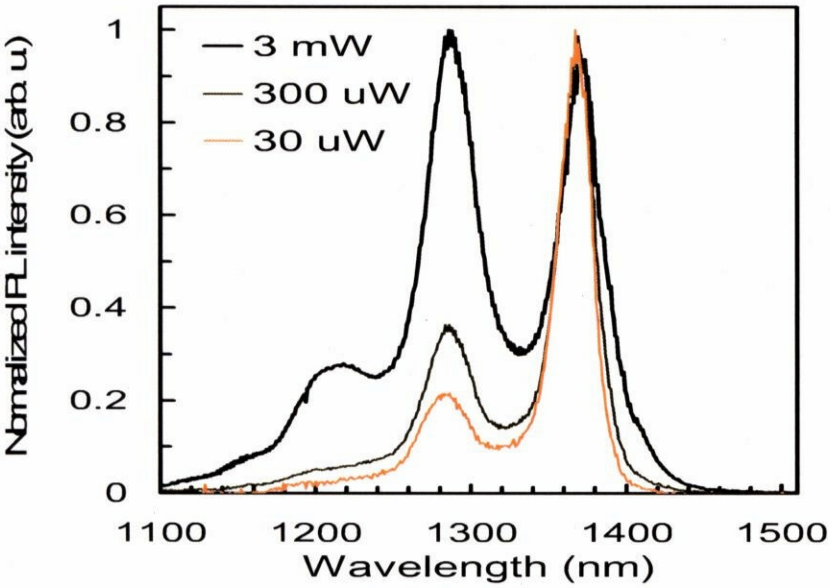


Fig.2-6 Macro PL spectra of low density (~$10^8 cm^{-2}$) QD sample at different excited powers

Next, micro PL measurements were performed with the sample held at 5K in a continuous flow helium cryostat. A continuous-wave helium-neon laser (λ= 632.8nm) was used as a pump laser. The pump laser was focused onto the sample surface through an objective lens. The diameter of the focused spot of the pump laser was about 4 um. The PL signals were collected through the same objective lens and coupled to a multimode optical fiber using a lens. The fiber led the signals to the entrance slit of a single-grating monochromator. Finally, the dispersed signals were measured using an InGaAs detector array. Micro PL spectrum of low density (~$10^8 cm^{-2}$) QD sample was shown in Fig.2-7. As shown in Fig.2-7 (a), the PL spectrum exhibits very sharp peaks of which emission wavelengths vary from 1000nm to 1300nm. By high-resolution measurements using a triple-grating monochromator, we found that these sharp emission peaks came from individual quantum dots. (Fig. 2-7 (b)) From these results, we can conclude that single dot spectroscopy has been achieved without any structure.

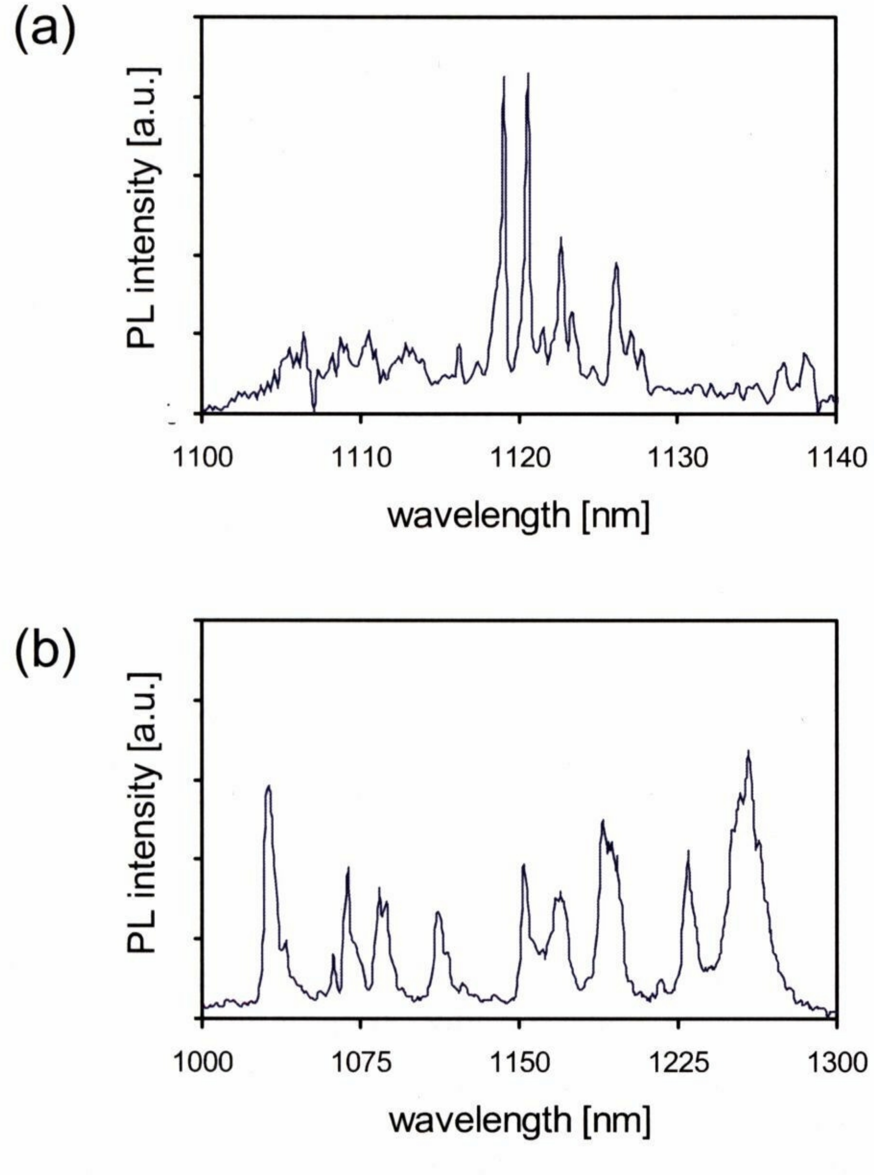


Fig.2-7 Micro PL spectra of QD sample which has low density. (a) narrow range spectrum (b) wide range spectrum

Fig.2-8(a) shows the laser power dependent micro PL spectra performed with Ti-Sa laser emitting at 800 nm. PL spectra show two emission peaks at 1157.76nm and 1159.33nm which are attributed to exciton(X) and biexciton(XX), respectively. The biexciton binding energy was calculated as about 1.45meV. At low pump power, X line has higher intensity than XX.

With increasing laser power, however, the intensity of XX line became higher than that of X line. The PL intensities of X and XX lines are plotted in Fig.2-8(b) as a function of excitation power. The square of X PL intensity was proportional to the XX PL intensity and it confirms that the XX line corresponds to biexciton emission. As a conclusion, exciton/biexciton behavior was clearly observed at low temperature. It reveals that low density quantum dots also have good carrier confinement.

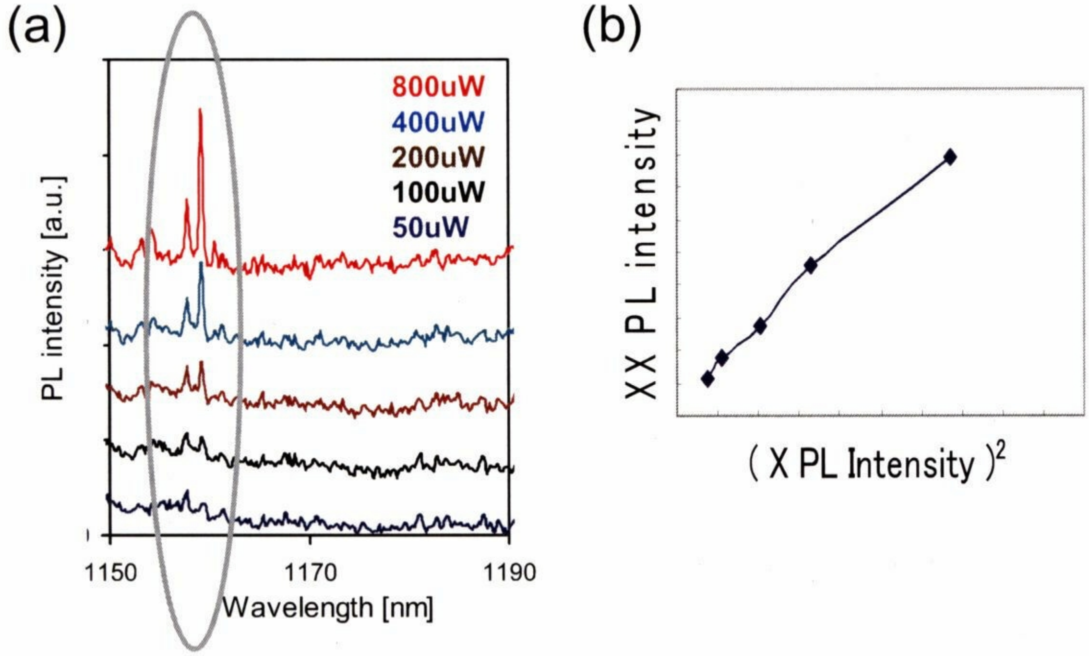
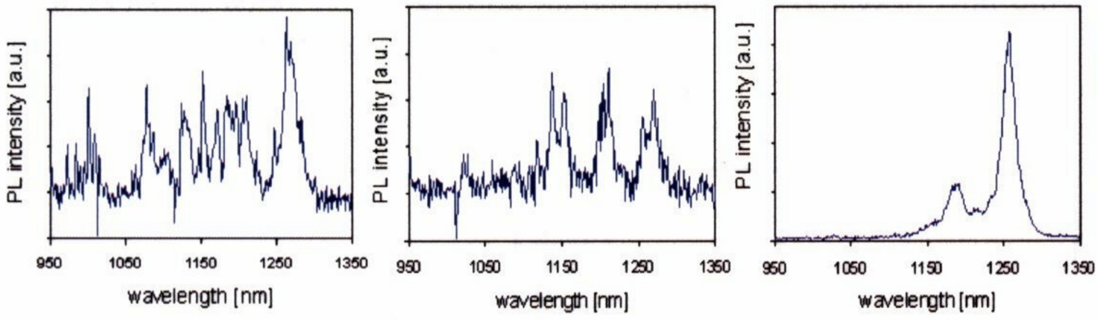


Fig.2-8(a) PL spectra at different excitation powers (b) dependence of the XX-PL intensity versus the X-PL intensity

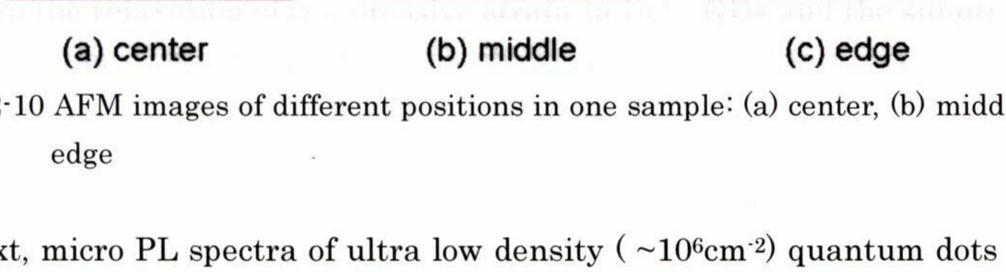
Then, we carried out micro PL measurements at 5K with ultra low density ($<10^7$cm^{-2}) samples. To perform the PL measurements, QD samples were also capped by 100nm thick GaAs capping layer. Micro PL spectra of low density ($\sim10^7$cm^{-2}) QD sample were shown in Fig.2-9.



(a) center (b) middle (c) edge

Figure.2-9 Micro PL spectra of low density (~10^{7}cm^{-2}) quantum dots at different positions: (a) center, (b) middle, (c) edge

As shown in Fig.2-9, the PL spectra exhibit very sharp emission peaks from individual quantum dots. Emission peaks from quantum dots increases when we approach to the edge, and finally QD emission peaks become ensemble in the edge due to the position dependence. Difference of QD density exists even in one sample due to the gradient of deposited source material. As shown in Fig.2-10, QD density of edge is hundred times higher than that of center in case of ultra low density (~10^{7}cm^{-2}).



(a) center (b) middle (c) edge

Fig.2-10 AFM images of different positions in one sample: (a) center, (b) middle, (c) edge

Next, micro PL spectra of ultra low density (~10^{6}cm^{-2}) quantum dots were measured. Fig.2-11 shows the micro PL spectra of ultra low density

($\sim 10^6 cm^{-2}$) quantum dots measured at different positions near in the middle. Only a single peak has been measured throughout the wide range (950nm-1400nm) using single-grating monochromator. It means that only a single dot exists in the laser spot (radius: ~2um).

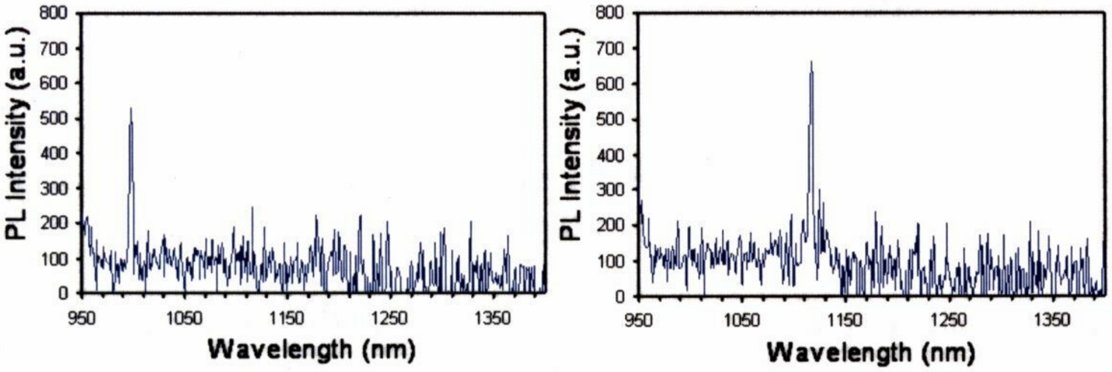


Figure.2-11 Micro PL spectra of low density ($\sim 10^6 cm^{-2}$) quantum dots at different positions near in the middle

2.4 Approach towards long emission wavelengths with SRL

We have succeeded in achieving ultra low density ($< 10^7 cm^{-2}$) quantum dots using low InAs coverage and high temperatures. For emission wavelengths, however, emission peaks which have wavelengths over 1.3um weren't measured in case of micro PL at 5K. In order to achieve long-wavelength emissions over 1.3um, we added InGaAs SRL (strain reducing layer) between InAs QD growth and GaAs capping layer. Using the InGaAs SRL between the InAs and GaAs, the band gap energy of InAs QDs is shrunken due to the relaxation of compressive strain in InAs QDs and the suppression of quantum confinement effect, as shown in Fig.2-12 .As a result, the PL peaks of InAs QDs shifts towards a longer wavelength.

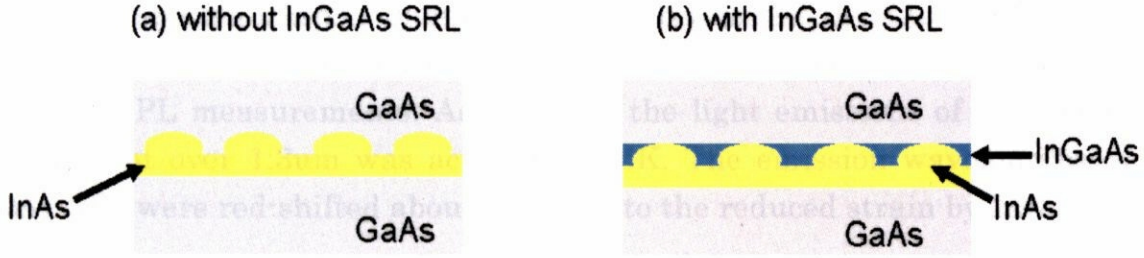


Figure.2-12 Schematic illustrations of self-assembled InAs QDs : (a) without InGaAs SRL, (b) with InGaAs SRL

We performed the QD growth under the same growth conditions as ultra low density (~10^7cm^{-2}) quantum dots except that the dots were capped by InGaAs SRL before capped by GaAs capping layer. In content of InGaAs SRL was 12 percent and the thickness of SRL was about 4nm. Fig.2-13 shows the macro PL spectrum of InAs quantum dots embedded in InGaAs SRL measured at room temperature. Emission peak which corresponds to the ground state transition was observed at 1.43um.

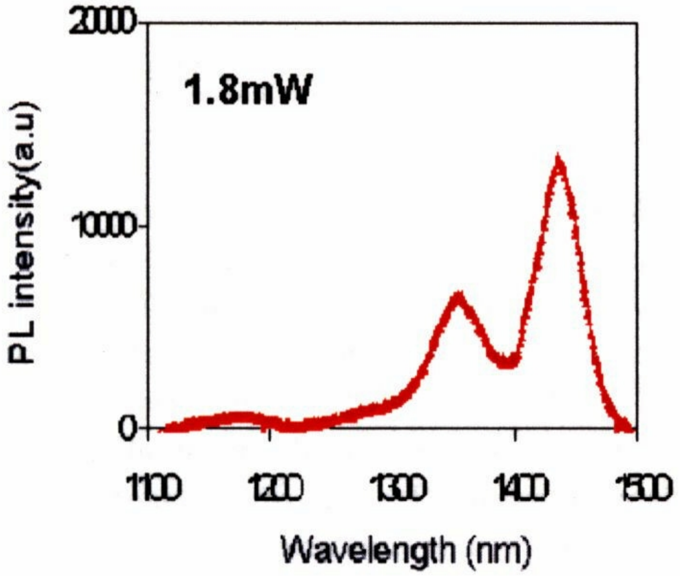


Figure.2-13 Room temperature macro PL spectrum of InAs quantum dots embedded in InGaAs SRL.

Next, Micro PL measurements were carried out at 5K. Fig.2-14 shows the micro PL spectra of InAs quantum dots embedded in InGaAs SRL. Single grating monochromator and triple grating monochromator were both used for micro PL measurements. As a result, the light emissions of InAs QDS emitting at over 1.3um was achieved at 5K. The emission wavelengths of InAs QDs were red-shifted about 1um due to the reduced strain by InGaAs SRL.

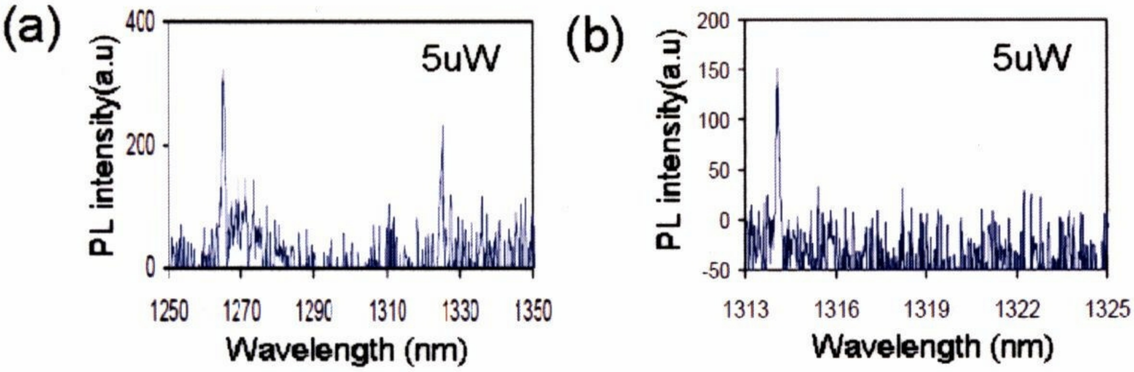


Figure.2-14 Micro PL spectra of InAs quantum dots embedded in InGaAs SRL
(a) by single monochromator (b) by triple monochromator

2.4 Conclusion remarks

In this chapter, we have successfully grown self-assembled QDs which have low density and long emission wavelength by metal organic chemical vapor deposition. First, low density quantum dots (~10^8cm^{-2}) were achieved using high growth temperature. High growth temperature leads to a reduction in QD density and also increasing in QD size. With these low density quantum dots, we performed the macro PL measurements at room temperature and micro PL measurements at 5K. Both PL measurements proved the good optical quality of low density quantum dots. Particularly, in the micro PL measurements at 5K, single dot spectroscopy has been achieved without any structure and clear exciton/biexciton behavior has been observed. Next, we fabricated ultra low density (<10^7cm^{-2}) quantum dots using low InAs coverage. As a result of micro PL, only a few peaks from individual dots has been achieved. For ultra low density growths~10^6cm^{-2}, only a single peak has been observed throughout the wide range wavelength. Such ultra low QD density makes the fabrication of single photon sources easy. Then we have succeeded to achieve the light emissions over 1.3um at 5K using InGaAs strain reducing layer. The emission wavelengths of InAs QDs were red-shifted about 1um due to the reduced strain by InGaAs SRL.