Effect of GaP and $In_{0.4}Ga_{0.6}P$ Insertion Layers on the Properties of InP Nanostructures Metal-Organic Vapor Phase Epitaxy

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***Abstract*— The effect of increasing GaP and InGaP insertion layers thickness (0-4) monolayers (MLs) to improve the structural and optical properties of InP self-assembled quantum dots (SAQDs) on GaAs (001) substrate grown by metal-organic vapor phase epitaxy was reported. The growth of thin GaP and InGaP insertion layers between $In_{0.49}Ga_{0.51}P$ buffer and InP QDs layer reduced the mean height and size fluctuation and increased the density of InP QDs. A maximum QDs density of 4.2×10^9 cm^{-2} and better and smaller QDs size and uniformity had been achieved at 2 ML GaP and InGaP insertion layers. The blue-shift of the PL peak was enhanced by insertion of GaP and InGaP layers. Due to InGaP insertion layer, a more blue-shift of the PL peak emission was also observed. InGaP insertion layer led to better QDs quality and higher PL intensity compare to that of GaP insertion layer.**

***Keywords*— InP, GaP, InGaP, Self-assembled Quantum Dots (SAQDs), Metal-Organic Vapor Phase Epitaxy (MOVPE), Atomic Force Microscopy (AFM), Photoluminescence (PL)**

I. Introduction

SAQDs grown using molecular beam epitaxy (MBE) or metalorganic vapor phase epitaxy (MOVPE) have recently attracted much interest from the view point of both fundamental physics and device applications in devices like semiconductor lasers, photo-detectors, optical memories etc.[1]. The direct formation of QDs on planar substrates using Stranski-Krastanov (S-K) growth has been introduced to achieve defect-free QD materials [2]. In particular, in order to achieve the predicted high efficiencies in QDs device applications, the QDs must be uniform in size and periodically distributed in all three-dimensions.

Advantageous of QD-based optoelectronic devices are the formation of defect-free, ordered arrays of uniform quantum dots, conditions realized in the InP/$In_{0.49}Ga_{0.51}P$ system. InP SAQD growths have also been investigated on GaAs and GaP substrates by several groups [3-7]. The lattice mismatch between InP and $In_{0.49}Ga_{0.51}P$ (lattice matched to GaAs) of 3.8% is also provided sufficient strain to form QDs via the SK mechanism. InP QDs grown on GaAs by insertion of III-V compound layers are less well studied than InAs QDs grown on GaAs by insertion of III-V compound layers. We here review the main experimental evidence of InP QDs embedded in InGaP matrices grown on GaAs (100) substrates by insertion of GaP and InGaP layers. QD (or island) densities ~10^9 cm^{-2} and size distribution and optical properties of InP QDs have been reported. In the theoretical model of the S-K growth mode, QD growth depends both on the strain and the surface condition of the layer upon which the dots are grown [8-10]. Therefore, the insertion of GaP and InGaP layers between $In_{0.49}Ga_{0.51}P$ and InP QDs layers are also expected to change the morphology and growth characteristics of the InP SAQDs. Various growth parameters, such as the growth temperature, growth time, V/III ratio, and the substrate oriention angle, are not changed and (2-4) ML GaP and InGaP layers are inserted to characterize structural and optical properties of InP QDs by atomic force microscopy (AFM) and photoluminescence (PL) [11-13]. Otherwise, GaP and InGaP, compressive strained materials on GaAs, have been reported to improve the structural and optical properties of InP QDs.

II. Experimental Details

In this study, quantum dots composed of InP embedded in $In_{0.49}Ga_{0.51}P$ matrix were carried out in a horizontal MOVPE reactor AIXTRON, AIX200/4 with a rotating substrate holder on nominally (001) oriented GaAs substrate. The inlet of the reactor is divided into two parts: Group-III precursors were introduced from the upper inlet and group-V precursors were introduced from the lower inlet. Hydrogen gas was used as the carrier gas for precursors and as coolant between the inner reactor and the outer tube. The reactions occur in a rectangular inner liner tube, which has a graphite rotator as a sample susceptor. During MOVPE growth, GaAs substrates were placed at the center of the susceptor. For InP QDs on GaAs substrate growth, trimethylgallium (TMGa) and trimethylindium (TMIn), tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP) were used as source precursors. Epitaxial growth conditions were a total pressure of 100 mbar,

H_2 total flow rate of 13,000 SCCM (SCCM denotes cubic centimeter per minute at standard pressure), temperature of 610 °C, and V/III ratio of source precursors of 18 for InP. Lattice-matched $In_{0.49}Ga_{0.51}P$/GaAs structures are becoming major III-V semiconductor systems because, they have lower reactivity with oxygen, and more reduced DX centers and lower interfacial recombination rates, compared to AlGaAs/GaAs systems. Fabrication of InP SAQDs in InGaP/GaAs systems is difficult by metal organic vapor phase epitaxy (MOVPE), mainly due to the exchange between As and P. The other causes that contribute to the difficulty include the ordering effect of InGaP and the segregation of In in the InGaP layer. Schematic representation of the InP QDs structure embedded in InGaP barrier grown on (001) GaAs substrate was depicted in Fig. 1.

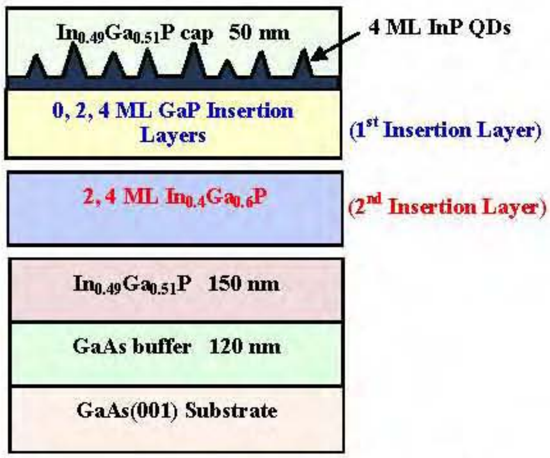

Fig. 1 Schematic diagram of the vertical layer structure of InP QDs grown on (001) GaAs substrate by insertion of GaP & InGaP layer

120 nm GaAs buffer layers were grown on semi-insulating GaAs (001) substrates at 610 °C. After the growth of GaAs buffer, growth of 150 nm lattice-matched $In_{0.49}Ga_{0.51}P$ layers was followed at the same temperature. In all growth process, the growth temperature was fixed at 610 °C. Then, 0 - 4 MLs GaP insertion layer was deposited to improve QDs size uniformity. Finally, the single-layer of self-assembled InP QDs was grown at a growth rate of 0.5 ML/s by depositing 4 ML of InP. After the growth of InP QDs, 50 nm cap of InGaP followed in the case of samples planned for PL measurements. For comparison of GaP insertion layer (IL), another InGaP (2-4) ML insertion layers were inserted between GaP and $In_{0.49}Ga_{0.51}P$ buffer layers in the next growth structure. Insertion of GaP and InGaP layers in the materials system InP/InGaP/GaAs by the Stranski-Krastanow technique in MOVPE technique is less well studied than other material systems. We here review the structural, morphological and optical properties of InP QDs due to insertion of 0, 2, 4 MLs GaP insertion layer by using atomic force microscopy (AFM) and photoluminescence (PL). The AFM measurements were performed by using a nanoscope in close-contact mode. PL measurement was carried out using the 532 nm line of solid state laser. The PL signal was collected by an InGaAs photo-detector.

III. Results and Discussion

A. Structure Properties of InP Quantum Dots by Atomic Force Microscopy (AFM)

The AFM images of the InP QDs grown on GaP and InGaP ILs are shown in Fig. 2 (a) – (e). The average height and diameter of InP QDs without GaP IL are 25 nm and 85 nm. Both size and height are generally decrease by increasing the thickness of GaP insertion layer. The sample with 2 ML GaP insertion layer showed a significantly improved size, height dispersion and homogeneity. The dot density increases from 2.3×10^9 cm^{-2} to 4.2×10^9 cm^{-2} due to insertion of 0 ML - 2 ML GaP layers and then decrease again to 3.3×10^9 cm^{-2} due to insertion of 4 ML GaP layer. The maximum density in 4.2 $\times 10^9$ cm^{-2} and smallest uniform InP QDs were obtained with 2 ML thickness of GaP insertion layer. After insertion of 2 ML GaP layer thickness, the QDs size was quite increase and density was decrease again. This observation indicated that QDs density first increased with increasing of GaP insertion layer thickness and then it saturated at 2 ML GaP insertion layer thickness. Such behavior showed the nuclei centers first

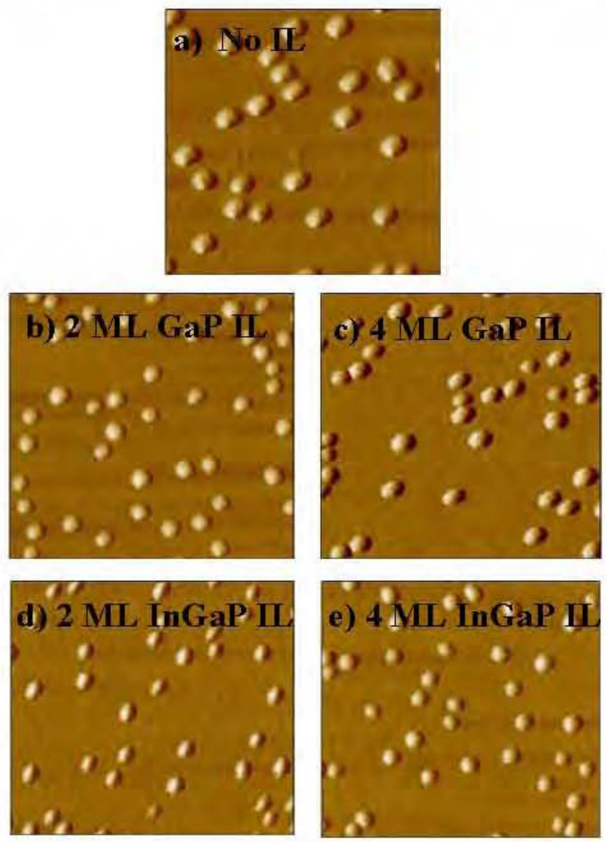

Fig. 2 Typical (1μm × 1μm) scan range AFM images of InP QDs embedded in InGaP barrier with GaP and InGaP insertion layers (a) No IL (b) 2 ML GaP IL (c) 4 ML GaP IL (d) 2 ML InGaP IL (e) 4 ML InGaP IL

increased with the increase of GaP insertion layer thickness from 0 ML to 2 ML, afterwards nucleation was completed and further increased in the thickness did not significantly increase the density of QDs. It is likely that the incorporation efficiency of In during the deposition of GaP layer reduces as the strain increases.

For reasons of comparison, samples with InGaP ILs were fabricated. The comparison of density and diameter of InP QDs grown with GaP and InGaP insertion layers are shown in Fig. 3(a) and (b). By using an InGaP IL, the average InP QD height and diameter are reduced to 16 nm and 50 nm and these values are also less than the size of GaP IL samples [14]. The introduced strain in the lower $In_{0.49}Ga_{0.51}P$ barrier strongly influences the InP QD growth, in a sense that the same amount of material is deposited but is rearranged in more and smaller QDs. This behavior becomes also obvious in the QD density, compared to the case with GaP IL (highest InP QD density: 4.2×10^9 cm^{-2}) the density is reduced to 3.6×10^9 cm^{-2}. Since the QDs growth conditions are the same, the smaller the QDs size and reduced density for the samples grown with InGaP IL results in less incorporation of the material. On the InGaP surface, there could be an indium segregated layer which may be favorable for the nucleation of InP QDs leading to increased QDs density. The GaP insertion layer may consume this segregated indium layer thereby block preferential nucleation sites. As a result, besides the QDs density increases and mean QDs height, the QDs size fluctuation is also decreases.

Diameter and height histograms of InP QDs that were extracted from 1×1 μm^2 AFM images are shown in Fig. 3 and 4. Generally, we can see a better size uniformity and low size fluctuation of InP QDs in InGaP IL sample results. The GaP IL samples show less uniformity and more fluctuate to compare that the results of InGaP ILs. The average height of all samples was nearly the same. The two samples with 2 and 4 MLs of GaP insertion layer are the same average height at about 17 nm and the same average diameter at about 80 nm. The sample without insertion layer showed a significantly improved size, height dispersion and homogeneity. When GaP and InGaP insertion layers are grown between QDs and $In_{0.48}Ga_{0.52}P$ layer, the height of the InP QDs decrease and the dots become more uniform in terms of size and composition distribution due to suppression of the exchange reaction as noted in the AFM images. According to the similar effect of QDs diameter, the segregated indium atom may react with P bond during the growth of InP QDs and forms additional InP which increased the QD density and its uniformity. Furthermore, the size and height fluctuation was minimal under the effect of strain compensation GaP and InGaP insertion layers.

Comparing GaP and InGaP insertion layer effects on InP quantum dots size (diameter) distribution are shown in Fig. 5. In comparison of size of these two layers, it is note that the quantum dots densities are increased, the average size diameters are decreased by insertion of GaP and InGaP insertion layers. A significant changes of size and diameter results at 2 ML GaP and InGaP insertion layer thickness. After insertion of 2 ML, InP QDs size a little bit decrease in sample

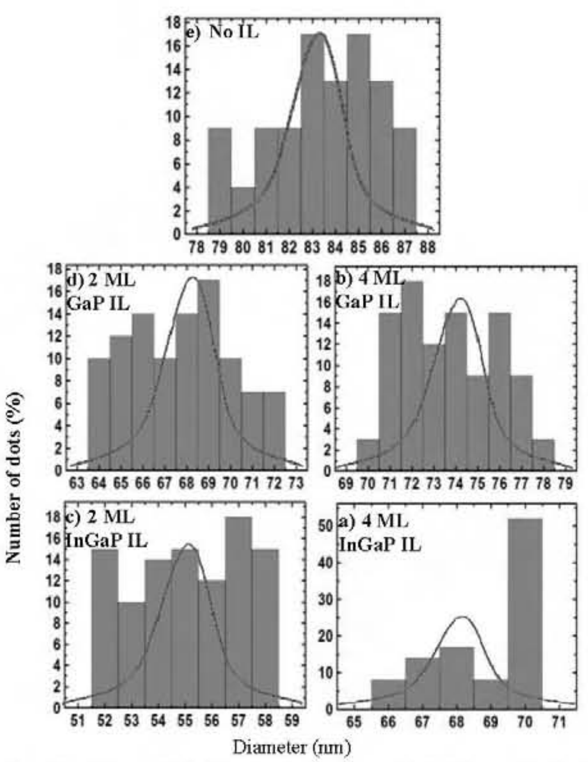

Fig. 3 Size (diameter) distribution histograms of InP QDs on (a) No IL (b) 2 ML GaP IL (c) 4 ML GaP IL (d) 2 ML InGaP IL and (e) 4 ML InGaP IL

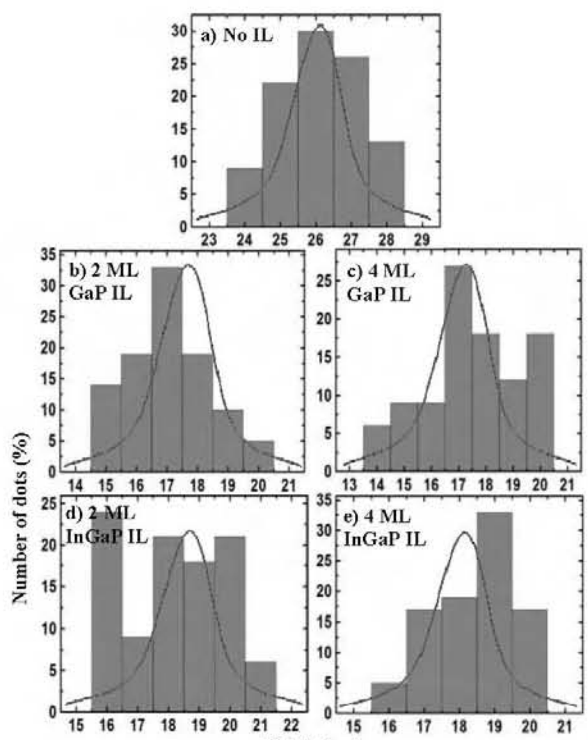

Fig. 4 Height distribution histograms of InP QDs on (a) No IL (b) 2 ML GaP IL (c) 4 ML GaP IL (d) 2 ML InGaP IL and (e) 4 ML InGaP IL

with 4 ML GaP insertion layer thickness although growth conditions are the same. This implies that it is due to a difference in the rate of As/P exchange during the growth of the quantum dots. Group V exchange during the growth of quantum dots affects mainly the nucleation density through an increase in supersaturation. Therefore, InP quantum dots size and densities depend on the thickness of GaP and InGaP insertion layers at the same growth conditions. As the number of insertion layers increases, the amount of strain in the structure also increases and the potential for strain relaxation becomes critical.

Another important parameter in the growth of semiconductor III-V quantum dots is the dots density. Due to insertion of GaP and InGaP insertion layers, the dots density increase and size decrease. As a results of GaP insertion layer samples, the dots density increases to 4.2×10^9 cm^{-2} by insertion of 2 ML GaP IL and then decrease again to 3.3×10^9 cm^{-2} by insertion of 4 ML GaP insertion layer. This is believed to be a result of competition between island nucleation and subsequent growth and coalescence. Fig. 6 shows the relation of dot density of InP QDs as a function of the GaP and InGaP insertion layer thickness. It is observed that with increasing GaP and InGaP ILs thickness, the QDs density increases and

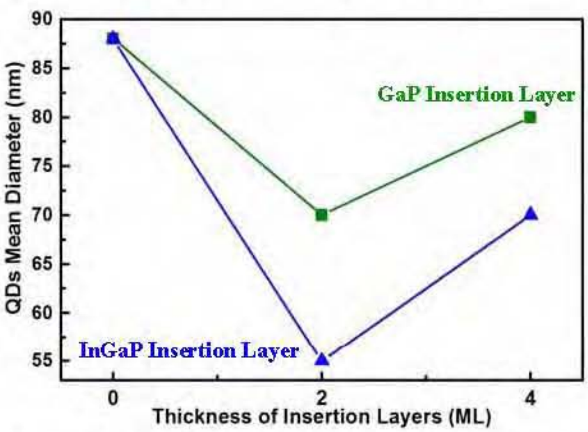

Fig. 5 Comparison of diameter effect of GaP and InGaP ILs on InP SAQDs embedded in InGaP grown at 610 °C

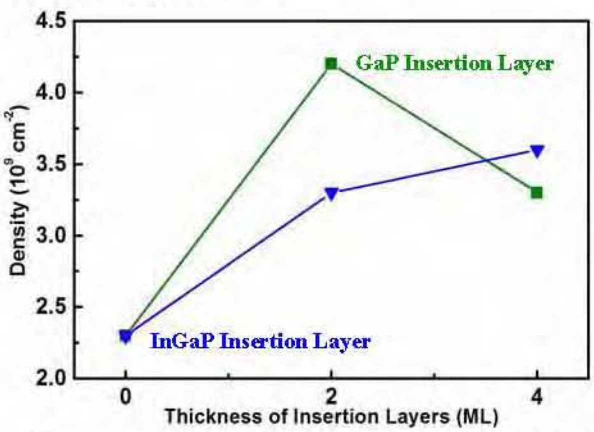

Fig. 6 Comparison of density effect of GaP and InGaP ILs on InP SAQDs embedded in InGaP grown at 610 °C

the relation of dot density of InP QDs as a function of the GaP height and diameter decrease [15]. This is also an expected result and is due to an increased supersaturation at the onset of nucleation which leads to a higher nucleation density. Since the QDs growth conditions are the same, the smaller QD height and diameter and increased density for the sample grown with the GaP and InGaP interlayers indicates that the insertion of the 2-4 MLs GaP and InGaP layers results in less incorporation of the material. The incorporation efficiency of In during the deposition of an GaP and InGaP layers reduces as strain increases [16].

B. Optical Properties of InP Quantum Dots by Photoluminescence (PL)

The room temperature (RT) PL spectra of InP QDs grown on GaP and InGaP ILs are shown in Fig. 7. The ensemble PL measurements reveal already drastically changed optical properties of the InP QDs grown with InGaP IL compared to samples with GaP IL. The PL spectrum without insertion layer shows PL peak at 814 nm and this InP QDs PL peak is overlapping with GaAs buffer photoluminescence peak. After insertion of 2-4 ML GaP layers, the PL intensity decreases and blue-shift noticeably with a peak at around 780 nm. Since the more QDs size fluctuation of GaP IL samples, broader the PL linewidth as can be seen from the PL spectra.

When the InGaP layer is inserted between the GaP buffer and the underneath InGaP buffer, a significant increase in PL intensity is observed while the linewidth of the spectrum remained almost unchanged from that of GaP IL samples. Due to the height of the QDs reduces and the dots become more uniform in terms of size, the PL spectra result in a blue shift of the PL emission wavelength. At the same time, gallium can also diffuse from the InGaP IL to the QDs leading to more blue shift in the PL emission wavelength. In both GaP and InGaP ILs, 2 ML thickness is noticeably improved intensity among other thicknesses. It indicates that an increased number of optically active InP QDs at this layer thickness. In the PL

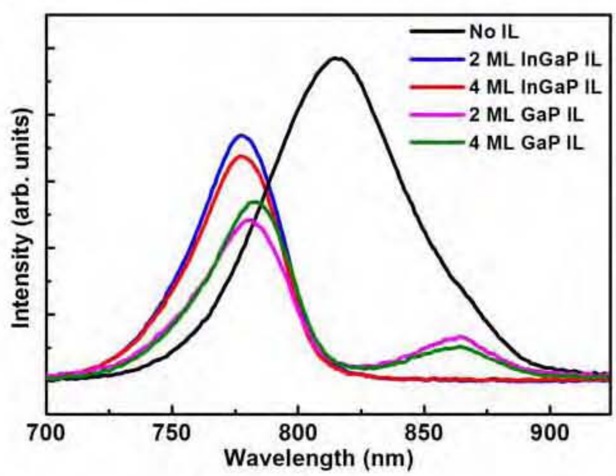

Fig. 7 The room temperature PL spectra of the InP QDs grown on the InGaP barrier with 2- 4 ML thick GaP and InGaP ILs.

spectra of InGaP IL samples, the PL emission of InP QDs is at 777 nm. This red spectral range is also preferable to generate highest photon detection efficiency for single-photon detectors. Additionally, the InP QDs with GaP and InGaP ILs must influence the optical properties of possible quantum optic devices which have to be carried out in future work.

IV. Conclusion

We have investigated the effects of GaP and InGaP insertion layers on the structural and optical properties of InP QDs by using MOVPE. The insertion of 2- 4 ML GaP and InGaP layers achieves slightly increase density and it also reduces the size and height of QDs that were the better conditions for InP QDs. Thin GaP and InGaP insertion layers effect on InP QDs led to a blue-shift of the PL peak. As a result of InGaP IL samples, besides the decrease of QDs density and mean diameter, the QDs size fluctuation also decreases and thus the broad of PL linewidth reduces and PL intensity increases. Insertion of InGaP IL is also achieved more blue shift in the PL emission wavelength, compared to the case with GaP IL. Under the same growth conditions, 2 ML ILs thickness is the optimum where QDs mean size and fluctuation are minimum while giving the higher PL intensity than other thickness of GaP and InGaP ILs. Since GaP and InGaP ILs improve the structure and PL quality of the InP QDs.

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