

# THE EFFECT OF THIN GAP INSERTION LAYER ON INP NANOSTRUCTURE GROWN BY METAL-ORGANIC VAPOUR PHASE EPITAXY

Soe Soe Han,<sup>1</sup> Somsak Panyakeow,<sup>1</sup> Somchai Ratanathammaphan,<sup>1\*</sup> Akio Higo,<sup>2</sup> Wang Yunpeng,<sup>3</sup> Momoko Deura,<sup>3</sup> Masakazu Sugiyama<sup>3,4</sup> and Yoshiaki Nakano<sup>2,3</sup>

1. Semiconductor Device Research Laboratory (NanoTec CoE), Department of Electrical Engineering, Chulalongkorn University, Bangkok 10330, Thailand
2. Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo, Japan
3. Department of Electrical Engineering and Information Systems, School of Engineering, The University of Tokyo, Tokyo, Japan
4. Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Tokyo, Japan

The effect of thin GaP insertion layers on the structural and optical properties of InP/In<sub>0.49</sub>Ga<sub>0.51</sub>P self-assembled quantum dots (SAQDs) on GaAs (001) substrate grown by metal-organic vapour phase epitaxy has been reported. The properties of InP/In<sub>0.49</sub>Ga<sub>0.51</sub>P SAQDs are modified when a thin (1–4 ML) GaP layer is inserted underneath the InP quantum dots (QDs). Deposition of the GaP insertion layer affects the dot dimension and improves the size uniformity. The density, dimension and uniformity of InP QDs strongly depend on the GaP insertion layer thickness. This variation in QD size is a result of a material nucleation effect caused by atomic intermixing between the InP QDs and underlying GaP insertion layer and surface energy. The insertion of GaP layer led to tuning the emission wavelength and narrowing of full width at half maximum (FWHM) when they are characterised by PL measurements at room temperature.

**Keywords:** InP, self-assembled quantum dots (SAQDs), metal-organic vapour phase epitaxy (MOVPE), atomic force microscope (AFM), photoluminescence (PL)

## INTRODUCTION

Many efforts were spent in recent years on the realisation of formation and physical properties of self-assembled quantum dots (SAQDs) for a variety of device applications like semiconductor lasers, photodetectors and quantum computation (Bayer et al., 2001; Li et al., 2003; Shchukin et al., 2004). One of the approaches used to achieve single-photon generation is based on the emission by semiconductor quantum dots (QDs). In the future, one can think of a simple QD device for computer or networking applications. For these purposes, optically or electrically addressable single QD would be needed on a mass production scale which favours metal-organic vapour-phase epitaxy (MOVPE) due to its several advantages (DenBaars et al., 1994; Lie and Wang, 2001). Current silicon based single-photon detectors have their highest photon detection efficiency in the red spectral range (Lie and Wang, 2000). Therefore, it is prefer-

able to fabricate single QDs emitting at such wavelengths. The light source in this spectral region can be obtained from InP QDs embedded in In<sub>0.49</sub>Ga<sub>0.51</sub>P structures (Eberl et al., 1997; Parssinen et al., 1999). However, InP/In<sub>0.49</sub>Ga<sub>0.51</sub>P SAQDs on GaAs are usually formed with poor size uniformity compared to that of InAs/GaAs QDs. As a consequence, inhomogeneous broadening in optical spectra due to the randomness in the dot sizes has been a difficult issue limiting potential benefits. In the theoretical model of the Stranski-Krastanow (S-K) growth mode, QD

\*Author to whom correspondence may be addressed.

E-mail address: rsomchai@chula.ac.th

Can. J. Chem. Eng. 9999:1–4, 2012

© 2012 Canadian Society for Chemical Engineering

DOI 10.1002/cjce.21648

Published online in Wiley Online Library

(wileyonlinelibrary.com).

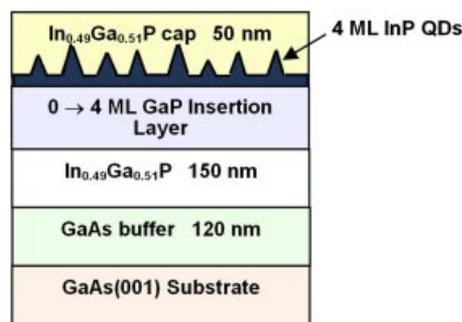
growth depends both on the strain and the surface condition of the layer upon which the dots are grown. In practical, the growth parameters, such as growth temperature (Jung et al., 2006) and QD layer thickness (Lee et al., 2004), affects the QD dimension and size distribution. Another method to avoid the bimodal size distribution is an introduction thin insertion layer between the QD and matrix layers to compensate the strain in QDs and to modify the surface. In the case of MOVPE grown InP/In<sub>0.49</sub>Ga<sub>0.51</sub>P SAQDs, a bimodal size distribution for the coherent islands has often been observed at low coverage of InP (Zhang et al., 2003). Nevertheless, the island size still remains large and hence the areal density is low. Since large dots may introduce misfit dislocations and low areal density of dots gives poor optoelectronic efficiency, growth of small size, high density and highly uniform InP/In<sub>0.49</sub>Ga<sub>0.51</sub>P SAQDs becomes imperative (Mishra and Shealy, 1994; Seifert et al., 1997). The strain in InP/In<sub>0.49</sub>Ga<sub>0.51</sub>P SAQD structure is a compressive strain. GaP, with a smaller lattice constant than that of In<sub>0.49</sub>Ga<sub>0.51</sub>P, and InP should be preferable to compensate for the strain in InP/In<sub>0.49</sub>Ga<sub>0.51</sub>P system due to the tensile strain of GaP/In<sub>0.49</sub>Ga<sub>0.51</sub>P. Hence, insertion of GaP layers between In<sub>0.49</sub>Ga<sub>0.51</sub>P and InP QDs layers is also expected to change the morphology, characteristics and optical properties of the InP SAQDs.

In this article, we present an experimental study of the effect of GaP insertion layer thickness on the structural and optical properties of InP QDs in Ga<sub>0.51</sub>In<sub>0.49</sub>P matrix grown on GaAs substrates by MOVPE via S-K growth mode. The structural and optical properties of InP QDs are examined via atomic force microscope (AFM) and photoluminescence (PL).

## EXPERIMENTAL DETAILS

In this study, the samples composed of InP embedded in In<sub>0.49</sub>Ga<sub>0.51</sub>P matrix were carried out on nominally (001) oriented GaAs substrate in a horizontal MOVPE reactor (AIXTRON, AIX200/4) with a rotating substrate holder. The inlet of the reactor is divided into two parts: group III precursors were introduced through the upper inlet and group V precursors were introduced through 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 performed in a rectangular inner liner tube, which had a graphite rotator as a sample susceptor. During MOVPE growth, GaAs substrates were placed at the centre of the susceptor. Trimethylgallium (TMGa), trimethylindium (TMIn), tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP) were used as precursors.

Epitaxial growth conditions were a total pressure of 100 mbar, H<sub>2</sub> total flow rate of 13 000 sccm (cubic centimetre per minute at standard temperature and pressure), temperature of 610°C and V/III ratio of source precursors of 18 for InP. Firstly, 120 nm GaAs buffer layers were grown on semi-insulating GaAs (001) substrates at 610°C. After the growth of GaAs buffer, the growth of 150 nm lattice-matched In<sub>0.49</sub>Ga<sub>0.51</sub>P layers was followed at the same temperature. Then, a 0–4 ML thick GaP insertion layer was deposited. Next, the formation of self-assembled InP QDs was performed at a growth rate of 0.5 ML/s by depositing 4 ML of InP. For the PL measurement, other samples with an additional 50 nm In<sub>0.49</sub>Ga<sub>0.51</sub>P cap layer were grown repeatedly under the same conditions. We examined the effect of GaP insertion layer thickness on structural, morphological and optical properties of InP QDs by AFM and PL. Schematic representation of the InP QDs structure was depicted in Figure 1.



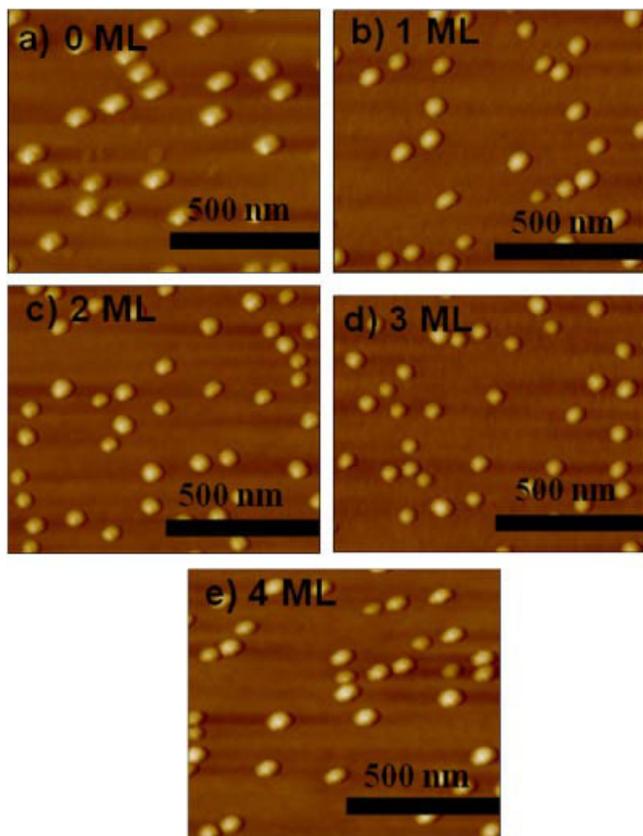
**Figure 1.** Schematic diagram of the vertical layer structure of InP QDs embedded in InGaP barrier grown on (001) GaAs substrate.

## RESULTS AND DISCUSSION

### Effect of GaP Insertion Layer on Size and Density of InP SAQDs

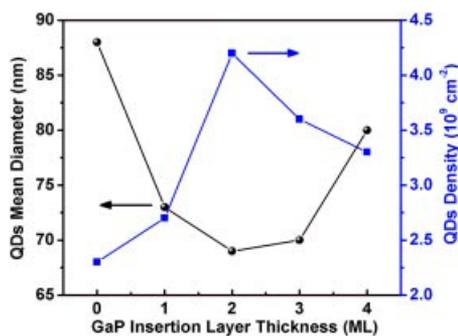
In order to investigate the role of GaP insertion layer on the characterisation of size and density of InP SAQDs, we have performed the measurement of AFM. Figure 2a–e shows 1  $\mu\text{m}$   $\times$  1  $\mu\text{m}$  AFM images of InP QDs grown with 0–4 ML GaP insertion layer. Both height and diameter generally decrease with increasing the thickness of GaP insertion layer. The average height and diameter of InP QDs without GaP sample are 27 and 87 nm. The distribution of the dots' widths and heights on GaP samples reveals that average height and diameter of smallest (biggest) QDs are 13 nm (27 nm) and 66 nm (87 nm), respectively. These average values are extracted from all 0–4 ML GaP samples. This result is verified that the insertion of the GaP layer give rise to the opportunity to control size of QDs. Figure 3 summarises the changes in the density and mean diameter of QDs with varying GaP insertion layer thickness. Initially, the mean diameter of the QDs is decreased continuously with increasing GaP thickness from 0 to 2 ML. The mean diameter of the QDs at 0, 1 and 2 ML GaP are 87, 73 and 63 nm, respectively. In case of 3–4 ML GaP insertion layer, the mean diameter increases to 78 and 80 nm, respectively. This effect is considered that the material nucleation step at 2D–3D transition caused by atomic intermixing between the InP QDs and the underlying insertion layers (Zhang et al., 2003; Lever et al., 2004). The difference in nucleation enthalpy between InP QDs and GaP insertion layer is responsible for the difference QD size on these samples. Because the morphology of InP QDs depends on the difference of surface energy and strain of each conditions. In this case, the GaP layer thickness variation affects the strain energy and surface energy (Park et al., 2004). Therefore, GaP surface energy will be difference from that of In<sub>0.49</sub>Ga<sub>0.51</sub>P, which changes the nucleation of the QDs.

Another important parameter in the growth of semiconductor III–V QDs is the dot density. The dot density increases from  $2.3 \times 10^9$  to  $4.2 \times 10^9 \text{ cm}^{-2}$  due to the insertion of 0–2 ML and then decrease again to  $3.6 \times 10^9$  and  $3.3 \times 10^9 \text{ cm}^{-2}$  due to insertion of 3 and 4 ML GaP layers, respectively. The maximum density of  $4.2 \times 10^9 \text{ cm}^{-2}$  and the small uniform InP QDs were obtained with 2 ML GaP. When the thickness of GaP is over 2 ML, the QDs density decreased again. QDs density first increased with increasing of GaP insertion layer thickness and then saturated at 2 ML GaP. It is also shown that two (2D)-to three dimension (3D) transition occurred sooner on the GaP layer while the QD size become smaller. The nuclei centres first increased with the increase of GaP thickness from 0 to 2 ML, the nucleation was performed

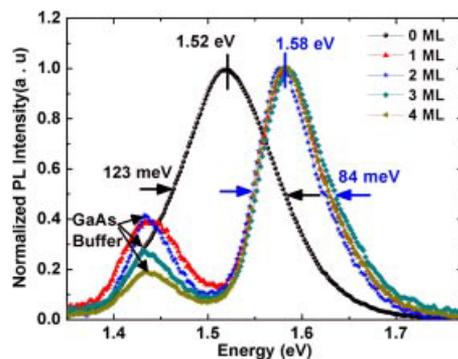


**Figure 2.** Typical ( $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) scan range AFM images of InP QDs embedded in InGaP barrier with (a) 0 ML, (b) 1 ML, (c) 2 ML, (d) 3 ML and (e) 4 ML GaP layers.

with increasing density until entering saturation. The InP QDs grown on GaP layer are slightly smaller in diameter with increase GaP layer thickness. Because GaP layer causes increase the surface energy and strain energy. Then, the density decreases due to the increasing of dislocation cluster with the increase GaP thickness (GaP > 2 ML). The interdiffusion between InP QD and GaP layer during growth also reduces the strain in QDs and modifies the composition of QDs. The interdiffusion also depends on GaP thickness. In this condition, the density decreases with increasing diameter. This observation indicated that the size and density of InP QDs strongly depends on the GaP thickness due to the strain and surface energy difference of each condition (Lever et al., 2004).



**Figure 3.** The average diameter and density of InP QD as a function of GaP insertion layer thickness.



**Figure 4.** The room temperature PL spectra of the InP QDs grown on the InGaP barrier with 0–4 ML thick GaP insertion layer between the InP QDs and the InGaP barrier.

## Optical Characterisation

In order to further investigate the phenomenon related to the effect of GaP insertion layer, we have characterised the optical properties by PL measurements at room temperature (298 K). The evolution of the PL spectra of InP QDs as a function of the thickness of the GaP insertion layer is shown in Figure 4. It shows that the InP QDs give strong PL, which in fact dominated the spectra from the samples. The InP QDs without GaP insertion layer shows PL peak centred at 1.52 eV and this PL peak is a superimposition of GaAs buffer layer and InP QDs PL peaks. After insertion of 1–4 ML GaP layers, InP QDs PL peaks are observed separately with GaAs buffer layer PL peaks. The split in the spectrum is caused by the improvement of QD size distribution with GaP interlayer. When a GaP layer is introduced, the PL peak blue-shifts noticeably with PL peak centred at 1.59 eV. This is mainly attributed to the reduction in the QD sizes arising from the effect of the insertion of GaP layer. Since lattice constant of GaP is smaller than that of InP and  $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$ . Thus, the strain in GaP is a tensile strain while the InP QD layer suffers a compressive strain. The strain caused by the lattice mismatch between InP QDs and GaP layers on  $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$  is concentrated partly in the InP dot and partly in the surrounding GaP layer. Therefore, the strain compensation between compressive strain in the InP QDs and the tensile strain in the GaP layer is shifted towards the surrounding  $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$  matrix. The reduced dimension in these InP QDs causes a blueshift. However, the variation in PL peak dependence on the thickness of the GaP interlayer, could not be observed in this case because of the smaller valence band offset of InP/GaP (Kent et al., 2002) than that of InP/ $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$  and the interdiffusion of group III at InP/GaP interface. The FWHM of the PL peaks are measured to be 123 and 84 meV for the samples without and with GaP insertion layers, respectively. A narrower FWHM value indicates that the samples with GaP insertion layer have a greater degree of dot size uniformity than that of the sample without insertion layer. Due to the insertion of GaP layer, a better uniformity and a smaller QD size leading to a narrower FWHM and a blueshift of the PL peaks might influence the optical properties of possible quantum optic devices which have to be carried out in future work.

## CONCLUSION

The role of GaP insertion layer on the properties of MOVPE grown InP/ $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$  QDs has been studied by atomic force microscopy and PL. The density and size of InP QDs strongly

depends on the GaP insertion layer thickness. The effect of thin GaP insertion layers on InP QDs led to a blue-shift of the PL peak. The blueshift of the PL peak is observed from 1.52 to 1.58 eV for without GaP layer and with GaP interlayer, respectively. In addition, the FWHM of the PL peak decreases by inserting the GaP insertion layer.

## ACKNOWLEDGEMENTS

The author wishes to thank ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net), the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (EN264A), Chulalongkorn University and University of Tokyo for the support of this work.

## REFERENCES

- Bayer, M., P. Hawrylak, K. Hinzer, S. Farad, M. Korkussinski, Z. R. Wasilewski, O. Stern and A. Forchel, "Coupling and Entangling of Quantum States in Quantum Dot Molecules," *Science* **291**, 451–453 (2001).
- DenBaars, S. P., C. M. Reaves, V. Bressler-Hill, S. Varma, W. H. Weinberg and P. M. Petroff, "Formation of Coherently Strained Self-Assembled InP Quantum Islands on InGaP/GaAs (001)," *J. Cryst. Growth* **145**, 721–727 (1994).
- Eberl, K., A. Kurtenbach, M. Zundel, J. Y. Jin-Phillipp, F. Phillipp, A. Moritz, R. Wirth and A. Hangleiter, "Self-Assembling InP Quantum Dots for Red Lasers," *J. Cryst. Growth* **175–176**, 702–706 (1997).
- Jung, S. I., H. Y. Yeo, I. Yun, J. Y. Leem, I. K. Han, J. S. Kim and J. I. Lee, "Photoluminescence Study on the Growth of Self-Assembled InAs Quantum Dots: Formation Characteristics of Bimodal-Sized Quantum Dots," *Physica E* **33**, 280–283 (2006).
- Kent, P. R. C., L. W. Hart Gus and A. Zunger, "Biaxial Strain-Modified Valence and Conduction Band Offsets of Zinc-Blende GaN, GaP, GaAs, InN, InP, and InAs, and Optical Bowing of Strained Epitaxial InGaN Alloys," *Appl. Phys. Lett.* **81**, 4377–4379 (2002).
- Lee, S. J., S. K. Noh, J. W. Choe and E. K. Kim, "Evolution of Bimodal Size-Distribution on InAs Coverage Variation in As-Grown InAs/GaAs Quantum-Dot Heterostructures," *J. Cryst. Growth* **267**, 405–411 (2004).
- Lever, P., H. H. Tan and C. Jagadish, "InGaAs Quantum Dots Grown With GaP Strain Compensation Layer," *J. Appl. Phys.* **95**, 5710–5714 (2004).
- Li, X. Q., Y. W. Wu, D. Steel, D. Gammon, T. H. Stievater, D. S. Katzer, D. Park, C. Piermarocchi and L. J. Sham, "An All-Optical Quantum Gate in a Semiconductor Quantum Dot," *Science* **301**, 809–811 (2003).
- Lie, D. Y. C. and K. L. Wang, "Chapter 1 SiGe/Ge Heterostructures for Si-Based Nanoelectronics," in "Handbook of Advanced Electronic and Photonic Devices and Materials 2," H. S. Nalwa, Ed., Academic Press, San Diego (2000), pp. 1–69.
- Lie, D. Y. C. and K. L. Wang, "Chapter 4 SiGe/Ge Processing," in "Semiconductors and Semimetals 73," R. K. Willardson and E. R. Weber, Eds., Academic Press, San Diego (2001), pp. 151–197.
- Mishra, U. K. and J. B. Shealy, "InP-Based Hemts: Status and Potential," in "Proceedings of the 6th International

- Conference on InP and Related Materials," Santa Barbara (1994), pp. 14–17.
- Park, S. K., J. Tatebayashi and Y. Arakawa, "Structural and Optical Properties of High-Density ( $>10^{11}/\text{cm}^2$ ) InAs QDs With Varying Al(Ga)As Matrix Layer Thickness," *Physica E* **21**, 279–284 (2004).
- Parssinen, A., J. Jussila, J. Ryyänen, L. Sumanen and K. A. I. Halonen, "A 2-GHz Wide-Band Direct Conversion Receiver for WCDMA Applications," *IEEE J. Solid-State Circuits* **34**, 1893–1903 (1999).
- Seifert, W., N. Carlsson, J. Johansson, M. E. Pistol and L. Samuelson, "In Situ Growth of Nano-Structures by Metal–Organic Vapour Phase Epitaxy," *J. Cryst. Growth* **170**, 39–46 (1997).
- Shchukin, V., N. N. Ledentsov and D. Bimberg, "Epitaxy of Nanostructures," Springer, New York (2004), Chapter 3, pp.315–334.
- Zhang, X. B., R. D. Heller, M. S. Noh and R. D. Dupuis, "Effect of the InAlGaP Matrix on the Growth of Self-Assembled InP Quantum Dots by Metalorganic Chemical Vapor Deposition," *Appl. Phys. Lett.* **83**, 1349–1351 (2003).

---

*Manuscript received April 21, 2011; revised manuscript received October 26, 2011; accepted for publication December 15, 2011.*