Mid-infrared Emissive InAsSb Quantum Dots Grown by Metal-organic Chemical Vapor Deposition

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Abstract

InAsSb islands/quantum dots (QDs) emit at wavelength >2.8μm were self-assembled on InP substrate by using metalorganic chemical vapor deposition (MOCVD). Instead of using arsine, the safer organic tertiarybutylarsine (TBAs) was used as the arsenic source in the growths. Effects of the growth conditions, i.e. substrate temperature and the growth rate, on the InAsSb QD formations have been studied. A narrow temperature window from 450°C to 470°C was found for growing the high quality InAsSb QDs. The InAsSb rings instead of islands/dots were formed using the conventional Stranski-Krastanow (S-K) growth mode if the growth rate was low or grew InAsSb for a longer time. By increasing the V/III ratio for the InAsSb growth, InAsSb islands/dots were formed with the same growth rate. To reduce the dot size and increase the InAsSb QD density, an alternative interruption-growth (AIG) method was proposed and investigated. Using the AIG growth method, much higher dot density of the InAsSb QDs has been received, achieved about 3×10^{9} cm^{-2} which is about 10 times of that of the "QDs" grown by using the conventional S-K growth method. Strong photoluminescence emissions of the InAsSb islands/dots were received. At room temperature, emission wavelength of the InAsSb islands/dots was measured at >2.8μm.

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I. INTRODUCTION

With a quasi zero dimensional structure, semiconductor quantum dots (QDs) have attracted much research attention. The unique physical properties of semiconductor QDs make them promising for novel optoelectronic devices applications[1,2],e.g. lasers and single photon emitters, etc. But most works on semiconductor QDs have focused on the InAs/GaAs material system at wavelength of 1.3μm[3.5] for optical communications and the InAs QDs grown on InP substrate to obtain the light emitters in the telecom wavelength region ~1.55μm[6,7,8]. Recently, attempts to use InAs nanostructures based on InP substrates to extend the wavelength further into the mid-infrared region >2.0μm have received more attention, because mid-infrared lasers are very attractive for applications in molecular spectroscopy, remote sensing of atmospheric and planetary gases, as well as lidar atmospheric detection and ranging[9,10,11],etc. InAs QDs and quantum-dash lasers have been demonstrated recently at various wavelengths from 1.60 to 2.04μm[12,13,14]. But the emission wavelength of the InAs QDs grown on InP is limited to <2.28μm[15,16].

To extend the emission wavelength further longer for the mid-infrared devices, narrower bandgap semiconductor structures, e.g. In(As)Sb and the related compounds grown on GaSb substrates, have been intensively investigated[17]. Only limited reports on In(As)Sb QDs so far have been published[18-20]. However, photoluminescence (PL) at wavelengths as long as 3.5μm from the InSb QDs grown on an InAs matrix has been publised[18] and InSb QDs with the dot density as high as $4\times10^{10}/\mathrm{cm}^2$ grown on InP have been achieved by using molecular-beam epitaxy (MBE).[19]

Typically, self-assembled InSb QDs using metal-organic chemical vapor deposition (MOCVD) growth have the area density less than $5\times10^9/\mathrm{cm}^2$. Different from that of the MBE growth, QD nucleation in MOCVD growth is basically an equilibrium process. Additionally, in MOCVD growths, high growth temperature is needed to crack the precursors. But the InSb bond is very weak and the indium adatoms have high mobility, which result in big InSb islands of low density in MOCVD growths of InSb QDs. It has been reported that the InAsSb nano-structures changed shapes from QDs to quantum wires (QWRs) and even quantum wells (QWs) as the Sb fraction in the MOCVD growths was increased[20]. These results suggest that a specific method for controlling the shape of the formed InAsSb QDs on InP substrates is necessary.

Among different epitaxy growth techniques, MOCVD is recognized as a key technology for manufacturing optoelectronic devices due to its high quality growth, short downtimes, high throughput, and availability to large scale processing, etc. In conventional MOCVD growths of III-V semiconductors, high toxic hydride arsine(AsH_3) and phosphine (PH_3) are used as group V As- and P-precursors. To improve the process safety, alternative group V sources with less toxicity have been investigated in MOCVD growths. Organo-arsine and phosphine, such as tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP), are used for replacing AsH_3 and PH_3 in MOCVD growths. Devices made from the structures grown by MOCVD using TBA and TBP as arsenic and phosphine sources exhibit state-of-the-art performance.[21,22]

In this research, MOCVD growth of InAsSb QDs on InP (001) substrate by using TBA and TBP as arsenic and phosphine precursors were studied in detail. Effects of the growth temperature and growth rate on the formation of the InAsSb QDs have been studied. An alternative interruption-growth (AIG) of InAsSb QDs method for improving the dot formation has been proposed and investigated. The work shows that InAsSb rings, instead of dots or islands were formed with a low InAsSb growth rate by using conventional Stranski-Krastanow (S-K) self assembly growth mode. Large size InAsSb islands could be formed with a high V/III ratio based on conventional S-K growth mode. The alternative interruption-growth (AIG) of InAsSb QDs has been verified for improving the dot density and uniformity in self-assembled InAsSb QD growths.

II. EXPERIMENT

All samples in this research were grown in a horizontal MOCVD reactor (Aixtron, AIX200) with gas foil rotation of the susceptor. The metal-organic sources used in the growths were TBA, TBP, trimethylantimony(TMSb), and trimethylindium (TMIn). High purity (99.999%) hydrogen gas purified by a MonoTorr phase II Getter column with dew point below $-100^{o}C$ was used as the carrier gas. The reactor pressure for all the growths was set at 20 mbar. The total gas flow in the reactor was Q_{tot} =3.1slm. Epi-ready InP semi-insulating substrates oriented in $(001)\pm0.1^{o}$ direction were used for all the growths.

Before starting the epitaxy growth, the InP substrate was annealed inside the reactor with H_2 environment at $700^{o}C$ for 5 min. Then a 0.3μm InP buffer layer was grown on the InP substrate at 630 ^{o}C. After that, the substrate temperature was lowed down for growing the InAsSb QDs. In this study, the InAsSb QDs were grown at the temperature range from 430 ^{o}C to 500 ^{o}C, and the TMIn inlet flux was varied from 9×10^{-6}mol/min to 2.7×10^{-5}mol/min to change the growth rate. The antimony source (TMSb) flow for all the growths was kept at the

TMSb/V ratio of 0.84. After the InAsSb QD growth, the heater was switched off to cool down the system. The TBA and TMSb sources flux were kept open during the cooling down to prevent decomposition of the grown sample's surface until the temperature was below 300 ^{o}C. Surface morphology of all the samples was studied by using Nanoscope III atomic force microscope (AFM). Emission of the grown InAsSb QDs was measured though photoluminescence (PL). For the PL measurement, the samples were excited by a 488 nm Ar^+ laser, and the emission of the samples was detected by a cooled PbS photodetector.

III. RESULTS AND DISCUSSION

Figures 1 shows the $3\times3\mu m^2$ top surface AFM images of the InAsSb QDs grown via the conventional S-K growth mode with different InAsSb growth rates. During the InAsSb QD growth, when the reactor temperature reached the InAsSb growth temperature of 470 ^{o}C, the TBP precursor was closed for 3 seconds before started the InAsSb growth by switching on the TBAs, TMSb and TMIn precursors simultaneously. TMIn source was closed to stop the growth when the InAsSb growth reached the targeted layer thickness. Before switching off the heater to cool down the system, TBAs and TMSb were kept opened during the post-growth interruption for forming the InAsSb QDs self-assembly. In this study, the post-growth interruption time was kept same of 10 seconds for all the growths. The V/III ratio was kept 6.5.

Sample R1102 and sample R1108 were grown with the same InAsSb growth rate by keeping the TMIn flow same. But for sample R1108, the InAsSb layer was grown for 2.4 seconds, while for sample R1102, it was grown for 3.5 seconds. Sample R1113 was grown with a much lower InAsSb growth rate by reducing the TMIn flux to one third of that for growing sample R1102 and sample R1108. To receive the same InAsSb layer thickness, the growth time of sample R1113 was increased to 9 seconds. Large size, the diameter >200nm, InAsSb nanostructures with very low density of less than 5×10^8 cm^{-2} have been received for all the three samples. Increased the InAsSb growth time, lower density and larger diameter of the InAsSb nanostructures were formed. A very good inverse linear relationship between the InAsSb "dot" density grown versus the growth time (or lower growth rate) has been received as shown in Figure 2. This suggests that the high mobility of In adatoms at the growth temperature enables the In adatoms to migrate easily on the growth surface. It is interested to observe that when the InAsSb growth time is increased from 2.4 seconds for R1108 to 3.5 seconds for R1102, the formed nanostructure of R1108 were changed to rings from the islands/dots of R1102. When prolonged the InAsSb growth time further to 9 seconds of sample

R1113, a larger diameter, lower density rings were received. For sample R1109, the input source flux V/III ratio was increased to 13.8 which was two times of that for growing the other samples. The InAsSb nanostructures formed of R1109 were changed back to islands from rings. In this growth, the InAsSb layer was grown for 6 seconds. In order to grow same thick InAsSb layer, the TMIn flux was reduced to 1.28×10^{-5}mol/min which is about half of that for growing sample R1102. Oval shape dots or islands were received for sample R1109. The dots/islands density of this sample is higher than that of sample R1113 which was grown for longer time, 9 seconds.

In order to increase the dot density, reduce the dot size and improve the formed InAsSb QD shape, an alternative interruption-growth (AIG) method was employed. In this growth method, the InAsSb QDs growth was done by periodically supply TMIn precursor and TBAs precursor with interruptions in between. Figure 3 compares the inlet TMIn flux supply in the conventional S-K self-assembly InAsSb QDs growth and in the AIG InAsSb QD growth. In the conventional S-K growth, TBAs and TMSb were continuously supplied. The InAsSb growth was done by switching on the TMIn for 6 seconds, then, it was closed and the InAsSb QDs were formed self-assembly during the post-growth interruption before cooling down the system. While in the AIG InAsSb QD growth, TMSb was always opened, but TMIn and TBAs was alternatively supplied with interruptions. To compare the growths, for both growths, the total InAsSb layer was grown with same 2 to 3 monolayer (ML) thick for all the samples.

Figure 4 shows the 3D AFM images of the InAsSb QDs grown at different temperatures by using the AIG growth mode. It shows that InAsSb islands/dots were received for all the growths by using the AIG growth method, no ring structures were observed in these growths. The formed InAsSb dots/islands size and density are much depended on the growth temperature. Figure 5 shows the dot/island density of the samples received versus the growth temperature. At high growth temperatures, large InAsSb islands with lower density were obtained. This is due to the longer diffusion length of the adatoms at high temperature.[23] During the post growth interruption, larger islands grew further by consuming small islands in the island-coarsening process. Low density dots/islands were formed when substrate temperature was below 450°C. This is because the diffusion coefficients of In adatoms are smaller, which leads to lower growth efficiency.[24] Therefore, the materials available for growing the InAsSb were reduced when the growth temperature was below 450 °C, which resulted in the low density InAsSb dots formed.

Emissions of the InAsSb islands/QDs grown by using the conventional S-K growth (sample R1108) and by the AIG method (sample R1119) were measured at different temperature by photoluminescence (PL). The measured PL spectra the two samples at different temperatures of are shown in Fig. 6(a) and Fig. 6(b), respectively. Strong emissions at the wavelength around 2.8μm were received from the two samples. For sample R1108 which was grown by the conventional S-K mode, large blue shift of its emission wavelength was observed when the temperature was lowered. At the same time, the full width of the half maximum (FWHM) of its PL spectrum became narrower when measured at lower temperature. This is because of the large size InAsSb islands formed of the sample. With the diameter of the islands beyond >200nm, there is no quantum confinement effect of the InAsSb islands. The emission from these islands is similar to that of the InAsSb bulk material. While for sample R1119, no shift of its PL emission peak wavelength was observed when the temperature was reduced. This shows the strong quantum confinement of the InAsSb QDs of the sample. Relatively wide emission spectrum of the sample is because of the variation of the sample's QD size. It also shows that at high temperature, two emission peaks of the sample were observed. The higher photon energy emission, P2, is because of the transition at the excited energy levels of the InAsSb QDs. At high temperature, the thermal excitation to higher energy becomes stronger, which results the higher energy transition emission of the InAsSb QDs.

IV. CONCLUSIONS

InAsSb nanostructures grown on InP substrate by MOCVD using TBAs and TMSb with different growth conditions have been studied. It has been found that there is narrow a growth temperature window, 450 ^{o}C - 470 ^{o}C, for forming the high quality InAsSb nanostructures. Out of this temperature range, very large islands with low density will be formed. InAsSb rings instead of dots were formed by using the conventional S-K growth mode when the growth time was relatively long. Longer the growth time, the formed InAsSb rings had larger diameters, but with lower density. This can be improved by increase the V/III ratio. An alternative interruption-growth of InAsSb QDs has been proposed to form InAsSb QDs self-assembly at 470 ^{o}C with very much higher density and smaller dot size. PL measurement shows that both the InAsSb nanostructures formed by using conventional S-K mode and the AIG mode emitted ~2.8μm at room temperature. But the emission peak of the conventional S-K grown sample blue shift when lowered the temperature, which shows no quantum confinement of the large islands formed. The emission peak of the AIG grown sample did not shift with the temperature shows the strong quantum confinement of the InAsSb QDs formed.

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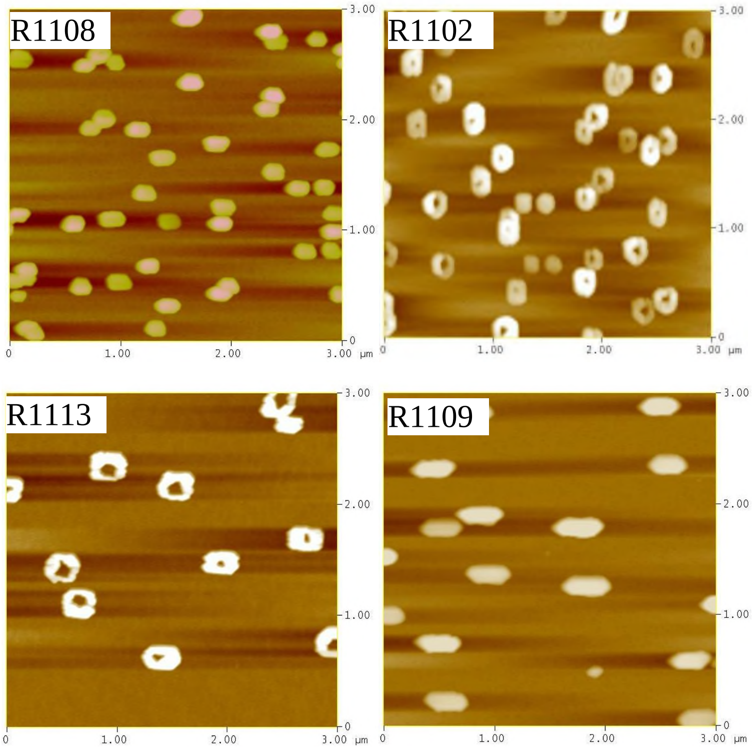


Figure 1 Top-view 3×3μm^2 AFM images of the InAsSb QD samples grown at 470^{o}C. Sample R1102 and R1108 have the same InAsSb growth rate, but different growth time. Sample R1109 and Sample R1113 was grown at lower growth rate but with longer time to keep the InAsSb layer thickness same as that of R1102.

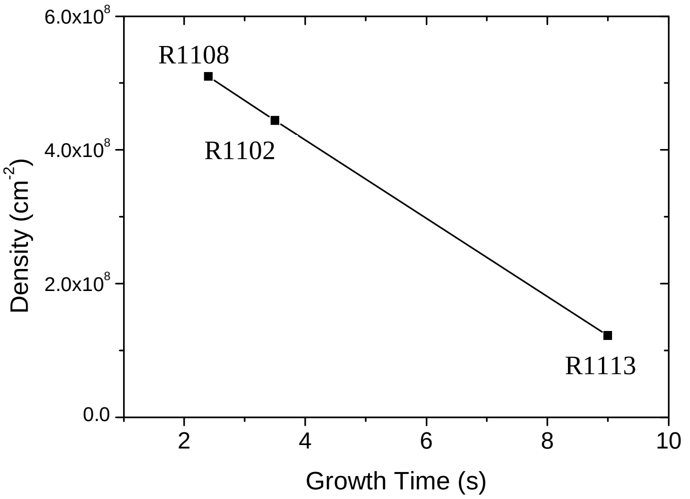


Figure 2 The density of InAsSb nanostructure grown by S-K mode versus the InAsSb growth time. The substrate temperature was 470 ^{o}C and V/III ratio was 6.5.

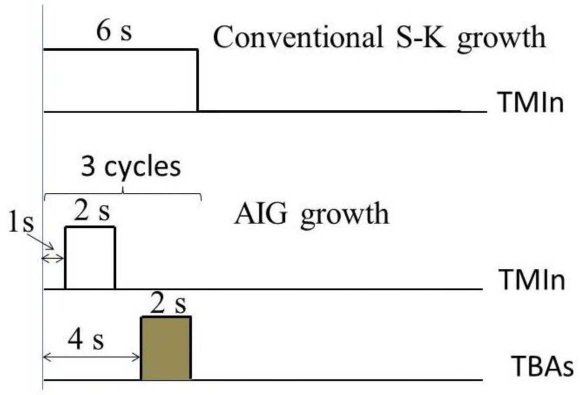


Figure 3 Comparison of the MO sources' flow between the conventional S-K InAsSb QD growth and the AIG InAsSb QD growth.

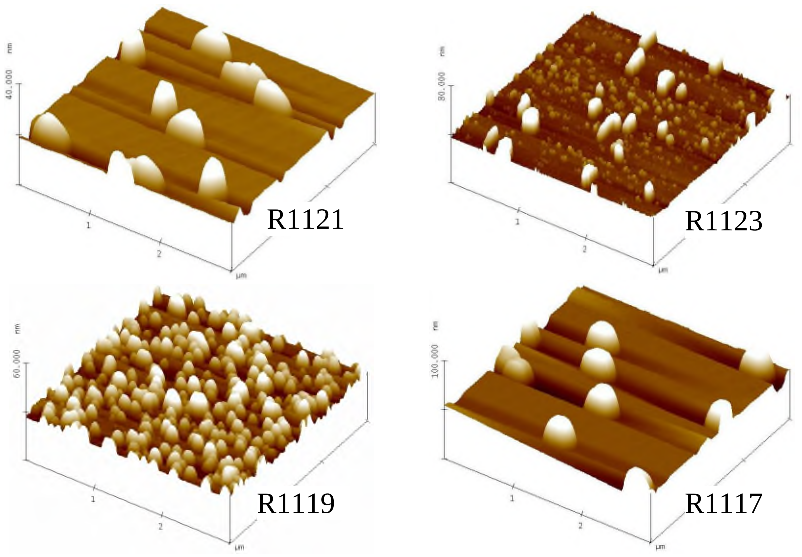


Figure 4 3D 3×3μm^2 AFM images of the InAsSb QD samples grown by AIG growth at different temperatures. R1121, R1123, R1119 and R1117 were grown at 430^{o}C, 450^{o}C, 470^{o}C and 500^{o}C, respectively.

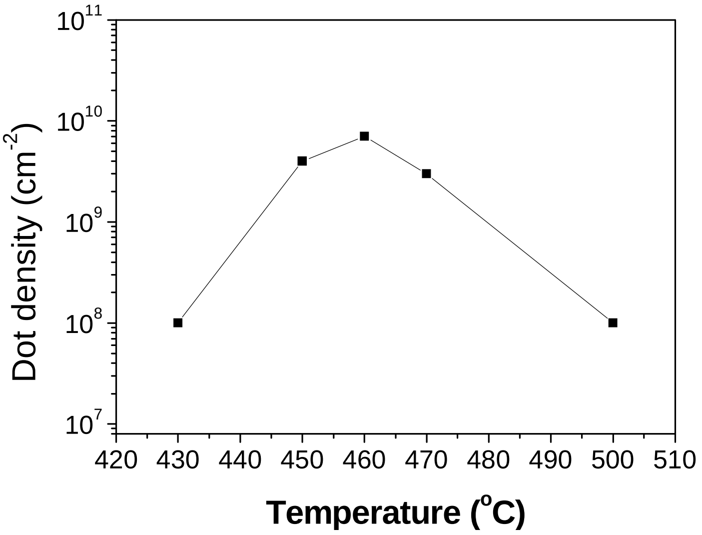
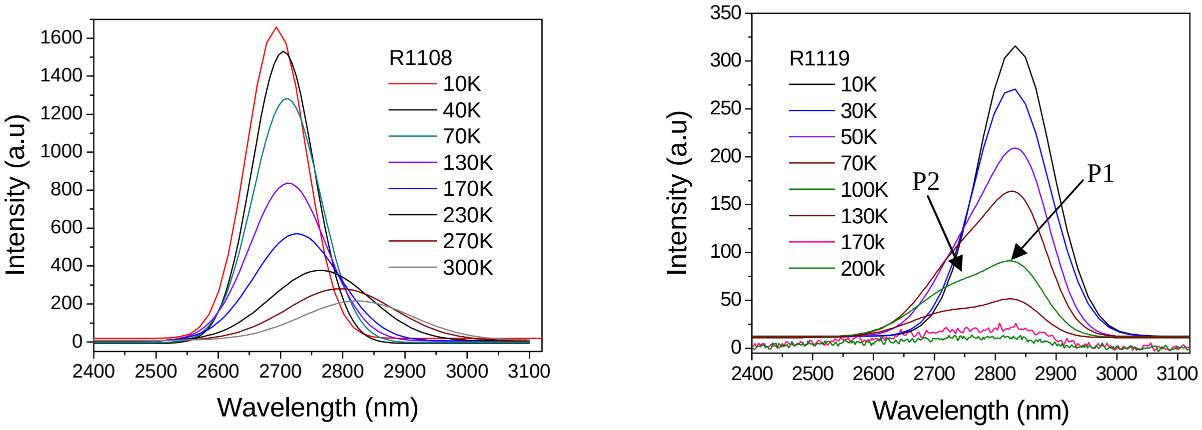


Figure 5 The InAsSb QD density grown by AIG mode versus the substrate temperature. The TMIn flux was 9×10^{-6}mol/min and V/III ratio was 6.5 for the growths.



(a) (b)

Figure 6 Photoluminescence spectra of the InAsSb QDs grown by (a) conventional S-K method and (b) AIG method measured at different temperatures.

References

[1] D. Bimberg, M. Grundmann, and N. N. Ledentsov, Quantum Dot Heterostructures, (Wiley, Chichester, 1999), chapter 4.

[2] Victor M. Ustinov, Alexey E. Zhukov, Anton Yu. Egorov, Nikolai A. Maleev, Quantum Dot Lasers, (Oxford University Press, 2003).

[3] D. L. Huffaker, G. Park, Z. Zou, O. B. Shchekin, and D. G. Deppe, Appl. Phys. Lett. **73**, 2564 ~1998

[4] S. Kiravittaya, A. Rastelli, O.G. Schmidt, Self-assembled InAs quantum dots on patterned GaAs(0 0 1) substrates: formation and shape evolution, Appl. Phys. Lett. 87 (2005) 243112.

[5] Y. Qiu, P. Gogna, S. Forouhar, A. Stintz, and L. Lester, Appl. Phys. Lett. **79**, 3570 (2001).

[6] R. H. Wang, A. Stintz, P. M. Varangis, T. C. Newell, H. Li, K. J. Malloy, and L. F. Lester, IEEE Photonics Technol. Lett. **13**, 767 (2001)

[7] S. Barik, H.H. Tan, C. Jagadish, Comparison of InAs quantum dots grown on GaInAsP and InP, Nanotechnology 17 (2006) 1867–1870

[8] N. Sritirawisarn, F.W.M.van Otten, P.E.D.SotoRodriguez, J.L.E. Wera, R.Notzel, “Formation of two-dimensional InAs quantum dot arrays by self-organized anisotropic strain engineering on InP (3 1 1)B substrates”, Journal of Crystal Growth 312 (2010) 164–168

[9] Jaakko Sormunen,* Juha Riikonen, Marco Mattila, Jouni Tiilikainen, Markku Sopanen, and Harri, Lipsanen, “Transformation of Self-Assembled InAs/InP Quantum Dots into Quantum Rings without Capping”, *Nano Lett.*, *5* (8), pp 1541–1543, (2005)

[10] Akaishi, M., Okawa, T., Saito, Y., Shimomura, K, “Wide Emission Wavelength InAs/InP Quantum Dots Grown by Double-Capped Procedure Using MOVPE Selective Area Growth”, IEEE Journal of Selected Topics in Quantum Electronics, Vol.14, Issue: 4, pp. 1197 - 1203 (2008)

[11] Junji Kotani, Peter J. van Veldhoven, and Richard Nötzel, “Mid-infrared emission from InAs quantum dots, wells and dots on well nanostructures grown on InP (100) by metal organic vapor phase epitaxy”, J. Appl. Phys. **106**, 093112 (2009);)

[12] J.R. Mialichi, N.C.Frateschi, “Shorter wavelength emission with InAs quantum dots growth directly on large bandgap quaternary(In0.68Ga0.32As0.7P0.3) barriers for high current injection efficiency”, Journal of Crystal Growth 312 (2010) 2279–2283

[13] R. Schwertberger, D. Gold, J. P. Reithmaier, and A. Forchel, IEEE Photonics Technol. Lett. 14, 735 (2002).

[14]Y. Qiu, D. Uhl, R. Chacon, and R. Q. Yang, Appl. Phys. Lett. **83**, 1704 (2003)

[15]S. Forouhar, A. Ksendzov, A. Larsson, and H. Temkin, Electron. Lett. 28, 1431, (1992)

[16]Zongyou Yin, Xiaohong Tang*, Wei Liu, Daohua Zhang, “Effects of $In_xGa_{1-x}As$ confinement layer on InAs quantum dots formation and their emission wavelength”, *J. of Appl. Phys.*, Vol.100, July, (2006) Jul 15 No.2, 033109

[17]R. M. Biefeld, Mater, Sci. Eng., R. **36**, 105 (2002)

[18] K. Suzuki and Y. Arakawa: Phys. Status Solidi B 224 (2001) 139.

[19] Y. Qiu, D. Uhl and S. Koo: Appl. Phys. Lett. 84 (2004) 263.

[20] K. Kawaguchi, M. Ekawa, T. Akiyama, H. Kuwatsuka, M. Sugawara, J. Crystal Growth 291 (2006) 154.

[21] H. B. Serreze, J. A. Baumann, L. Bunz, R. Schachter and R. D. Esman, Appl. Phys. Lett. 55, 2532 (1989).

[22] B. X. Bo, X. H. Tang, B. L. Zhang, G. S. Huang, Y. C. Zhang and S. C. Tjin, J. Crys. Growth, 268, 415 (2004).

[23] A. A. El-Emawy, S. Birudavolu, P. S. Wong, Y.-B. Jiang, H. Xu, S. Huang and D. L. Huffaker, J. Appl. Phys. 93, 3529 (2003).

[24] C. C. Hsu, Y. F. Yang, H. J. Ou, E. S. Yang and H. B. Lo, Appl. Phys. Lett., 71, 3248 (1997).