

# Mid-infrared emissive InAsSb quantum dots grown by metal–organic chemical vapor deposition

Cite this: *CrystEngComm*, 2013, 15, 604

Tang Xiaohong,<sup>\*a</sup> Zhang Baolin<sup>b</sup> and Yin Zongyou<sup>a</sup>

InAsSb islands/quantum dots (QDs) emitting at wavelength  $>2.8 \mu\text{m}$  were self-assembled on InP substrate by using metal–organic chemical vapor deposition (MOCVD). Instead of using arsine, the safer organic *tert*-butylarsine (TBAs) was used as the arsenic source in the growth process. 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  $450 \text{ }^\circ\text{C}$  to  $470 \text{ }^\circ\text{C}$  was found for growing high quality InAsSb QDs. InAsSb rings instead of islands/dots were formed using the conventional Stranski–Krastanow (S–K) growth mode if the growth rate was low or if InAsSb was grown 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 achieved, about  $3 \times 10^9 \text{ cm}^{-2}$ , 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 observed. At room temperature, the emission wavelength of the InAsSb islands/dots was measured at  $>2.8 \mu\text{m}$ .

Received 10th August 2012,  
Accepted 4th November 2012

DOI: 10.1039/c2ce26271a

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## 1. 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,<sup>1,2</sup> *e.g.* lasers, single photon emitters, *etc.* But most works on semiconductor QDs have focused on the InAs–GaAs material system at wavelength of  $1.3 \mu\text{m}^{3-5}$  for optical communications and InAs QDs grown on InP substrate to obtain light emitters in the telecom wavelength region  $\sim 1.55 \mu\text{m}$ .<sup>6-8</sup> Recently, attempts to use InAs nanostructures based on InP substrates to extend the wavelength further into the mid-infrared region  $>2.0 \mu\text{m}$  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,<sup>9-11</sup> *etc.* InAs QDs and quantum-dash lasers have been demonstrated recently at various wavelengths from  $1.60$  to  $2.04 \mu\text{m}^{12-14}$  but the emission wavelength of the InAs QDs grown on InP is limited to  $<2.28 \mu\text{m}$ .<sup>15,16</sup>

To extend the emission wavelength further 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.<sup>17</sup> Only limited

reports on In(As)Sb QDs so far have been published.<sup>18-20</sup> However, photoluminescence (PL) at wavelengths as long as  $3.5 \mu\text{m}$  from the InSb QDs grown on an InAs matrix has been published<sup>18</sup> and InSb QDs with the dot density as high as  $4 \times 10^{10} \text{ cm}^{-2}$  grown on InP have been achieved by using molecular-beam epitaxy (MBE).<sup>19</sup>

Typically, self-assembled InSb QDs using metal–organic chemical vapor deposition (MOCVD) growth have an area density less than  $5 \times 10^9 \text{ cm}^{-2}$ . 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 results in big InSb islands of low density in MOCVD growths of InSb QDs. It has been reported that the InAsSb nano-structures changed shape from QDs to quantum wires (QWRs) and even quantum wells (QWs) as the Sb fraction in the MOCVD growth was increased.<sup>20</sup> 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, availability to large scale processing, *etc.* In conventional MOCVD growth of III–V semiconductors, highly toxic hydride arsine ( $\text{AsH}_3$ ) and phosphine ( $\text{PH}_3$ ) 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 growth. Organo-arsine and phosphine,

<sup>a</sup>OPTIMUS, Photonics Centre of Excellence, School of Electrical & Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore.  
E-mail: [exhtang@ntu.edu.sg](mailto:exhtang@ntu.edu.sg)

<sup>b</sup>College of Electronic Science & Engineering, Jilin University, Changchun, China

such as *tert*-butylarsine (TBAs) and *tert*-butylphosphine (TBP), are used for replacing AsH<sub>3</sub> and PH<sub>3</sub> in MOCVD growth. Devices made from the structures grown by MOCVD using TBAs and TBP as arsenic and phosphine sources exhibit state-of-the-art performance.<sup>21,22</sup>

In this research, MOCVD growth of InAsSb QDs on InP (001) substrate by using TBAs and TBP as arsenic and phosphine precursors was 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 a conventional S–K growth mode. The AIG of InAsSb QDs has been verified for improving the dot density and uniformity in self-assembled InAsSb QD growth.

## II. Experiment

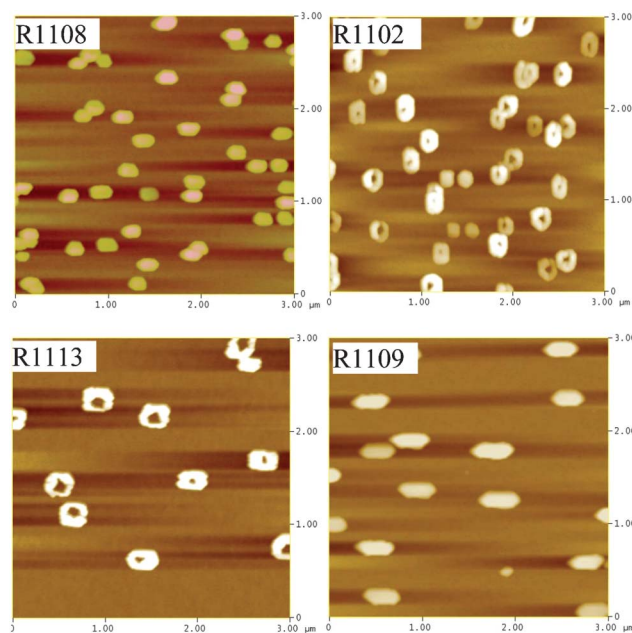
All samples in this research were grown in a horizontal MOCVD reactor (Aixtron, AIX200) with gas foil rotation of the susceptor. The metal–organic sources used in the growths were TBAs, TBP, trimethylantimony (TMSb), and trimethylindium (TMIn). High purity (99.999%) hydrogen gas purified by a MonoTorr phase II Getter column with dew point below –100 °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  $Q_{\text{tot}} = 3.1$  slm. *Epi*-ready InP semi-insulating substrates oriented in (001)  $\pm 0.1^\circ$  direction were used for all the growth processes.

Before starting the epitaxy growth, the InP substrate was annealed inside the reactor with a H<sub>2</sub> environment at 700 °C for 5 min. Then a 0.3  $\mu\text{m}$  InP buffer layer was grown on the InP substrate at 630 °C. After that, the substrate temperature was lowered for growing the InAsSb QDs. In this study, the InAsSb QDs were grown in a temperature range from 430 °C to 500 °C, and the TMIn inlet flux was varied from  $9 \times 10^{-6}$  mol min<sup>-1</sup> to  $2.7 \times 10^{-5}$  mol min<sup>-1</sup> 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 TBAs 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 °C. Surface morphology of all the samples was studied by using a Nanoscope III atomic force microscope (AFM). Emission of the grown InAsSb QDs was measured through photoluminescence (PL). For the PL measurement, the samples were excited by a 488 nm Ar<sup>+</sup> laser, and the emission of the samples was detected by a cooled PbS photodetector.

## III. Results and discussion

Fig. 1 shows the  $3 \times 3 \mu\text{m}^2$  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 °C, the TBP precursor was closed for 3 s before starting 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 open during the post-growth interruption for formation of the InAsSb QDs self-assembly. In this study, the post-growth interruption time was kept the same at 10 s for all the growths. The V : III ratio was kept at 6.5.

Sample R1102 and sample R1108 were grown with the same InAsSb growth rate by keeping the TMIn flow same. However, for sample R1108, the InAsSb layer was grown for 2.4 s, while for sample R1102, it was grown for 3.5 s. 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 s. Large size, with the diameter  $>200$  nm, InAsSb nanostructures with a very low density of less than  $5 \times 10^8 \text{ cm}^{-2}$  have been obtained for all the three samples. Upon increased InAsSb growth time, a lower density and larger diameter of the InAsSb nanostructures were formed. A very good inverse linear relationship



**Fig. 1** Top-view  $3 \times 3 \mu\text{m}^2$  AFM images of the InAsSb QD samples grown at 470 °C. Sample R1102 and R1108 have the same InAsSb growth rate, but different growth times. Sample R1109 and sample R1113 were grown at a lower growth rate but with a longer time to keep the InAsSb layer thickness the same as that of R1102.

between the InAsSb “dot” density grown *versus* the growth time (or lower growth rate) has been obtained as shown in Fig. 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 interesting to observe that when the InAsSb growth time is increased from 2.4 s for R1108 to 3.5 s for R1102, the formed nanostructure of R1108 was changed from the islands/dots to the rings of R1102. When prolonging the InAsSb growth time further to 9 s for sample R1113, larger diameter, lower density rings were obtained. 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 of R1109 were changed back to islands from rings. In this growth, the InAsSb layer was grown for 6 s. In order to grow the same thickness of InAsSb layer, the TMIIn flux was reduced to  $1.28 \times 10^{-5} \text{ mol min}^{-1}$ , which is about half of that for growing the sample R1102. Oval shaped dots or islands were obtained for sample R1109. The dot/island density of this sample is higher than that of sample R1113, which was grown for longer time, 9 s.

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 supplying TMIIn and TBAs precursors with interruptions in between. Fig. 3 compares the inlet TMIIn 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 TMIIn for 6 s, then it was closed and the InAsSb QDs were formed by self-assembly during the post-growth interruption before cooling down the system. Meanwhile in the AIG InAsSb QD growth, TMSb was always opened, but TMIIn and TBAs were alternately supplied with interruptions. To compare the growths, for both growths, the

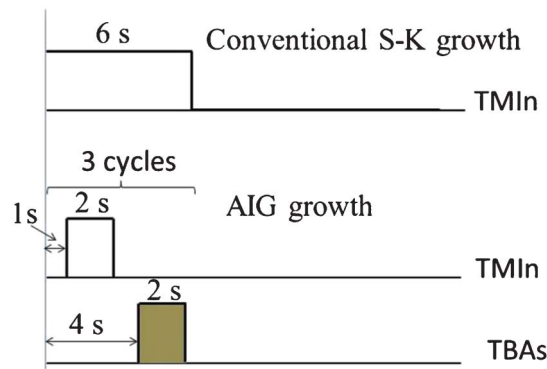


Fig. 3 Comparison of the MO sources' flow between the conventional S–K InAsSb QD growth and the AIG InAsSb QD growth.

total InAsSb layer was grown with same 2 to 3 monolayer (ML) thickness for all the samples.

Fig. 4 shows the 3D AFM images of the InAsSb QDs grown at different temperatures by using the AIG method. It shows that InAsSb islands/dots were obtained for all the growths by using the AIG method, no ring structures were observed in these growths. The formed InAsSb dot/island size and density are much dependent on the growth temperature. Fig. 5 shows the dot/island density of the samples obtained *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.<sup>23</sup> 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 the substrate temperature was below 450 °C. This is because the diffusion coefficients of In adatoms are smaller, which leads to lower growth efficiency.<sup>24</sup> Therefore, the materials available for growing the InAsSb were reduced when

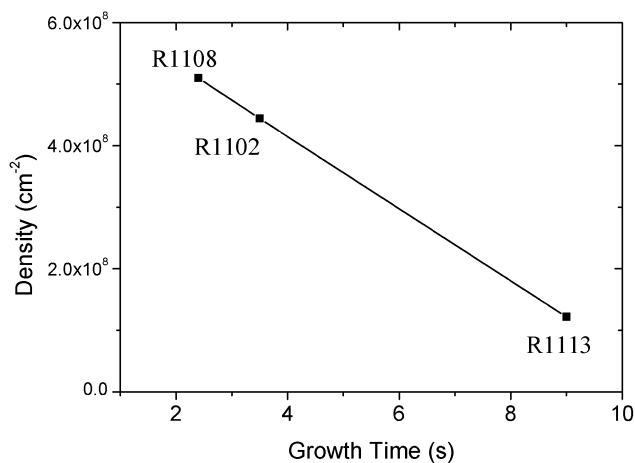


Fig. 2 The density of InAsSb nanostructure grown by S–K mode *versus* the InAsSb growth time. The substrate temperature was 470 °C and  $V : III$  ratio was 6.5.

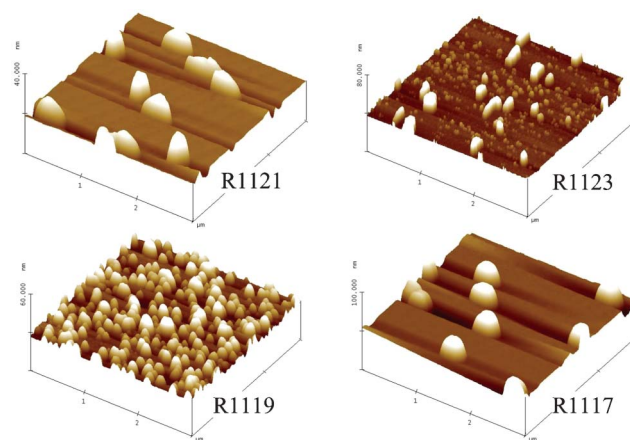
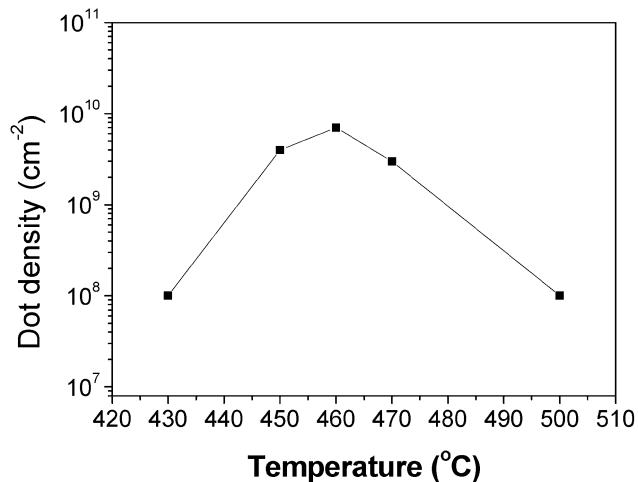


Fig. 4 3D  $3 \times 3 \mu\text{m}^2$  AFM images of the InAsSb QD samples grown by AIG growth at different temperatures. R1121, R1123, R1119 and R1117 were grown at 430 °C, 450 °C, 470 °C and 500 °C, respectively.



**Fig. 5** The InAsSb QD density grown by AIG mode versus the substrate temperature. The TMIn flux was  $9 \times 10^{-6} \text{ mol min}^{-1}$  and V : III ratio was 6.5 for growth.

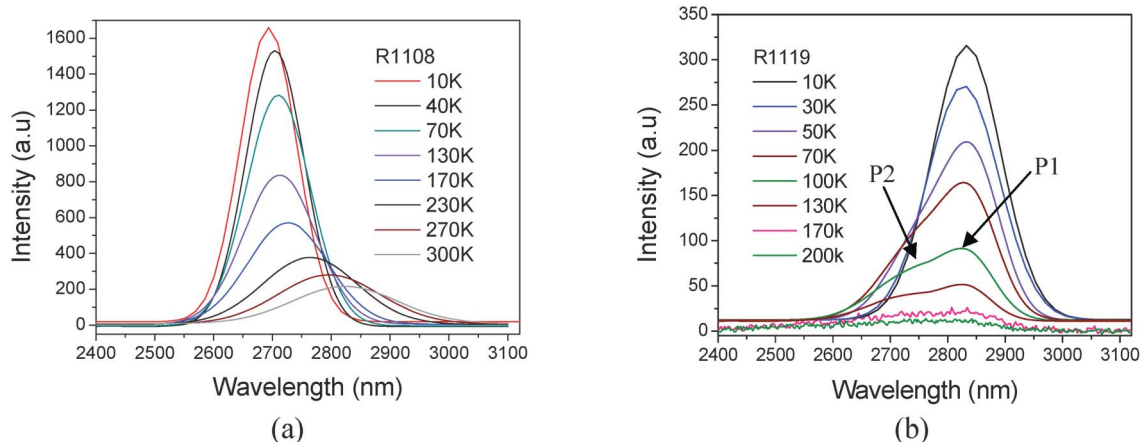
the growth temperature was below 450 °C, which resulted in the low density of InAsSb dots formed.

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 temperatures by photoluminescence (PL). The measured PL spectra of the two samples at different temperatures are shown in Fig. 6(a) and (b), respectively. Strong emissions at the wavelength around 2.8  $\mu\text{m}$  were obtained from the two samples. For sample R1108, which was grown by the conventional S–K mode, a 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 sized InAsSb islands formed in the sample. With the diameter of the islands above >200 nm, there is no quantum confinement effect of the InAsSb islands. The emission from these islands is similar to

that of the InAsSb bulk material. Meanwhile 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. The 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 a narrow growth temperature window, 450 °C–470 °C, for forming 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. With longer growth time, the formed InAsSb rings had larger diameters, but with lower density. This can be improved by increasing the V : III ratio. An alternative interruption growth of InAsSb QDs has been proposed to form InAsSb QDs self-assembly at 470 °C with very much higher density and smaller dot size. PL measurements show that both the InAsSb nanostructures formed by using conventional S–K mode and the AIG method emitted at  $\sim 2.8 \mu\text{m}$  at room temperature but the emission peak of the conventional S–K grown sample blue shifted when the temperature was lowered, which shows no quantum confinement of the large islands formed. The emission peak of the AIG-grown sample did not shift with the temperature, showing the strong quantum confinement of the InAsSb QDs formed.



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

## Acknowledgements

The authors would like to thank Madam Neo Bee Geok for helping on the AFM measurement. This research was sponsored by the Agency for Science, Technology and Research, Singapore.

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