Influence of As_4 flux on the growth kinetics, structure, and optical properties of InAs/GaAs quantum dots

A. Garcia,[a)] C. M. Mateo, M. Defensor, and A. Salvador
Condensed Matter Physics Laboratory, National Institute of Physics, University of the Philippines, Diliman, 1101 Quezon City, Philippines

H. K. Hui, C. B. Boothroyd, and E. Philpott
Institute of Materials Research and Engineering, 3 Research Link, Singapore

(Received 30 April 2007; accepted 6 August 2007; published online 11 October 2007)

We report the effects of variations in As_4 growth flux on the evolution of molecular beam epitaxy grown InAs quantum dots (QDs) and their structures and optical properties. For InAs QDs grown under As-stable conditions, evaluated through photoluminescence and atomic force microscopy (AFM) measurements, it is evident that QD size increases with As_4 pressure along with improvement in size uniformity. Furthermore, transmission electron microscopy measurements for InAs layers of critical thicknesses ($\sim$1.7 ML) showed decreasing QD density with increasing As_4 pressure accompanied by a strong reduction in photoluminescence (PL) integral intensity. These show that high As_4 fluxes suppress InAs QD formation while the decreasing PL intensity seems to indicate cluster formation that features nonradiative recombination. AFM measurements show larger and denser QDs for samples grown at higher As_4 pressures. These are explained on the basis of adatom condensation during surface cooling and the influence of As_4 pressure on indium incorporation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2785969]

I. INTRODUCTION

The study of quantum dots has allowed immense development in the physics of zero-dimensional (0D) structures. The technological potential of quantum dot (QD)-based devices owing to their superior optical and electronic properties has become the main driving force for further studies in this field. Taking advantage of the inherent strain among heterostructures, quantum dots are grown via self-assembly (i.e., Stranski-Krastanow mode) through molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). The practicality of QD-based devices at room temperature applications, however, imposes several requirements from the growth standpoint, particularly on QD size and uniformity.[1] Various investigations have been reported on the study of QD size control[2–6] as the ability to control the height, shape, and lateral dimension of QDs affords structures that emit in the technologically important wavelengths of 1.3 and 1.55 μm. No less important than size control is the demand for QD uniformity. Devices that require the strictest spectral constraint, with the exception of QD lasers, will rely on the uniformity of quantum dots and as such any significant fluctuation in size or volume is undesirable. In the InAs/GaAs quantum dot system, enhanced uniformity is observed on vertically coupled quantum dot samples,[7,8] on samples grown by migration enhanced epitaxy under In (no As) flux,[9] and for QDs grown with As_2 instead of As_4 species.[10] Independent control of size and density distributions in the upper QD layer in bilayer samples has also been reported.[7] Similar studies exploring the effects of various parameters such as growth rates,[11] growth temperature,[12] annealing,[13,14] AlAs,[15] and $In_xGa_{1-x}As$ capping layers[16,17] on the structure and luminescence characteristics of QDs have been conducted.

Curiously, the effect of arsenic growth flux (As_2 or As_4) on InAs/GaAs systems is scarcely investigated except for one of the early studies conducted by Ledentsov *et al.*[18] which showed that higher or lower As fluxes suppressed the formation of dots.

In this study, we report a detailed investigation on the effects of As_4 flux on the growth kinetics and the optical and structural characteristics of InAs quantum dots grown on GaAs (100) substrates by MBE, particularly with regard to size evolution, QD density, and uniformity.

II. EXPERIMENTS

The layers were grown on n^+-GaAs (100) substrates using a solid source Riber 32P MBE system equipped with a 12 keV reflection high energy electron diffractometer (RHEED). After oxide desorption, a 0.6-μm-thick Si-doped GaAs buffer layer containing 20–30 periods of AlAs/GaAs superlattice was grown at 580 °C to shield the layers from substrate impurities and smoothen the surface prior to the deposition of dots. The growth temperature was slowly ramped down to 490 °C during the last 100 nm of the buffer layer, followed by InAs deposition. The amount of deposited InAs was determined from RHEED signal in accordance with Ref. 19, wherein the appearance of so-called *chevrons* in the $[1\bar{1}0]$ azimuth corresponded to a critical coverage of 1.7 ML (monolayer) at this growth temperature for a total deposition time t_c. Immediately upon observation of critical coverage, the In cell was closed and the InAs layer was subjected to a 10 s growth interrupt (G.I.) under flowing As_4

[a)]Electronic mail: agarcia@nip.upd.edu.ph

followed by another InAs deposition for the same duration t_c and, finally, an overgrowth with 100 nm Si-doped GaAs. On this cap layer, a second InAs QD layer was grown in an exactly similar manner but at a higher As_4 flux. In all, three QD layers were grown at various values of As_4 flux for each sample, and two samples (S1 and S2) were prepared this way, covering As_4 flux range of $1.6P_0$–$8.4P_0$. In this study, $1.6P_0$ corresponds to an As_4 pressure which is 1.6 times over the value where the transition from As-rich to Ga-rich growth takes place. To investigate the effect of varying As_4 flux during growth interrupt, another sample (S3) containing three QD layers was grown in the same manner described above but *without the subsequent InAs regrowth* following the growth interrupt stage. Finally, a control sample (S4) containing three layers of identically grown InAs QD layers was prepared to determine whether the relative positions of the QD layers with respect to the surface affect the photoluminescence (PL) peak positions and intensities.

All InAs QDs in this study were grown at 490 °C at a fixed In flux and capped with 100 nm Si-doped GaAs (for PL measurements) except for those intended for atomic force microscopy (AFM) measurements. For these uncapped layers, the growth temperature was rapidly ramped down to room temperature upon growth of InAs. Two QD layers for AFM under $2.3P_0$ and $8.4P_0$ were grown in this manner. We note that the cap layers for the other samples were grown at different V/III flux ratios corresponding to the changes in As_4 flux (Ga flux was fixed). The thickness (100 nm) of the cap layer was meant to minimize if not eliminate any templating and/or stacking effects between QD layers that could lead to vertical coupling.

PL measurements were performed using the 488 nm line of Ar^+ laser with the output signal collected by a Spex 500 spectrometer using a Ge photodiode employing standard lock-in techniques. It was necessary to etch the samples sequentially in order to probe the buried QD layers. For this purpose we used 1:3:150 ($NH_4OH:H_2O_2:H_2O$) solution by volume at an etch rate of about 90 Å/s for GaAs. Finally for S3, cross section transmission electron microscopy (XTEM) images are correlated with PL data to evaluate the effect of As_4 during growth interrupt.

III. RESULTS AND DISCUSSION

Figure 1 presents the PL spectra for sample S1, corresponding to the lowest range of As_4 flux used in this study, $1.6P_0$–$5P_0$. The broad spectra indicate wide size distributions while broadening toward higher wavelengths accompanied by a redshift in PL peak positions suggests increase in QD size with As_4. To visualize size increase, we utilized Gaussian fitting curves showing three dominant size distribution modes labeled SQD, MQD, and LQD (for purposes of distinction), corresponding to their respective relative sizes (small, medium, and large). The increasing emission wavelength [Figs. 1(a)–1(c)] translates to a decrease in quantum confinement which is an indication of increasing QD size. In addition, a low density of smaller QDs starts to appear in the PL spectrum for the layer grown at $5P_0$ [indicated by an arrow in Fig. 1(c)]. No broadening is observed in the low

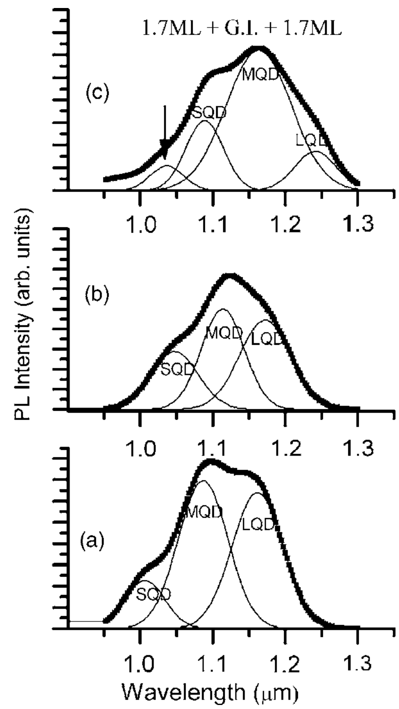

FIG. 1. PL spectra for sample S1 (three GaAs-capped QD layers) grown at (a) $1.6P_0$, (b) $3.2P_0$, and (c) $5P_0$ where P_0 corresponds to As_4 pressure at the Ga-rich to As-rich growth transition point. The increase in PL emission wavelengths with As_4 pressure indicates increasing QD size over the entire multimodal distribution with small, medium, and large QDs labeled SQD, MQD, and LQD, respectively, based on Gaussian fitting curves. The peak marked by the arrow in (c) represents the appearance of small QDs in addition to the three modal sizes.

wavelength side of the spectrum. This size increase can be explained by the minimal In desorption at high As_4 flux[20] and at relatively low temperatures. In incorporation is therefore enhanced and the In adatoms are probably bonded preferentially to existing islands. A similar behavior can be seen in Fig. 2 for sample S2 grown at a higher As_4 flux range of $4.4P_0$–$8.4P_0$. Comparing Figs. 1 and 2, we see an improved

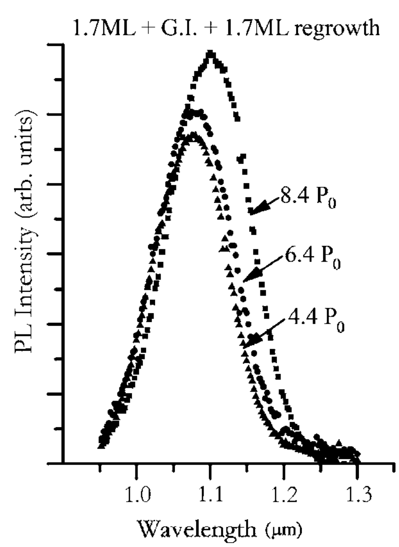

FIG. 2. PL spectra for sample S2 (three GaAs-capped QD layers) showing broadening at higher wavelengths with increasing As_4 flux indicating QD size increase.

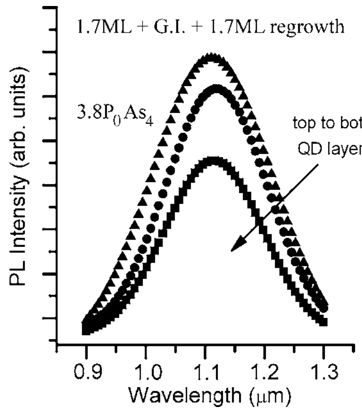

FIG. 3. PL spectra of sample S4 (three identically grown GaAs-capped QD layers) showing the decrease in integral intensity of buried QD layers.

uniformity in QD size distribution for S2, in addition to the increased QD size with As_4 pressure. We estimate a 46% reduction in full width at half maximum (FWHM) value for S2 relative to S1. The lowest As_4 flux used in this study corresponds to As_4/In ratio of ~200 well into the As-stable condition regime. Accordingly, strain relaxation under As-stable conditions starts with the formation of coherent islands while misfit dislocation formation that leads to the suppression of island growth is characteristic of In-stable conditions.[21] Our results are in perfect agreement with the former case.

GaAs cap layers have been known to affect the size and shape evolution of dots. The anisotropic formation of InAs on GaAs can lead to elongation of the dots[22] and shape transformation has been reported from square-based pyramids to lens-shaped dots after GaAs regrowth.[23] A study on the effect of thin GaAs cap layer resulted into reduction in height and density of QDs.[3] In our case, aside from a small reduction in PL intensity for buried layers, we observed consistent and reproducible effect of the 100 nm GaAs spacer layers for QDs grown at a relatively higher flux of $3.8P_0$. This is seen in Fig. 3, the PL spectra for sample S4 consisting of three QD layers grown identically at this As_4 flux. Hence, we attribute the observed redshifts in PL emission as due exclusively to increased QD size. The nonconformity of our results with those of Ref. 3 where In segregation from the wetting layer to the GaAs layer was considered to be the cause for QD volume reduction may be due to the relatively low growth temperature of 490 °C used in our study that renders the thermally driven In segregation to be ineffective.

In Fig. 4 we compare the AFM micrographs of two uncapped QD layers grown at As_4 fluxes of $2.3P_0$ [(a) and (c)] and $8.4P_0$ [(b) and (d)]. A most notable difference between the two layers is the high concentration of clusters for the layer grown at the lower As_4 flux as seen in Fig. 4(a). Such lateral coupling indicates that In is preferentially incorporated into large dots already present and further enhanced under low arsenic conditions. This mechanism also explains the apparent low coverage seen in Fig. 4(a). However, as can be seen in Fig. 4(c), a large portion of these "uncovered" areas is in fact populated by small coherent dots, whose growth is hampered by the above-mentioned preferential In

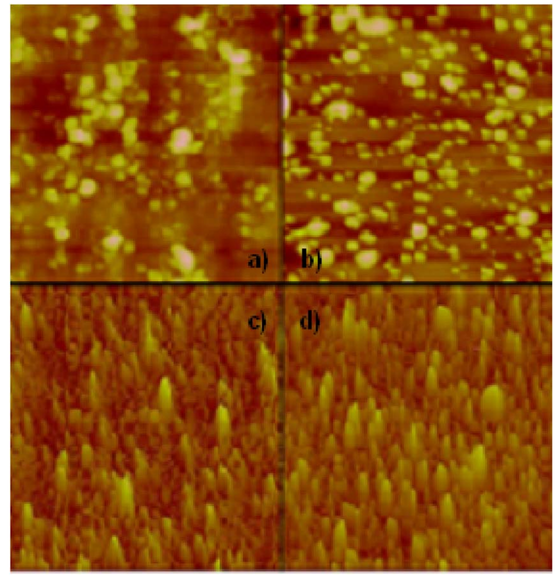

FIG. 4. (Color online) 2×2 μm^2 AFM areal and three-dimensional (3D) micrographs of QD layers grown at $2.3P_0$ [(a) and (c)] and $8.4P_0$ [(b) and (d)]. Improved uniformity and density can be seen for the QDs at higher As_4 flux.

incorporation. Figure 4(b) shows the areal micrograph of QDs grown at higher As_4 flux and it can be seen that the density of clusters is significantly reduced leading to a more uniform size distribution [Fig. 4(d)] and larger coherent dots.

We now focus on the origin of the increase in size and density of the uncapped QDs. The effect of cooling of uncapped surfaces has been previously studied and it was found that QD size increases due to surface adatom condensation onto existing InAs islands.[24] However, the observed size increase in our study cannot be fully attributed to this phenomenon because (i) the uncapped samples in this study were cooled *rapidly* to 300 °C severely limiting adatom diffusion and condensation on preexisting islands and (ii) QD size increase is observed even for capped QDs (samples S1 and S2) as indicated by the *redshift* in PL peak position seen in Fig. 1. This means that some other mechanism(s), such as the one described above, is (are) in effect. Comparing the densities of QDs, we found from Fig. 4 that the layers grown at higher As_4 flux have a higher concentration than the lower As_4 flux layer. Such increase in QD density is consistent with the results of the study conducted by Ledentsov *et al.*[25] and is accordingly due to adatom condensation. The speed of the cooling process in this case imposes a limitation on the effective diffusion length of In adatoms which therefore condense to form new islands rather than being incorporated into existing islands. This is particularly true for surfaces of low island density before cooling starts. As can be seen in Fig. 5, QD density is significantly low for InAs layers grown at higher As_4 fluxes (sample S3). Therefore, adatom condensation will strongly be manifested in the formation of new islands, hence the increase in density for uncapped QDs grown at high As_4 fluxes. It is also evident from the integral intensities of the PL peaks in Fig. 5 that the dots grown at high As_4 fluxes are dominated by cluster formations as reported in Ref. 18.

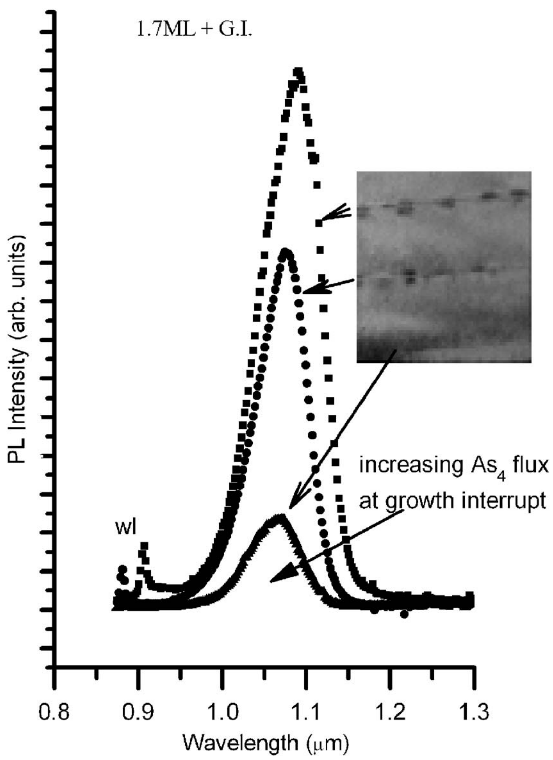

FIG. 5. 10 K PL spectra and bright-field cross-sectional TEM micrograph for sample S3 showing decrease in QD density with increasing As_4 flux and a significant reduction in integral PL intensity.

IV. CONCLUSION

In conclusion, we found that InAs quantum dots grown under As-stable conditions increase in size with As_4 pressure, in addition to enhanced size uniformity. Furthermore, InAs layers of critical thicknesses ($\sim$1.7 ML) showed decreasing QD density with increasing As_4 pressure accompanied by a strong reduction in PL integral intensity. High As_4 fluxes therefore suppress InAs QD formation while at the same time inducing cluster formation that features nonradiative recombination. Higher density QDs resulted from growth of uncapped QDs at high As_4 pressures due to adatom condensation during surface cooling, while volume increase is due to the influence of As_4 pressure on indium incorporation.

ACKNOWLEDGMENTS

This project is funded in part by the Philippine Council for Advanced Science and Technology Research and Development (PCASTRD) and the International Center for Materials Research (ICMR), Asia Materials Network. A.G. acknowledges the support of the University of the Philippines Baguio.

[1]D. Bimberg, M. Grundmann, and N. Ledentsov, *Quantum Dot Heterostructures* (Wiley, Chichester, 1999).
[2]J. S. Kim, J. H. Lee, S. U. Hong, W. S. Han, H. S. Kwack, J. H. Kim, and D. K. Oh, J. Appl. Phys. **94**, 2486 (2003).
[3]F. Ferdos, S. Wang, Y. Wei, A. Larsson, M. Sadeghi, and Q. Zhao, Appl. Phys. Lett. **81**, 1195 (2002).
[4]M. V. Maximov, A. F. Tsatsul'nikov, B. V. Volovik, D. S. Sizov, Yu. M. Shernyakov, I. N. Kaiander, A. E. Zhukov, A. R. Kovsh, S. S. Mikhrin, V. M. Ustinov, Zh. I. Alferov, R. Heitz, V. A. Shchukin, N. N. Ledentsov, D. Bimberg, Yu. G. Musikhin, and W. Neumann, Phys. Rev. B **62**, 16671 (2000).
[5]H. Y. Liu and M. Hopkinson, Appl. Phys. Lett. **82**, 3644 (2003).
[6]K. Takehana, F. Pulizzi, A. Patane, M. Henini, P. C. Main, L. Eaves, D. Granados, and J. M. Garcia, J. Cryst. Growth **251**, 155 (2003).
[7]I. Mukhametzhanov, R. Heitz, J. Zeng, P. Chen, and A. Madhukar, Appl. Phys. Lett. **73**, 1841 (1998).
[8]H. Heidemeyer, S. Kiravittaya, C. Muller, N. Y. Jin-Philipp, and O. Schmidt, Appl. Phys. Lett. **80**, 1544 (2002).
[9]J. D. Song, Y. M. Park, J. C. Shin, J. G. Lim, Y. J. Park, W. J. Choi, I. K. Han, J. I. Lee, H. S. Kim, and C. G. Park, J. Appl. Phys. **96**, 4122 (2004).
[10]T. Sugaya, T. Amano, and K. Komori, J. Appl. Phys. **100**, 063107 (2006).
[11]P. B. Joyce, T. J. Krzyzewski, G. R. Bell, T. S. Jones, S. Malik, D. Childs, and R. Murray, J. Cryst. Growth **227–228**, 1000 (2001).
[12]S. Liang, H. L. Zhu, and W. Wang, J. Appl. Phys. **100**, 103503 (2006).
[13]Q. W. Mo, T. W. Fan, Q. Gong, J. Wu, Z. G. Wang, and Y. Q. Bai, Appl. Phys. Lett. **73**, 3518 (1998).
[14]D. Z. Hu, D. M. Schaadt, and K. H. Ploog, J. Cryst. Growth **293**, 546–549 (2006).
[15]F. Ferdos, S. Wang, Y. Wei, M. Sadeghi, Q. Zhao, and A. Larsson, J. Cryst. Growth **251**, 145 (2003).
[16]K. Nishi, H. Saito, S. Sugou, and J. S. Lee, Appl. Phys. Lett. **74**, 1111 (1999).
[17]J. S. Kim, P. W. Yu, J. I. Lee, J. S. Kim, S. G. Kim, J.-Y. Leem, and M. Jeon, Appl. Phys. Lett. **80**, 4714 (2002).
[18]N. N. Ledentsov, M. Grundmann, N. Kirstaedter, O. Schmidt, R. Heitz, J. BÖhrer, D. Bimberg, V. M. Ustinov, V. A. Shchukin, A. Yu. Egorov, A. E. Zhukov, S. Zaitsev, P. S. Kop'ev, Zh. I. Alferov, S. S. Ruvimov, A. O. Kosogov, P. Werner, U. GÖsele, and J. Heydenreich, Solid-State Electron. **40**, 785 (1996).
[19]Ch. Heyn, Phys. Rev. B **64**, 165306 (2001).
[20]J. M. Van Hove and P. I. Cohen, Appl. Phys. Lett. **47**, 726 (1985).
[21]A. Trampert, A. Tournie, and K. H. Ploog, Phys. Status Solidi A **145**, 481 (1994).
[22]S. Sauvage, P. Boucaud, F. H. Julien, J.-M. Gerard, and J.-Y. Marzin, J. Appl. Phys. **82**, 3396 (1997).
[23]Y. Nabetani, T. Ishikawa, S. Noda, and A. Sakai, J. Appl. Phys. **76**, 347 (1994).
[24]R. Leon, J. Wellman, X. Z. Liao, J. Zou, and D. J. H. Cockayne, Appl. Phys. Lett. **76**, 1558 (2000).
[25]N. N. Ledentsov, V. A. Shchukin, D. Bimberg, V. M. Ustinov, N. A. Cherkashin, Y. G. Musikhin, B. V. Volovik, G. E. Cirlin, and Zh. I. Alferov, Semicond. Sci. Technol. **16**, 502 (2001).