Another Origin of Bimodal Size Distribution in InAs Self-Assembled Quantum Dots

Bhavtosh Bansal*, M. R. Gokhale, A. Bhattacharya and B. M. Arora
Department of Condensed Matter Physics and Materials Science,
Tata Institute of Fundamental Research, 1 Homi Bhabha Road, Mumbai-400005, India
(Dated: March 23, 2022)

The evolution of InAs quantum dots grown on InP substrates by metal-organic vapour phase epitaxy is studied as a function of InAs coverage. Under specific growth conditions, the onset of the two- to three-dimensional transition is seen to proceed via two distinct pathways: through (i) an abrupt appearance of quantum dots as expected in the usual Stransi-Krastanov growth picture and (ii) a continuous evolution of small surface features into well developed quantum dots. The average size of the features in both these families increases with coverage, leading to a bimodal distribution in dot sizes at an intermediate stage of growth evolution that eventually becomes a unimodal distribution as more material is deposited. Complementary information obtained from independent measurements of photoluminescence spectra and surface morphology is correlated and is found to be independently consistent with the picture of growth proposed.

PACS numbers: 68.65.Hb, 78.67.Hc, 81.07.Ta, 68.37.Ps, 81.15.Gh

The semiconductor heterostructures grown via the strain-mediated Stranski-Krastanov (S-K) route[1, 2] have been of special interest. The resulting self assembled clusters are extremely small (~10nm, hence called quantum dots), coherently strained (hence optically active) and have a size dispersion that may be acceptable for their use in real optoelectronic devices, e.g., [3, 4]. The S-K transition has been systematically studied in most III-V semiconductors of interest (e.g. InAs/GaAs, GaSb/GaAs[13]). While the growth route may be rationalized by energetic considerations that predict an initial two-dimensional growth followed by an abrupt appearance of three-dimensional clusters upon the ‘wetting layer’[1], the actual process of self-assembly is complicated by kinetic effects, substrate conditions and orientation, a non-quiescent wetting layer during growth evolution, alloying and long-ranged substrate-mediated elastic interactions. For example, it has also been observed, though not consistently by different groups, that there may be redistribution of matter leading to a decrease in the quantum dot (QD) size with coverage. Often a bimodal size distribution[5,12] has also been observed at an intermediate growth stage. Although many of these phenomena have been described in terms of elastic energy barriers corresponding to change in shape and a maximum permissible size for quantum dots beyond which they are dislocated, the complex growth evolution of self-assembled dots, especially under far from equilibrium (usual) growth conditions, is still very much an open problem despite more than a decade of extensive work.

In this paper, we focus on InAs/InP self-assembled QDs grown by metal-organic vapour phase epitaxy (MOVPE)[14,15]. The samples are studied at different stages of evolution by independently studying and quantitatively correlating the morphology and the optical emission spectra. Contrary to many of previous reports, we have, on samples grown under more non-equilibrium conditions (lower coverage, 450°C and higher growth rate ~1-2 monolayers(ML) per second) where surface kinetics may be an important limiting step, observed that the 2D-3D transition is not completely abrupt and proceeds via two different pathways. This study also yields a different picture for bimodality in the QD’s size distribution.

Growth was carried out using low pressure (100 torr) MOVPE on n+ doped (001) “epi-ready” InP substrates in a horizontal reactor with hydrogen as the carrier gas. Group III and V sources were trimethyl-indium and arsine and phosphine respectively. Prior to InAs growth, an InP buffer layer was grown first at 625°C and then with the temperature continuously ramped down and stabilized to 450°C. InAs layers were grown at a relatively low temperature of 450°C at a growth rate[16] of approximately 1.8ML/s. A pair of samples was grown with identically deposited InAs layer in two growth runs. In the first case, the sample was taken out of the reactor after InAs deposition itself to enable a study of surface morphology and in the second case a InP cap layer was grown for samples used for photoluminescence study. For these samples, about 50 Å InP was deposited at the InAs deposition temperature to avoid any further ripening during the higher temperature overgrowth. Surface features were studied ex-situ using an atomic force microscope (AFM) in contact mode, typically within a few hours of sample growth. The PL spectra were measured at ~25 K at low enough excitation power (~0.5W/cm²) to preclude any subband filling and were corrected for the system response using a standard black body source.

Fig. 1 (inset) shows 1µm × 1µm AFM scans for samples with progressively increasing InAs coverage in Fig. 1(a) to (d). The histograms of the island heights corresponding to these AFM images are shown in the main Fig. 1. All well-separated (~20nm) convex features with heights above two ML were counted here. Fig. 1(a) depicts an early stage of growth. Here we observe that along with very few (~5 × 10⁶ cm⁻²) well developed
(height > 8 nm) QDs, there are many small surface features of minimum height of ~14Å and a mean height of 26Å contributing to a large number of counts at low heights. Furthermore, in Fig. 1(b)-(c), we observe that these small surface features are stable and continuously grow in size as more material is deposited. Therefore, with incremental coverage, Fig. 1(b)-(d), the morphology evolves as (i) matter is accreted by all pre-existing features making them grow in size (ii) new well-developed QDs of height ~8nm are spontaneously generated (usual S-K transition). Growth via two independent pathways naturally leads to a bimodal size distribution at an intermediate stage of growth, Fig. 1(c). The role of existing (two- and quasi-three-dimensional) surface features during the S-K transition has been much discussed in Refs. 6, 7, and 17. Here these surface corrugations are only being connected to dots which continuously evolve in size and we have not examined their role, if any, as precursors to abruptly generated well developed dots (S-K transition).

The above mentioned picture of growth evolution is independently observed in optical properties. Fig. 2 shows the low temperature PL spectra measured on the four similarly grown but capped samples. Along with the characteristic PL from well-developed dots, the PL spectrum also shows a wetting layer peak around 1.02−1.03 eV that is broadened towards lower energy by the emission from these optically active quasi-three-dimensional clusters. The spectrum in Fig. 2(c) shows almost three distinct peaks corresponding to the wetting layer and the two kinds of quantum dots. Finally, in the saturation regime (when the number of well resolved QDs does not increase with coverage), the distribution of the dot sizes is again roughly unimodal, but with a large dispersion.

The optical signature from the wetting layer was inferred by fitting two Gaussians, (corresponding to signals from WL and quasi-three-dimensional clusters) to the high energy PL peak. We observe that the wetting layer peak is constant to within 10 meV in Fig. 2(a)-(c). This low temperature PL peak at around 1.02−1.03 eV corresponds...
sponds to an approximately 4.5 ML strained InAs/InP quantum well. This value may be used to calibrate the thickness with the deposition time, which is otherwise difficult to estimate with sub-ML precision in a typical MOVPE set-up without in-situ diagnostic tools. It is worth pointing out that there has been a wide variation in the reported value of the wetting layer thickness for InAs/InP, with the lower limit being ~1ML. With a lower growth temperature, the wetting layer thickness is expected to be (exponentially) larger than its equilibrium value, since the former is inversely dependent on the deposition temperature. Because 450°C is among the lower reported growth temperatures for InAs dots, a thicker wetting layer is naturally expected. Remarkably, a recent reflection high energy electron diffraction study on 2D-3D transition in MBE grown InAs/InP films, reports for growth at 450°C, a value of the wetting layer thickness that is very similar to what we have inferred from the PL spectra.

Finally, in Fig. 2(d), the wetting layer PL shifts to a higher energy, ~1.10 eV indicating the well known narrowing of wetting layer in the saturation regime.

The observed PL spectra from QDs should in principle be derivable from the quantitative analysis of the AFM images. Using published ground state energy calculations for InAs/InP QDs, the expected emission spectra from large dots are shown in Fig 2(open squares). While there is a good quantitative agreement without any fitting parameter for the expected and observed spectral features from large dots (those above the size cut-off depicted by dotted lines in Fig. 1), the PL from the smaller features in each histogram did not agree as well and is therefore not shown in Fig 2. It has been previously established that the capping process can considerably change the morphology of the individual quantum dots and it is likely that the smaller dots are more affected by capping and compositional changes due to the As/P exchange during the early stage of InP overgrowth.

Implications: We have observed that the 2D-3D transition is not abrupt and the bimodality in the QD’s size distribution at an intermediate stage of growth is a consequence of the growth evolving via two distinct pathways. These two observations are contrary to previous studies on InAs/GaAs and InxGa1−xAs/GaAs where the 2D-3D transition had been found to be abrupt and thermodynamically first-order with the surface coverage playing the role of a critical parameter. An abrupt appearance of quantum dots beyond a critical coverage has also been theoretically reproduced within a rate equation based model.

Bimodality in dot sizes also implies that the QDs ensemble cannot be characterized by a single length scale (e.g., mean island size) during most of the evolution and rules out the very attractive possibility of data collapse onto a universal scaling function during intermediate stages of growth. Absence of scaling at an intermediate growth stage has actually been observed by

It is instructive to (visually) separate the heights histograms in Fig. 1 at the minima between the two modes (dotted lines in Fig. 1). Fig. 3 is the corresponding plot of cluster densities in these two families (S-K dots and continuously evolving clusters) as a function of coverage. The increase in the density of larger dots with coverage is abrupt, whereas the number of smaller features decreases with coverage due to coalescence. At large enough coverage the distribution becomes unimodal. Without invoking the existence of energy barriers, this is most simply understood as being due to the difference in growth rates of larger and smaller dots (due to their different volumes).

Among the various studies of growth evolution, the results in references, although on MBE grown InAs/GaAs, are qualitatively most similar to ours. Nevertheless there are some important differences both in data and interpretation of results. Firstly, the quasi-three dimensional clusters were thought to be precursors to all the quantum dots giving a common origin to the dots in both the families. Possibly due to a smaller strain in the InAs/InP system as compared to InAs/GaAs, we observe an uninhibited increase in size and a corresponding redshift in PL with coverage. This is in contrast with InAs/GaAs QDs, where a pronounced barrier seems to restrict the maximum dot size to ~8nm. This supports the general observation of larger dispersion in dot sizes and low temperature PL linewidths (~100meV) in InAs/InP.
The differences observed in growth evolution by different groups may be a result of differing substrate/buffer layer conditions. It is possible for the local roughness in the wetting layer surface to stabilize pre-existing quasi-three dimensional surface structures and determine the extent of bimodality at an intermediate growth stage. Many of the thermodynamic arguments used to describe the QD self-assembly are relevant only under quasi-equilibrium conditions of growth which many such previous experiments tried to maintain. Our results, on the other hand, are obtained under much higher growth rates, more typical growth conditions of quantum dots. Conclusions: Studying the growth evolution of MOVPE grown InAs/InP self-assembled quantum dots, we have observed that an alternate pathway for the 2D-3D transition exists which naturally explains the often observed bimodality in the quantum dots size distribution at an intermediate growth stage. Independent evaluations of the morphology and the photoluminescence spectra are consistent with the picture of growth presented.

We gratefully acknowledge J. John and Sandip Ghosh for their help with the AFM and PL measurements and Sandeep Krishna for his help with the development of the image processing software.

*Electronic Address: bhavtosh@tifr.res.in

[1] J. Stangl, V. Holy and G. Bauer, Rev. Mod. Phys. 76, 725 (2004)
[2] B. A. Joyce, D. D. Vvedensky, Mat. Sci. Eng. R 46 ,127 (2004).
[3] H. C. Liu, M. Gao, J. McCaffrey, Z. R. Wasilewski, and S. Fafard, Appl. Phys. Lett. 78, 79 (2001).
[4] Y. Qiu, D. Uhl, R. Chacon, and R. Q. Yang, Appl. Phys. Lett. 83, 1704 (2003).
[5] D. Leonard, K. Pond, and P. M. Petroff, Phys. Rev. B 50, 11687 (1994).
[6] A. Madhukar, p26 Nano-Optoelectronics Ed. M. Grundmann (Springer-Verlag, Berlin 2002). T. R. Ramachandran, R. Heitz, P. Chen, and A. Madhukar, Appl. Phys. Lett. 70, 640 (1997).
[7] P. Patella, A. Sgarlata, F. Arciprete, S. Nufris, P. D. Szkutnik, E. Placidi, M. Fanfoni, N. Motta and A. Balzarotti, J. Phys. Cond. Matt. 16, S1503 (2004). Sgarlata, [8] M.J. da Silva, A.A. Quivy, P.P. Gonzalez-Borrero, E. Marega Jr., J.R. Leite, J. Crystal Growth 241, 19 (2002).
[9] C. A. Duarte, E. C. F. da Silva, A. A. Quivy, M. J. da Silva, S. Martini, J. R. Leite, A. E. Meneses and E. Lauretto, J. Appl. Phys. 93, 6279 (2003).
[10] R. Leon and S. Fafard, Phys. Rev. B 58, R1726 (1998).
[11] A.G. Cullis, D.J. Norris, T. Walther, M.A. Migliorato, and M. Hopkinson, Phys. Rev. B 66, 081305 (R) (2002).
[12] A. Ponchet, A. Le Corre, H. L’Haridon, B. Lambert, and S. Salaün, Appl. Phys. Lett. 67, 1850 (1995).
[13] L. Müller-Kirsch, R. Heitz, U. W. Pohl, D. Bimberg, J. Husler, H. Kirmse, and W. Neumann, Appl. Phys. Lett. 79, 1027 (2001) Charbonneau,
[14] N. Carlsson, T. Junno, L. Montelius, M. -E. Pistol, L. Samuelson and W. Seifert, J. Cryst. Growth, 191, 347 (1998).
[15] H. Marchand, P. Desjardins, S. Guillon, J.-E. Pauliure, Z. Bourgioua, R. Y.-F. Yip, and R. A. Masut, Appl. Phys. Lett. 71, 527 (1997).
[16] This value of growth rate is inferred from the wetting layer PL in Fig.2(a).
[17] C. Preister and M. Lanno, Phys. Rev. Lett. 75, 93 (1995). C. Preister and M. Lanno, Curr. Opinion Sol. Stat. Mat. Sci. 2, 716, (1997).
[18] R. Leonelli, C. A. Tran, J. L. Brehner, J. T. Graham, R. Tabti, R. A. Masut, and S. Charbonneau, Phys. Rev. B 48, 11135 (1993).
[19] K. Kawaguchi, M. Ekawa, A. Kuramata, T. Akiyama, H. Ebe, M. Sugawara, and Y. Arakawa, Appl. Phys. Lett. 85, 4331 (2004).
[20] J. F. Girard, C. Dion, P. Desjardins, C. N Allen, P. J. Poole, and S. Raymond, Appl. Phys. Lett. 84, 3382 (2004).
[21] J. Johansson and W. Seifert, J. Cryst. Growth 234, 132 (2002), ibid., 132, 139 (2002).
[22] C. W. Snyder, J. F. Mansfield, and B. G. Orr Phys. Rev. B 46, 9551(1992).
[23] M. Gendry, C. Monat, J. Brault, P. Regreny, G. Hollinger, B. Salem, G. Guillot, T. Benyattou, C. Bruchevallier, G. Bremond, and O. Marty, J. Appl. Phys. 95, 4761 (2004).
[24] for example, G Abstreiter, P Schittenhelm, C Engel, E Silveira, A Zrenner, D Meertens and W Jager, Semicond. Sci. Technol. 11 1521 (1996).
[25] It must be noted that AFM images cover an area of 1µm² which is vastly different from the area sampled by the PL excitation source (∼ 1mm²). The comparison (which is further affected by InP overgrowth) is therefore necessarily qualitative.
[26] M. Holm, M-E. Pistol, and C. Pryor, J. Appl. Phys. 92, 932 (2002).
[27] P. B. Joyce, T. J. Krzyzewski, G. R. Bell, and T. S. Jones, Appl. Phys. Lett. 79, 3615 (2001).
[28] F. Ferdos, S. Wang, Y. Wei, A. Larsson, M. Sadeghi, Q. Zhao, Appl. Phys. Lett. 81, 1195 (2002).
[29] H. T. Dobbs, D. D. Vvedensky, A. Zangwill, J. Johansson, N. Carlsson, and W. Seifert, Phys. Rev. Lett. 79, 897 (1997).
[30] Y. Ebiko, S. Muto, S. Itoh, D. Suzuki, K. Shiramire, and T. Haga, Phys. Rev. Lett., 80, 2650 (1998).
[31] R. E. Rudd, G. A. D. Briggs, A. P. Sutton, G. Mediavilla-Ribeiro, and R. S. Williams, Phys. Rev. Lett. 90, 146101 (2003).
[32] F. M. Ross, J. Tesfay, and R. M. Tromp, Phys. Rev. Lett. 80, 984 (1998). F. M. Ross, R. M. Tromp, and M. C. Reuter, Science 286, 1931 (1999).
[33] C. Adelmann, B. Daudin, R. A. Oliver, G. A. D. Briggs, and R. E. Rudd, Phys. Rev. B 70, 125427 (2004).
[34] G. Costantini, A. Rastelli, C. Manzano, R. Songmuang, O. G. Schmidt, K. Kern, and H. von Känel, Appl. Phys. Lett. 85, 5673 (2004).