Photoluminescence evolution in InAs/InP quantum dots grown by MOVPE

Bhavtosh Bansal*, M. R. Gokhale, Arnab Bhattacharya and B. M. Arora

Department of Condensed Matter Physics and Materials Science
Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400005, INDIA

ABSTRACT

Self-assembled quantum dots of InAs have been grown on InP substrates by metal-organic vapour phase epitaxy. The effect of the growth temperature and the growth rate on the morphology and the optical properties of the quantum dots is studied using atomic force microscopy and photoluminescence spectroscopy. The spectral shape of the low temperature photoluminescence depends strongly on the growth conditions. A single peak, observed at a high growth rates, develops into two or even three distinct peaks for different samples grown at progressively lower growth rates. These findings weakly correlate with the observed size distribution of the quantum dots although the role of arsenic/phosphorous exchange at the Group-V sites may also be important. The temperature dependence of the photoluminescence spectra for the samples with a single peak is also discussed.

Keywords: Quantum dots, Indium Arsenide, Indium Phosphide, self-assembly, photoluminescence, MOVPE, Stranski-Krastanov growth

1. INTRODUCTION

There is currently considerable interest in self-assembled quantum dot structures for optoelectronic applications[1,2]. Self-assembled quantum dots are nanoscopic islands that are spontaneously generated in a few monolayers (ML) of strained hetero-epitaxial growth through the Stranski-Krastanov growth mechanism. That is, while the growth is initially two-dimensional, for deposition beyond a critical surface coverage of 1-2ML, the excess strain energy leads to generation of relaxed three-dimensional islands over a thin wetting layer of the same material. Stranski-Krastanov growth is observed when the deposited film is compressively strained with a relative lattice parameter mismatch between ~2-8%. For such self-assembled semiconductor quantum dots to have useful optical properties, the dots must be grown on and capped with a higher energy gap semiconductor. Remarkably, these two independent conditions are simultaneously fulfilled for many semiconductor systems, Si$_x$Ge$_{1-x}$/Ge, In$_x$Ga$_{1-x}$As/GaAs, InAs/InP, Ga$_x$In$_{1-x}$N/GaN, etc. Growth of self-assembled quantum dots is typically achieved using either molecular beam epitaxy (MBE) or metal-organic vapour phase epitaxy (MOVPE) since both these techniques provide ML level control during deposition.

The biggest advantage of growing quantum dots via the Stranski-Krastanov route is that such dots are coherent. Being virtually defect-free, these dots can give significant radiative recombination yields at wavelengths that can be tuned by an appropriate choice of the materials of the matrix, the embedded dots and their sizes. The goal of most optoelectronics motivated investigations on semiconductor quantum dots is to make the dots highly uniform in size, regular in position if possible and of controllable density. A first step toward this end is an understanding of nucleation, surface diffusion and related kinematic and thermodynamic aspects of the growth process.

With the above motivation, we have studied the changes in the photoluminescence spectra from InAs quantum dots, grown within an InP matrix, when the growth parameters (deposition rate, growth temperature, surface coverage) are varied. This system is a variant of the much more studied InAs/GaAs system[2]. The significant difference between the two is that the InAs/InP system involves an exchange of the anions across the growth interface. The effective energy gap of InAs/InP quantum dots can be tuned to 1.5 µm, making the system promising for fibre optic communication applications. The last couple of years have seen successful demonstrations of InAs/InP quantum dot lasers[3] and infrared detector structures.
2. EXPERIMENTAL

Growth was carried out using low-pressure metal-organic vapour phase epitaxy on n+ doped (001) InP substrates. Group III and V sources were trimethyl indium, phosphine and arsine respectively. The reactor pressure was 100 mbar with hydrogen as the carrier gas. InAs layers were grown at a relatively low temperature of 430-450 °C. Prior to the few ML InAs growth, an InP buffer layer was grown in three stages. First a 1500 Å of InP was deposited at 625 °C. Then 500 Å of InP was grown as the temperature was ramped down to the InAs growth temperature, followed by the growth of another 500 Å InP when the temperature had stabilized to the InAs growth temperature. In most cases, a pair of samples was grown with an 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. In the second case, the dots were further capped with InP. The capping process was done in two stages. First, about 50 Å InP was deposited at the InAs deposition temperature to avoid any further quantum dot evolution. Then another ~350 Å InP was grown with temperature continuously ramped up to 625°C. The capped samples were used in photoluminescence studies. The surface morphology of the uncapped dots was characterized by a NanoscopeIV atomic force microscope (AFM) in the tapping mode. The images were further analysed using WSI software (freeware) and a computer program developed in-house to identify the dots and analyze their statistical properties. Photoluminescence spectra were recorded between 20K and 300K using a McPherson grating monochromator and 325nm helium-cadmium laser as the excitation source. The power density was ~ 0.5W/cm². While this power is low enough, samples were also excited at 10% power (0.05Wcm⁻²) to rule out sub-band filling as the cause for multiple photoluminescence peaks. The measured spectra were corrected for the system response against a standard Oriel black-body source heated to 1350K.

3. RESULTS

3.1 Stranski-Krastanov Transition

![AFM image of quantum dots](image1.png)

![Photoluminescence spectrum](image2.png)

Figure 1(a) 2x2 µm AFM image of quantum dots during early stage of growth, right after the onset of the Stranski-Krastanov (SK) transition. (b) 25 K photoluminescence spectrum measured on an InP capped sample with InAs grown under the same conditions. Peaks A and B most probably correspond to signals from the two-dimensional wetting layer and the low density quantum dots respectively. A clear signal from the wetting layer indicates SK growth.

To ascertain that the growth does indeed take place via the Stranski-Krastanov mode, we have looked at the surface morphology and the PL spectra of the samples in the very early stages of the 2D to 3D transition. Figure 1 (b) is the low temperature photoluminescence spectrum at the onset of the self-assembled growth transition. For the given growth condition, (Growth rate = 1Å/s, substrate temperature = 450°C), the critical wetting layer thickness is observed to be ~1ML. This number is slightly smaller than the standard reported value of ~1.5 ML. A slight error in the calibration of
the growth rate cannot be ruled out because, unlike MBE where the thickness of the deposited material can be monitored with a monolayer precision using reflection high energy electron diffraction, our MOVPE system does not allow for an in-situ surface monitoring during growth. The difference may also be due to the growth in the present case being carried out at a lower temperature compared to the typical temperatures of \(-500^\circ\text{C}\)[5].

A clear signature of the wetting layer can be seen along with a very weak signal from the quantum dots in figure 1(b). The corresponding AFM image is shown in figure 1(a). It was observed that the quantum dot density could be continuously tuned between \(-4\times10^6\) to \(-2\times10^9\) cm\(^{-2}\) by increasing the quantity of deposited material up to 2ML, beyond which the islands began to coalesce and therefore reduce in density. Leonard, et. al[9] have proposed that the sudden onset of quantum dots' nucleation beyond a critical surface coverage may be looked upon as a thermodynamic phase transition, where the quantum dot density, \(\rho(\Theta)\) can be related to surface coverage, \(\Theta\), beyond the critical thickness \(\Theta_{\text{crit}}\), through a relation \(\rho(\Theta) = \rho_0 (\Theta - \Theta_{\text{crit}})^\alpha\). The value of the critical exponent, \(\alpha\), was found to be 1.71 for MBE grown InAs/GaAs system. Using the measured values of \(\Theta_{\text{crit}}=1\) ML and \(\rho_0=1.91\times10^{10}\) cm\(^{-2}\) (the island density before coalescence becomes important) we found that our experimental data could be well described by the same value of the critical exponent. This suggests that neither the growth route (MBE or MOVPE) nor the relative mismatch (InAs/GaAs \(\sim 7\%\), InAs/InP\(\sim 4\%\)) seem to be important beyond the critical coverage and the process of self-assembly is largely governed by kinematic factors.

### 3.2 Island density and growth conditions

Figure 2 shows the AFM scans of the surface of samples with self-assembled quantum dots prepared under different growth conditions for the same amount of material deposited. From this figure it is evident that the effect of increasing the growth temperature is the same as that of reducing the growth rate. This feature has been almost universally observed in most self-assembled growths and in fact, appears to be a generic property of the early stages in thin film growth. This relationship may thus also be of a purely kinetic origin (independent of the material systems, relative strain). The saturation density of clusters, \(N_0\) deposited on a high symmetry substrate, therefore can be written as only a function of the ratio of the growth flux to the adatom diffusion constant, \(N_0 \sim (R/D)\).

![Figure 2](image)

**Figure 2** AFM image of 1x1 µm\(^2\) area of the sample with quantum dots grown under different conditions. (a) GR=2.5 Å/s T=450°C, (b) GR=1 Å/s T=450°C, GR=1 Å/s T=430°C The effect of increasing the growth rate (a) is qualitatively similar to that of lowering the growth temperature (c).

The quantum dot configurations in Figure 2 (b) are closest to equilibrium among the three samples since here the diffusion constant (adatom mobility) is higher, compared to (c), and the growth much slower, compared to (a).

### 3.3 Photoluminescence evolution with growth rate

The low temperature PL spectra show an interesting variation as the growth rate is lowered. This is shown in figure 3. For samples grown at 2.5 Å/s, we observe a single peak (FWHM\(\sim 120\)meV), that considerably broadens as the growth rate is reduced. This is attributed to two causes. Firstly, we observed a much larger dispersion in the quantum dot sizes as the growth rate was lowered. From a quantitative analysis of our AFM images, there is also an indication of a natural
tendency of the InAs/InP quantum dots to preferentially arrange themselves in a bimodal distribution of sizes[6]. Lower growth rates allow for a longer time for the island structures to diffuse on the surface and reach to configurations that are closer to equilibrium, which in some cases may have a bimodal distribution of sizes.

Secondly, a lower growth rate also implies a longer time for the InP substrate to be exposed to arsine gas during growth. This can cause considerable alloying (i.e. formation of InAs\(_{1-x}\)P\(_x\)) in the exposed regions of the substrate and would imply a consequent change in the energy gap toward higher energies.

Figure 3: Photoluminescence spectra from three samples grown at different growth rates (GR) measured at 25K. Growth temperature=450\(^\circ\)C, A:GR=1.0 Å/s, B: GR =1.25 Å/s and C: GR=2.5 Å/s. A higher growth rate yields a single PL peak that splits into multiple peaks as GR is lowered.

3.4 Temperature dependence of PL spectra

Clearly, the sample with a single PL peak is the most suitable for optoelectronic applications. To understand the optical properties better, we shall now discuss its temperature dependent emission properties. Three (out of the eight) photoluminescence spectra measured at temperatures between 25-300K are shown in figure 4 (a). Although there is a slight asymmetry in shape, all the spectra could be reasonably fitted to a single Gaussian curve. These best fits were used to determine the peak energies and the full widths at half maximum (FWHM) shown in figure 4 (b).

While a drop in the magnitude of the peak with an increase in temperature is easily understood in terms of enhanced non-radiative recombination rates due to an increase in phonon number, the temperature dependence of the FWHM and the shift in the peak energy (figure 4 (b,c)) are more interesting. The temperature dependent shift in the PL peak position is an indication of the change in the energy gap, \(E_g(T)\). One may therefore use Varshni’s equation, \(E_g(T)=E_g(0)-\left[\alpha T^2/\beta +T\right]\), to parameterize this shift and compare the changes observed in quantum dot samples with the known temperature dependence of the energy gap of bulk InAs. In Varshni’s equation, \(E_g(0)\) is the zero temperature energy gap and \(\alpha\) and \(\beta\) are the Varshni parameters related to the average effects of the electron phonon interaction and the Debye temperature of the solid. While the confinement effects significantly change the effective zero temperature energy gap, the parameters \(\alpha\) and \(\beta\) may be, to a good approximation, assumed to be unchanged from their bulk values[7].
Figure 4 (a) Photoluminescence spectra measured at different temperatures. (b) The temperature dependence of the PL peak position. The two parallel curves are drawn with Varshni parameters $\alpha$ and $\beta$ for InAs, but with different values of the effective zero temperature gaps $E_g(0)$. (c) Corresponding FWHM at different temperatures.

Therefore, we have plotted the observed change in the PL peak positions along with the expected Varshni curves $\alpha$ and $\beta$. Have the bulk InAs values and $E_g(0)$ is a variable? Clearly, the temperature dependence for quantum dots is much larger than bulk InAs. On the other hand, the lower and the higher temperature regions of the data can be fitted to two different Varshni curves with slightly different values of the lowest state confinement energy, $E_g(0)$. This fact is indicative of a transfer of carriers from smaller to larger dots as the temperature is increased. The fast non-radiative relaxation of the excited electron-hole pairs can trap them in the local potential minima associated with smaller sized dots. At low temperatures, these carriers are unable to overcome the potential barrier and access the lower energy states available in larger dots.

The interesting anomaly in the magnitude of the FWHM measured at different temperatures also corroborates this reasoning. Qualitatively, the broad emission width at low temperatures corresponds to carriers being frozen in both the large and small dots. As the temperature is raised, radiative recombination occurs mostly within the larger dots as the electrons and holes are able to access many more lower energy states. Finally, of course the temperature broadening due to phonons becomes important and the FWHM continues to increase in magnitude.

It must be mentioned that these two facts have been previously observed and analogously explained by many other studies on quantum dots[8]. A quantitative study of these observations within a rate equation formalism will be reported elsewhere.

4. CONCLUSIONS

We have studied the growth of self-assembled InAs quantum dots on InP substrates using MOVPE. By varying the growth conditions, we could tune the density of self-assembled islands starting from $4 \times 10^8 \text{cm}^{-2}$ to $2 \times 10^9 \text{cm}^{-2}$. 
Moreover, the variation of island density with ML coverage appears to follow a very general relationship independent of the growth method or the relative lattice mismatch. We observed that increasing the growth rate has qualitatively the same effect as reducing the growth temperature. The above two facts indicate that many average aspects of the quantum dots’ self-assembly can be described using only very generic kinematic arguments. On the other hand, the spectral shape of the photoluminescence spectra is non-universal and very sensitive to the growth conditions. Results suggest a tendency for quantum dots to arrange themselves in a bimodal distribution of sizes as the growth conditions get closer to equilibrium. The temperature dependence of the PL spectra indicates an interesting non-thermal distribution of carriers that gives rise to a lowering in the FWHM as the temperature is increased from 25K up to ~100K. The anomaly in the temperature dependence of the inferred energy gap was also linked to this above observation.

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6. REFERENCES


*bhavtosh@tifr.res.in