

Chapter 2

Structural, Optical and Spectral Characterization of Single-Layer QDIPs

Abstract In this chapter, we have investigated the effect of growth pause on structural, optical and spectral properties of InAs/GaAs QD materials. Introduction of growth pause or ripening time changes the morphology of the QDs by altering effective epitaxial strain during the growth of QDs. Initially, we grew single-layer QD samples, with another QD layer on the top of the surface for structural characterization. Sample sets with two different InAs growth rates (0.032 and 0.197 ML/s) were grown on (100)-oriented GaAs substrates. Three samples, with 0, 25 and 50 s growth pause, were grown with each of the two growth rates, keeping all other growth parameters constant. We have examined the change of their optical and structural properties with different duration of growth pause. For device fabrication, we grew 10 mutually uncoupled QD layers sandwiched between Si-doped thick GaAs contact layers. In this case, the InAs dots were grown at 520 °C with a growth rate of 0.1 MLs⁻¹. Growth pauses of 0, 25 and 50 s were introduced for samples A, B and C, respectively. Finally, single-pixel photodetector devices were fabricated from as-grown A, B and C samples with standard fabrication procedures.

Keywords Growth pause • Scanning electron microscope • Photoluminescence

2.1 Introduction¹

In recent past, InAs/GaAs-based self-assembled QD heterostructures have drawn a great deal of attention from scientific community, especially in the field of optoelectronic devices such as laser, photodetector [1–6]. The performance of any such device depends upon its dot density, dot size and the uniformity of dot-size distribution. All of

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these characteristics depend on the optimization of growth parameters, such as the InAs growth rate, growth temperature, thickness of the InAs monolayer (ML), V/III ratio of the flux [7, 8]. It is a usual practice to grow single-layer QD heterostructures for optimization of different growth parameters. Another very important, but relatively less investigated parameter is the growth pause or ripening pause during the growth of the sample [9]. The growth pause is defined as the time interval between the end of QD deposition and subsequent deposition of the barrier. In the S–K growth mode, the formation of QDs is driven by the mass transport under partially strained condition, as the deposited layer (InAs) exceeds a certain critical thickness. The grown InAs QDs always have a tendency to interact with neighbouring QDs through the substrate under epitaxially strained condition. When delaying covering the QDs, i.e. introducing a growth pause, QDs are allowed to relax in an energetically favourable condition, as well as to interact with the surrounding QDs for longer time. QDs under such conditions show a ripening behaviour. So introduction of growth pause can effectively alter the morphology of the sample. In this work, we have investigated the effect of growth pause on single-layer InAs/GaAs QD heterostructures. We have grown two sets of sample - 1st set has three samples namely 2106, 2105 and 2100 with 0, 25 and 50 s of growth interruption respectively. These three samples were grown at the growth rate of 0.032 ML/s. The other set which has another three samples - 2109, 2108 and 2115 with 0, 25 and 50 s of growth interruption was grown at 0.197 ML/s growth rate. Two different growth rates were chosen to study the effect of growth rate on the morphology of the sample.

The later part of the work studied effect of thermal treatment on the sample. Rapid thermal annealing (RTA) of QD heterostructures at temperatures 600–800 °C is a popular post-growth treatment [10–15]. It is believed that RTA leads to a relatively homogenized size distribution in the QD ensemble, a relaxed strain distribution and a reduction in structural defects, thereby improving the optical properties of the sample [16–18]. We also investigated the effects of RTA on the optical properties of the QD samples with growth pauses at different temperatures.

2.2 Results and Discussion

2.2.1 Structural Characterization

Figure 2.1 shows the SEM images of samples grown with slow (#2106) and fast (#2109) deposition rates. The average dot density is 0.6×10^{10} dots per cm^2 and from 2.3×10^{10} dots per cm^2 for slow and fast growth-rate samples, respectively. Faster deposition helps produce a higher dot density due to the competition between the nucleation rate and nucleation probability.

For a lower growth rate, the growth process is dominated by the nucleation probability. The nucleation rate increases with the increment in growth rate, resulting in a higher dot density. At a very fast growth rate, the nucleation rate and nucleation probability reach a dynamic equilibrium, resulting in dot-density saturation [19].

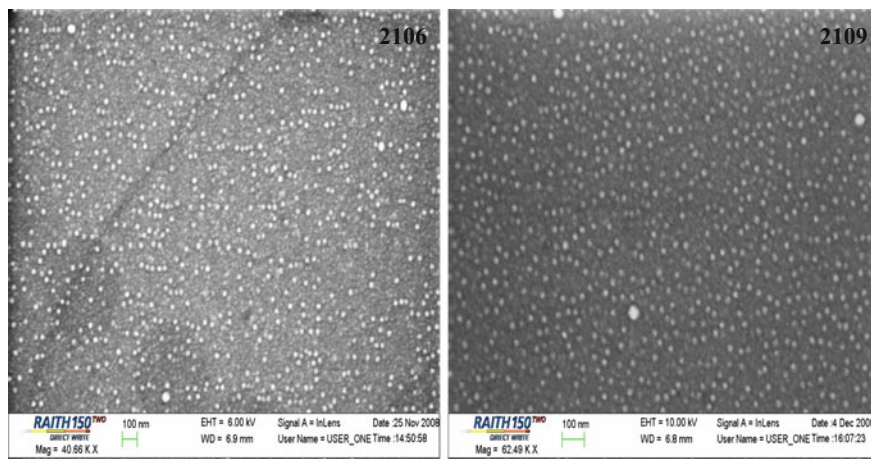


Fig. 2.1 Top view SEM images of dot distributions of samples 2106 and 2109. Reprinted from “Investigation of effect of varying growth pauses on the structural and optical properties of InAs/GaAs quantum dots heterostructure” *Superlattices and Microstructures*, Vol. 46, No. 4, pp. 611–617, October 2009 with permission from Elsevier

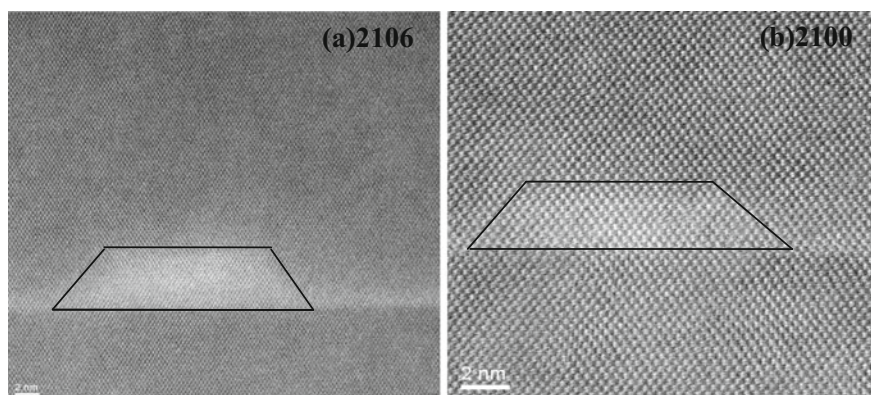


Fig. 2.2 STEM images of single QD grown at 0.032 ML/s with **a** 0 s and **b** 50 s of growth pause. Reprinted from “Investigation of effect of varying growth pauses on the structural and optical properties of InAs/GaAs quantum dots heterostructure” *Superlattices and Microstructures*, Vol. 46, No. 4, pp. 611–617, October 2009 with permission from Elsevier

Figure 2.2 shows STEM images of a QD in samples 2106 and 2100, and Fig. 2.3 shows the same for samples 2109 and 2115, where the atomic structure is revealed. TEM images were taken of different portions of each of the samples; the figures show only the best images of the QDs representing the structural features of the sample. The contrast in the TEM image appears due to the difference in average atomic number of the InAs QDs and GaAs. In dark-field mode, one can expect the

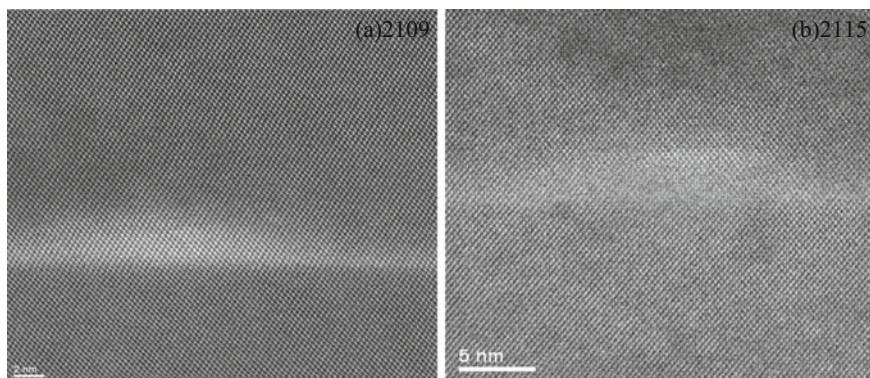


Fig. 2.3 STEM images of single QD grown at 0.197 ML/s with **a** 0 s and **b** 50 s of growth pause. Reprinted from “Investigation of effect of varying growth pauses on the structural and optical properties of InAs/GaAs quantum dots heterostructure” *Superlattices and Microstructures*, Vol. 46, No. 4, pp. 611–617, October 2009 with permission from Elsevier

InAs QDs will appear as brighter spot as shown in the images. The mechanism of dot formation is in accordance with the change in Gibbs free energy and the elastic relaxation energy [20].

In the STEM images, the fluctuation in contrast inside the dots arises from the inhomogeneity of In distribution within the dots. We can see from the images that in the first case, i.e. for slow growth rate, the shape of the quantum dots is trapezoidal. A compressive strain originated from the interface of the InAs QDs with the subsequent GaAs capping layer may be responsible for such trapezoidal shape.

The height and lateral size were in the range of 3–4 and 13–18 nm, respectively, for slower growth rate samples. Though the height of the dots remains almost constant, a slight increment in lateral dot size appeared as the growth pause gradually increased. Driven by epitaxial strain, some Indium-adatom migrate away from top of the QDs to the bottom, causing the increment in lateral size of samples subjected to a longer growth pause. For the faster growth rate, the QDs exhibit a shell-like structure, rather than a trapezoidal shape with larger lateral size seen in the earlier samples. The height varying from 3 to 4.5 nm with lateral size of these samples varies from 16 to 25 nm. The faster deposition rate causes quick build-up of strain energy at the bottom of the dots leading to an elongation of the lateral size. This is responsible for the shell-like appearance of the dots. The fading of the intensity at the dot apex along the interface between InAs and GaAs layers in each of the dot suggests an intermixing of In-Ga occurred.

2.2.2 Optical Characterization

The PL measurements of single-layer QD samples are shown in Figs. 2.4 and 2.5 that support the structural analysis. For both slow and fast growth-rate samples, two distinct peaks appear in the PL spectra. The lower and higher energy peaks are due to the transition from electron ground state (GS) to hole ground state and first excited electronic state to first excited ground state.

For slow growth-rate samples, distinct GS and first excited state energy peaks appear. A shift of the ground-state peak from 1.082 eV (~ 1146 nm) to 1.071 eV (~ 1158 nm) occurred with an increase in the duration of the growth pause. This redshift is the direct consequence of the formation of larger QDs with an increase of the growth pause [21]. The FWHM of the individual peak was measured after resolving the peaks by Gaussian function using Origin Pro-8 software. The measured FWHM of GS-emission peaks is found to vary from 30 to 40 meV. The GS energy peak and first-order excitation energy peak are not as distinct for samples with a faster growth rate. Figure 2.6 shows a shift of the ground-state peak from 1.471 eV (~ 1081 nm) to 1.12 eV (~ 1107 nm) when increasing the growth pause from 0 to 25 s, and then, a slight blueshift of ~ 8 nm occurs with a further increase in the growth-pause duration.

Introduction of a growth pause also allows Indium out-diffusing from the core region of dots, resulting in reduced In concentration and smaller dot size. The mechanism that occurs during dot formation can be described as a competition of two counter-phenomena. Initially, larger islands are formed at the expense of the interaction between neighbouring smaller QDs [8]. Larger size tends to lower the band gap of the dots, and thus, sample 2108 exhibits redshift in the emission wavelength when compared to sample 2109. For a growth pause longer than 25 s, at higher growth rates desorption of Indium-adatom from QDs dominates the surface diffusion, causing a change in the QD morphology and hence the blueshift.

Fig. 2.4 PL-emission energies for samples 2106, 2105 and 2100 at 8 K. Reprinted from “Investigation of effect of varying growth pauses on the structural and optical properties of InAs/GaAs quantum dots heterostructure” Superlattices and Microstructures, Vol. 46, No. 4, pp. 611–617, October 2009 with permission from Elsevier

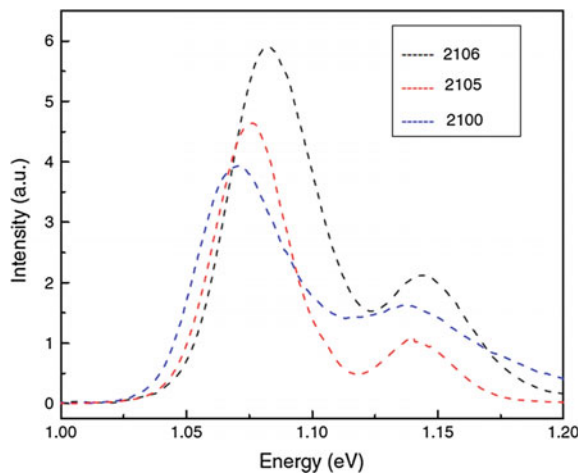
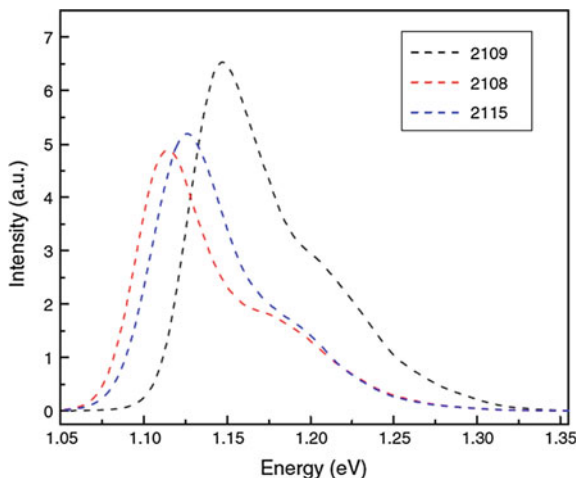


Fig. 2.5 PL-emission energies for samples 2109, 2108 and 2115 at 8 K. Reprinted from “Investigation of effect of varying growth pauses on the structural and optical properties of InAs/GaAs quantum dots heterostructure” Superlattices and Microstructures, Vol. 46, No. 4, pp. 611–617, October 2009 with permission from Elsevier



Faster growth rate induces QD size fluctuation and produces smaller dots, which causes a broadening of the linewidth of the emission peak (measured FWHM, 40–46 meV) and reduces the GS-emission wavelength. We believe that during longer growth pauses the dots have more time to interact with neighbouring dots under strained conditions and coalesce to produce larger dots which reduces dot density [22].

A similar trend appears when growing samples for device fabrication. The ground state of the PL-emission peaks for samples with 0, 25 and 50 s growth pauses (i.e. A, B and C) was observed at 1120.97, 1128.88 and 1124.78 nm, respectively, at 8 K. Thermal-activation energies calculated for each of the grown samples (A, B and C) from a typical Arrhenius plot are around 126, 117 and 89 meV for samples A, B and C, respectively, following a decreasing trend for an increase in growth-pause duration. This can be explained by the segregation of Indium from the dots towards the GaAs barrier. Intrusion of Indium-adatom in the GaAs barrier reduces the depth of the potential well, hence a gradual reduction in the activation energy. The presence of defect levels between dots and GaAs barrier during growth is another possible reason for low activation energy. Defect levels create non-radiative sites, causing degradation of sample luminescence. The existence of low activation energy for all three samples suggests the presence of non-radiative sites originating from defects and dislocations.

All three samples (A, B and C) were subjected to post-growth thermal treatment at 650, 700, 750 and 800 °C with an aim to improve the quality. Temperature-dependent PL was performed on each set of samples under identical experimental conditions, and results are compared to the as-grown sample of the same. The results are summarized in Fig. 2.6.

All three samples (A, B and C) showed significant enhancements in activation energy when annealed up to 700 °C. The thermal treatment enhanced the optical qualities by eliminating defects inside the samples. As the annealing temperature exceeded 700 °C, the thermal energy induced intermixing of InAs–GaAs, leading

Fig. 2.6 Comparison of activation energies among the annealed counterparts of samples of all growth-pause durations

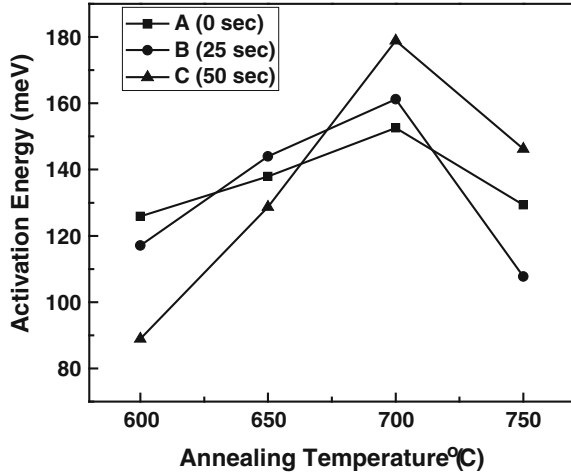
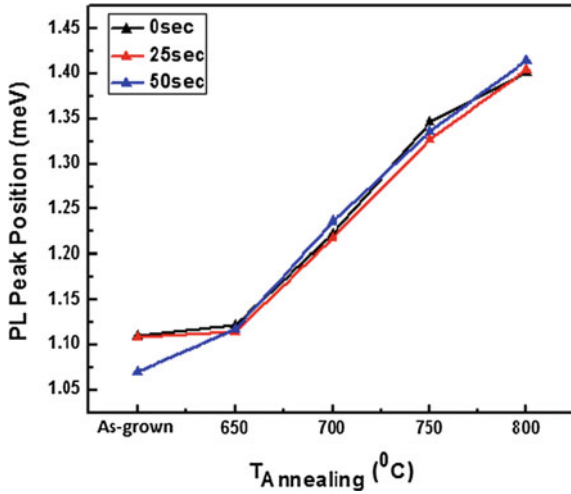


Fig. 2.7 Comparison of GS PL-emission peak of as-grown sample A, B and C and their annealed counterparts



to considerable amount of carrier escape and reducing the activation energy. The usual blueshift in the GS-emission wavelength of all three samples was observed when they were subjected to thermal annealing (Fig. 2.7).

It is evident that rapid thermal annealing causes significant change in the structural and optical properties of the as-grown heterostructure due to InAs dots–GaAs barrier intermixing. Since a particular QD heterostructure is tailored for specific uses, it is essential to develop a theoretical model to understand and predict the experimental variation in their optical properties with annealing. We have examined the experimental findings about the effect of annealing of 2106 sample with a theoretical perception in order to understand the phenomena in a better way [23]. The model was developed based on Fick's second equation.

$$\frac{\partial x(r, t)}{\partial t} = D \nabla^2 x(r, t)$$

where x denotes the mole fraction of In in $\text{In}_x\text{Ga}_{1-x}\text{As}$, and D the diffusion constant of InAs is assumed to be constant throughout. We assume the as-grown QD to be composed purely of InAs and use the following initial conditions for the above equation.

$x = 1$, in the QD and WL,

$x = 0$, in the barrier material.

The equation was solved in three dimensions by discretization in both time and space, with Dirichlet boundary conditions and annealing time $t = 30$ s to obtain the composition of the annealed heterostructure. To explain the variation of properties with annealing temperature T_a , we consider an Arrhenius-type temperature dependence of the diffusion coefficient.

$$D = D_0 \exp\left(-\frac{E_a}{kT_a}\right)$$

where the parameters D_0 are initial diffusion coefficient and $E_a = 1.23$ eV, respectively.

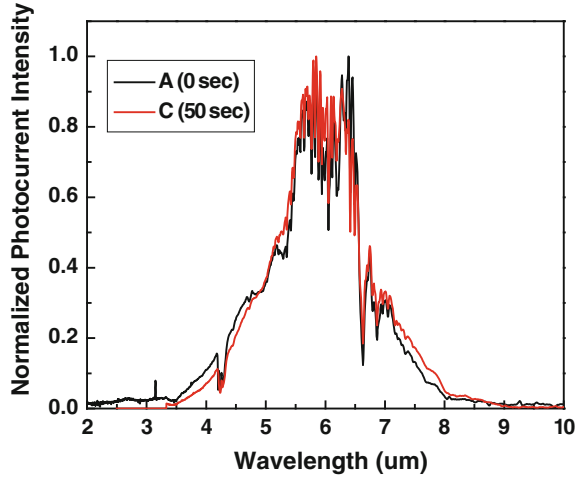
Subsequently, the corresponding band profiles were calculated, and their variation with annealing was examined. The band profiles were used to solve for carrier energy states from the Schrödinger equation, and we observed a well-correlated blueshift in PL peak energy. Operating within a similar framework, PL spectra from the QD ensemble in the heterostructure, annealed at different temperatures, were calculated. In addition to quantitatively reproducing the variation in PL spectra, our studies shed light on changes in strain effects and potential profiles in QD materials, which may form the basis for investigations into other phenomena induced by annealing.

2.2.3 Spectral Characterization of Device

We characterized photodetector devices made of as-grown sample A and C to check the effect of growth pause on performance of the device. The normalized photocurrent of devices A and C as a function of wavelength at low temperature (50 K) at a 0.6 V operating bias is depicted in Fig. 2.8.

The photocurrent response peak (~ 6.0 μm) is due to the transition of carriers between QD-bound states and the quasi-bound state of the In(Ga)As wetting layer. The broadness in the linewidth of the spectrum indicates reduced confinement of the energy levels, which may be associated with the presence of defects and dislocations. The spectral response peaks of the two samples nearly coincide. Clearly,

Fig. 2.8 Comparison of the spectral response results of devices A and C at 50 K



the difference in PL-emission peak is not so significant that can alter spectral response peak of the devices under consideration.

2.3 Conclusions

This study examined the effects of varying growth pauses on InAs/GaAs QD materials at two different growth rates, the effects of thermal annealing and the performance of single-pixel IR photodetector devices. The growth pause causes effective epitaxial strain to increase QD size. The optical behaviour of the samples reflects the changes in their morphology. Larger QDs decrease PL-emission energy. A small blueshift in the emission wavelength appears for samples grown at a higher growth rate and subjected to a longer ripening pause due to Indium desorption. Thus, the growth pause can serve as an important parameter in tuning the emission wavelength of InAs/GaAs QDs though the device performance may not be affected. The activation energy reduces with an increase in the duration of the growth pause due to intrusion of Indium-adatom from dots to the GaAs barrier and formation of non-radiative recombination sites that reduce the effective depth of the potential wells. Post-growth thermal treatment up to a critical limit (here 700 °C) removes these non-radiative sites and improves optical behaviour. No significant change in the spectral response of the photodetectors was observed with the introduction of growth pause.

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Structural, Optical and Spectral Behaviour of
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Applications for High-performance Infrared
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