Interdiffusion induced changes in the photoluminescence of In X Ga 1 − X As ⁄ Ga As quantum dots interpreted

Dipankar Biswas, Subindu Kumar, and Tapas Das

Citation: Journal of Applied Physics **101**, 026108 (2007); doi: 10.1063/1.2430510
View online: http://dx.doi.org/10.1063/1.2430510
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/101/2?ver=pdfcov
Published by the AIP Publishing

Interdiffusion induced changes in the photoluminescence of $In_XGa_{1-X}As/GaAs$ quantum dots interpreted

Dipankar Biswas,[a] Subindu Kumar, and Tapas Das
Institute of Radiophysics and Electronics, University of Calcutta, 92 A. P. C. Road, Kolkata 700009, India

(Received 13 July 2006; accepted 16 November 2006; published online 24 January 2007)

Interdiffusion in $In_XGa_{1-X}As/GaAs$ quantum dots (QDs) may occur during high temperature growth and processing, which may create problems in the ultimate device performance. It is simulated through successive high temperature annealing, and the changes at each stage are studied through photoluminescence (PL). Significant changes are observed in the peak energy, linewidth, and intensity of the PL spectra. These have been attributed to relaxation of strain, changes in the composition of $In_XGa_{1-X}As$, and size distribution of the QDs, which fail to establish proper understanding qualitatively and quantitatively. In this Communication we present appropriate interpretations of the changes in the observed PL through quantum mechanical concepts and computations. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2430510]

Interdiffusion of the third group elements in $In_XGa_{1-X}As/GaAs$ quantum dots (QDs) may occur during high temperature growth and device processing which affects the performance of the ultimate device adversely. Photoluminescence (PL),[1–7] being simple, is widely used for obtaining data from QDs of compound semiconductors subjected to interdiffusion which may be simulated artificially through annealing.

There are a number of reports[1–4] on the annealing of $In_XGa_{1-X}As/GaAs$ QDs. The experimental results of such reports agree strongly on one particular phenomenon, that is, the initially observed PL spectrum is very broad. After annealing, the PL peak undergoes a strong blueshift and the full width at half maximum (FWHM) decreases very significantly, while there is an increase in the intensity. It is also found that the FWHM decreases monotonically if the shoulder in the as grown sample[5] is not ignored. Typical PL spectra on annealing are depicted in Fig. 1.[1]

The complex process of annealing and interdiffusion in QDs has been ascribed mostly to relaxation of strain, homogenization of the size distribution of QDs, and reduction of dislocations and defects.[1,2,4] It is well established[8] that there is a decrease in the FWHM of the PL spectrum, as the deviation in the size distribution decreases, but there is no blueshift of the PL peak after such homogenization of the dot size. Due to strain, the conduction band offsets increase marginally[9] whose relaxation can cause minimal blueshift. So these arguments do not explain the observed strong changes in the PL spectra clearly.

The aim of this paper is to interpret theoretically the annealing induced changes in the PL spectra of $In_XGa_{1-X}As/GaAs$ QDs through suitable quantum mechanical models and concepts. We have emphasized on the changes of the shapes of the conduction and valence bands on annealing and the subsequent changes in the energy levels from which optical transitions take place.

While interpreting this interdiffusion related PL phenomenon, a very important point has been overlooked by the research workers in the field. As outlined very clearly,[10,11] when an $In_XGa_{1-X}As/GaAs$ single QD emerges from a strained layer crossing the critical thickness, initially a small three dimensional pyramid highly rich in indium is formed on the indium rich strained layer, as shown in Fig. 2(a). As the QD grows in size, the indium rich nucleus is covered by $In_XGa_{1-X}As$ layers which progressively become depleted of indium, as depicted in Fig. 2(b), and the indium rich bottom strained wetting layer loses its thickness. The dot is then covered with GaAs. It is quite difficult to visualize the band structure of an as grown $In_XGa_{1-X}As/GaAs$ QD. If we take a close look at the structure[11] from the GaAs substrate in the growth direction, at different vertical sections *a*, *b*, and *c* across the QD, as shown in Fig. 2(b), the conduction and valence bands have the nature of asymmetric triangular wells due to the strong gradient of the indium concentration at each section. The conduction band wells are shown in Fig. 2(b). The width varies at different sections *a*, *b*, and *c*, and the depth varies with the variation of indium concentration. The broad PL spectrum from the as grown single QD arises from the large number of transition levels available from the asymmetric triangular wells of widely different depths and widths as seen from quantum mechanical computations. Over and above this, the transitions from the dots of different

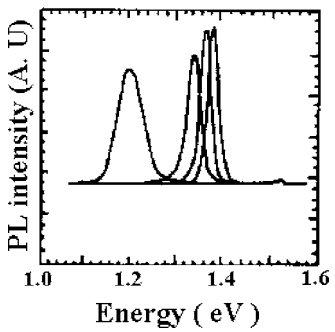

FIG. 1. Blueshifts in the PL from $In_XGa_{1-X}As/GaAs$ QDs on annealing.

[a]Electronic mail: diiibiswas@yahoo.co.in

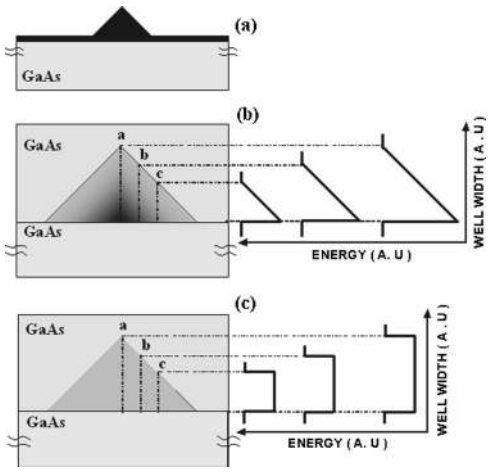

FIG. 2. Schematic illustration of the formation of a QD of $In_XGa_{1-X}As$ on GaAs. Darker shades indicate higher composition of X. (a) Initial nucleation of an indium-enriched island on strained alloy film on substrate. (b) Later stage, when the island has consumed alloy film, which becomes progressively indium depleted during growth. (c) Final stage, after annealing, showing the homogenization of indium and gallium. The corresponding conduction bands at different cross sections of the dot are also shown in (b) and (c).

sizes are superimposed to make the spectrum still broader.

On annealing, indium outdiffuses from the central core of the single dot to homogenize the distribution and the triangular wells under consideration, ultimately, after long annealing, leading to rectangular wells. The wells thus obtained have the same depth since the concentrations of indium and gallium have homogenized, as shown in Fig. 2(c), only the widths of the rectangular wells vary. The resulting PL arises from the transitions of these wells. Intermediate phases are trapezoidal wells, which have PLs intermediate between the triangular and the rectangular.[12]

Model quantum mechanical calculations were carried out for pyramidal $In_XGa_{1-X}As/GaAs$ QDs of square base,[10] the height being equal to 25 nm and the base being 40 nm. To keep the complexity within presentable limits, the variation of indium is assumed to have five concentrations of linear gradient from the central core to the outer periphery, $x=0.8$, 0.603, 0.405, 0.208, and 0.010 as shown in Fig. 3. After annealing the indium, with no outdiffusion into the barrier, it homogenizes throughout the QD to a value of $x=0.17$. The band gap E_g of $In_XGa_{1-X}As$ is determined from the empirical relation[13]

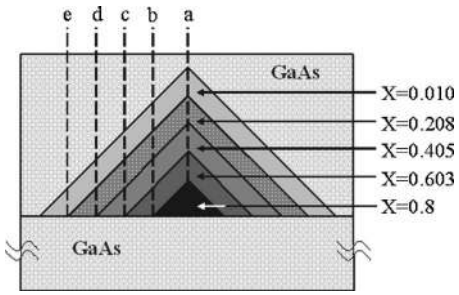

FIG. 3. Model of Fig. 2(b) showing the variation of indium which is assumed to be a linear gradient of five concentrations from the central core to the outer periphery.

TABLE I. Optical transition energies calculated for different asymmetric triangular wells with the effective masses of electrons, m_e^*, and holes, m_h^*, varying from $0.035m_0$ to $0.066m_0$ and from $0.410m_0$ to $0.450m_0$, respectively. The band offset ratio $E_C:E_V$ has been considered to be 60:40.

Well width (nm)	Indium mole fraction (x)	Transitions available	PL peak energy (eV)
25.00	0.8	$1\rightarrow1$	0.949
22.50	0.8	$1\rightarrow1$	0.965
20.00	0.8	$1\rightarrow1$	0.986
20.00	0.603	$1\rightarrow1$	1.102
17.50	0.603	$1\rightarrow1$	1.122
15.00	0.603	$1\rightarrow1$	1.148
15.00	0.405	$1\rightarrow1$	1.271
12.50	0.405	$1\rightarrow1$	1.297
10.00	0.405	$1\rightarrow1$	1.334
10.00	0.208	$1\rightarrow1$	1.445
7.50	0.208	⋯	⋯
5.00	0.208	⋯	⋯
5.00	0.010	⋯	⋯

$$E_g = 1.516 - 1.214x + 0.264x^2, \tag{1}$$

where x is the concentration of indium. The energy levels of the finite triangular and the rectangular quantum wells (QWs) of different depths and widths are calculated from the formulas[14,15] outlined below:

$$E_n = [(V_0\hbar/a)^2/(2m^*)]^{1/3}\alpha_n, \tag{2}$$

and

$$E_n = \frac{2P^2}{(P+1)^2}\left[\left(\frac{n\pi}{2}\right)^2 - \frac{1}{3(P+1)^3}\left(\frac{n\pi}{2}\right)^4 - \frac{27P-8}{180(P+1)^6}\left(\frac{n\pi}{2}\right)^6\right], \tag{3}$$

where $\alpha_n=[3\pi(n-1/4)/2]^{3/2}$, $P=[(2m^*V_0)^{1/2}/\hbar]a/2$, V_0 and a are the height and width of the well, respectively, and m^* is the effective mass of the carriers. For asymmetric triangular wells, the effective masses[16] of electrons, m_e^*, and holes, m_h^*, are varied from $0.035m_0$ to $0.066m_0$ and from $0.410m_0$ to $0.450m_0$, respectively, with the indium concentrations varying from 0.8 to 0.01. In case of the rectangular wells, m_e^* and m_h^* were taken to be $0.060m_0$ and $0.442m_0$, respectively. The band offset ratio $E_C:E_V$ was considered to be 60:40. Computations were for 6 K, around which most PL experiments are carried out. Computations at different sections of the as grown QD, as represented in Fig. 3, were carried out to find the energies of 1-1 transitions which are of importance at the low temperature. At the crossovers of the indium concentrations, computations for both the concentrations were done. Computations at the same sections of the rectangular wells were also carried out.

The probable 1-1 transition energy positions of the as grown and of the long annealed single QD are presented in Tables I and II, respectively. The highest and lowest energies of transitions were found which remain constant at e and a, respectively. At e indium is minimum, and the width of the well is also minimum, which gives rise to the highest transition energy, and at a the reverse happens.

TABLE II. Optical transition energies evaluated for a rectangular well with effective masses, $m_e^*=0.060m_0$ and $m_h^*=0.442m_0$, and the indium mole fraction, $x=0.17$. The band offset ratio $E_C:E_V$ has been considered to be 60:40.

Well width (nm)	Transitions available	PL peak energy (eV)
25.00	1→1	1.326
22.50	1→1	1.327
20.00	1→1	1.329
17.50	1→1	1.332
15.00	1→1	1.336
12.50	1→1	1.342
10.00	1→1	1.352
7.50	1→1	1.367
5.00	1→1	1.395

One may well note that the sections *b*, *c*, and *d* of Fig. 3 can have innumerable positions between *a* and *e*. So, Tables I and II depict only some of the large number of transitions which are probable. The intensities of the transitions will depend on various factors and are not of much concern for this work. From the tables it can be clearly seen that the transitions in the asymmetric triangular wells are widely distributed in the energy space, while for the rectangular wells, the transitions are blueshifted in energy and they bunch up in a narrow energy space. To consider a spread in the size distribution of the QDs,[8] computations on ±30% and ±40% variations in the dimensions of the sections were also carried out, which also accommodate the expected local undulations in the indium concentration. Figure 4 depicts the results of all such 1-1 transitions thus found for triangular and rectangular wells. The vertical lines as represented by *a* and *c* in Fig. 4 are the energy positions of probable optical transitions for the as grown and the long annealed QDs, respectively. The expected PL spectra corresponding to *a* and *c* are shown schematically through *b* and *d*, respectively, in Fig. 4. On annealing, the asymmetric triangular wells are converted into rectangular wells and the transitions cluster in a small energy space resulting in a narrow and blueshifted spectrum. For the same power density of the excitation in the PLs, approximately the same number of transitions are expected. So the intensity of the spectrum increases significantly. The nature of the theoretical results of Fig. 4 is similar to the experimental results[1] of Fig. 1.

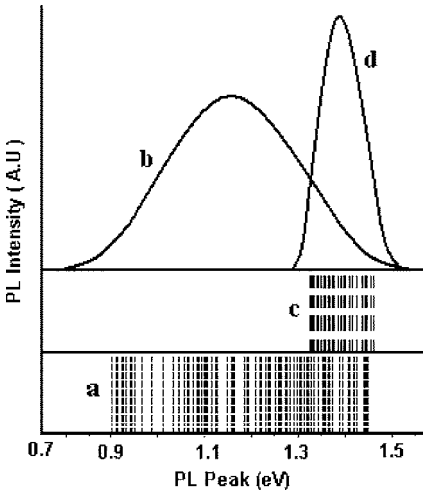

FIG. 4. Schematic diagram of the computed PL spectra for triangular and rectangular QWs corresponding to Tables I and II.

As discussed earlier, the transitions shown in Fig. 4 are some of the innumerable transitions that can occur since the dimensions of the QD and the indium concentration both vary continuously, but for each of *a* and *c* the highest and lowest transition energies which define the upper and lower limits of the observed spectrum remain constant. Pyramidal structures of different aspect ratios yield similar results.

To summarize, in this paper we have interpreted the changes in the PL spectra of $In_XGa_{1-X}As/GaAs$ QDs on annealing. The interpretations are centered on a necessary and important point that when a pyramidal QD starts growing, a nucleus of the pyramid is formed, which is very rich in indium. As the dot grows in size, the upper layers forming the dot are successively depleted of indium. Thus the conduction band and the valence band of an as grown QD observed from the substrate in the growth direction are asymmetric triangular wells, where there is a continuous variation of both indium and width. After long annealing, the indium composition in the dot is homogenized and the asymmetric triangular wells tend towards rectangular, where the variation is in the width only. The depth becomes constant. Quantum mechanical computations on the triangular band structures of the as grown QDs reveal that the optical transitions are spread out over energy, while the transitions in the rectangular wells of the annealed dots bunch up in a small energy space resulting in a blueshifted, narrow, and intensity enhanced PL spectrum. The theoretical PL results are very similar to experimental observations. This phenomenon is modified by the superposed effects of redistribution of the QD size, strain relaxation, and reduction of dislocations and defects.

[1] R. Leon, D. R. M. Williams, J. Krueger, E. R. Weber, and M. R. Melloch, Phys. Rev. B **56**, R4336 (1997).
[2] C. Lobo, R. Leon, S. Fafrad, and P. G. Piva, Appl. Phys. Lett. **72**, 2850 (1998).
[3] A. Babiński, J. Jasiński, R. Bożek, A. Szepielow, and J. M. Baranowski, Appl. Phys. Lett. **79**, 2576 (2001).
[4] R. Leon, Y. Kim, C. Jagadish, M. Gal, J. Zou, and D. J. H. Cockayne, Appl. Phys. Lett. **69**, 1888 (1996).
[5] E. C. Le Ru, J. Fack, and R. Murray, Phys. Rev. B **67**, 245318 (2003).
[6] B. Allen, D. Biswas, J. M. Pastor, L. Gonzalez, and J. M. Garcia, Phys. Status Solidi A **190**, 763 (2000).
[7] J. M. Pastor, D. Biswas, B. Allen, J. Bosch, L. Gonzalez, and J. M. Garcia, Phys. Status Solidi A **190**, 599 (2002).
[8] W.-Y. Wu, J. N. Schulman, T. Y. Hsu, and U. Efron, Appl. Phys. Lett. **51**, 710 (1987).
[9] N. Debber, D. Biswas, and P. Bhattacharya, Phys. Rev. B **40**, 1058 (1989).
[10] For example, see D. Bimberg, M. Grundmann, and N. N. Ledentsor, *Quantum Dot Heterostructures* (Wiley, Chichester, 1999).
[11] J. Tersoff, Phys. Rev. Lett. **81**, 3183 (1998).
[12] H. W. Shim *et al.*, Appl. Phys. Lett. **81**, 3552 (2002).
[13] W. P. Gillin, D. J. Dunstan, K. P. Homewood, L. K. Howard, and B. J. Sealy, J. Appl. Phys. **73**, 3782 (1993).
[14] For example, see D. Haar, *Problems in Quantum Mechanics* (Pion, 1975).
[15] D. L. Aronstein and C. R. Stroud, Jr., Am. J. Phys. **68**, 943 (2000).
[16] For example, see *Data in Science and Technology, Semiconductors Group IV Elements and III-V Compounds*, edited by O. Madelung (Springer-Verlag, Berlin, 1991).