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Presentation and experimental validation of a model for the effect of thermal annealing on the photoluminescence of self-assembled InAs/GaAs quantum dots

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We present a model for the effect of thermal annealing on a single-layer InAs/GaAs quantum dot (QD) heterostructure and study the corresponding variation in full photoluminescence (PL) spectrum. In/Ga interdiffusion due to annealing is modeled by Fickian diffusion and the Schrödinger equation is solved separately for electrons and holes to obtain ground state PL peaks of the heterostructure at different annealing temperatures. We theoretically examine the decrease in strain effects and carrier confinement potentials with annealing. PL spectra of the entire ensemble of QDs, annealed at different temperatures, are calculated from a lognormal distribution of QD heights derived from experimental atomic force microscopy (AFM) data. Results from our calculations, which illustrate the blueshift in emission wavelength and linewidth variation in PL with annealing, are in excellent agreement with experimental PL observations on the same samples. This highlights the potential of the model to assist in precisely engineering the optical properties of QD materials for specific device applications. Moreover, the simplicity of the model and its multiple useful features including computation of material interdiffusion, band profiles and full PL spectra make it a valuable tool to study annealing effects on QD heterostructures. © 2010 American Institute of Physics. [doi:10.1063/1.3431388]

I. INTRODUCTION

Self-assembled quantum dots (QDs) have been gaining increasing interest over the last years due to their discrete energy levels and delta-like density of states, which render them suitable for potential high-quality optoelectronic applications such as QD lasers and photodetectors. InAs/GaAs QDs grown in the Stranski–Krastanow mode are particularly well-studied in terms of their structural and optical properties and are being considered for applications in the IR region. A major difficulty that could arise in designing such applications using QD heterostructures is the nonuniform size distribution of QDs, which arises during growth. This results in significant broadening of optical response, an increase in laser threshold current and decrease in optical gain. The impact of a QD size distribution is most evidently seen in the photoluminescence (PL) spectrum of QD materials, in which the envelope of emissions of all QDs in the structure follows a distribution over emitted wavelengths, as opposed to an ideally desired sharp peak. Rapid thermal annealing (RTA) of as-grown QD heterostructures at temperatures 600–800 °C is one technique commonly used to reduce the linewidth and enhance the full intensity of the PL emission. 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 conferring desirable properties. The PL spectrum of InAs/GaAs QDs with annealing has been extensively studied in experiments on single as well as multilayer heterostructures with the interest of enhancing their potential for device applications.

Since QD materials are to be tailored for specific uses, it is essential to develop a theoretical model to study and predict the experimental variation in their optical properties with annealing. An approximate treatment of this problem is presented by Kumar et al. in which as-grown and annealed QDs are treated as triangular and rectangular quantum wells, respectively, thereby qualitatively explaining trends in PL peak energy with annealing. In another work, modeled PL peaks are used to derive information about QD dimensions. In this paper, we present modeling and simulations of the In/Ga interdiffusion process in single-layer InAs/GaAs QDs subjected to annealing, and for the first time, study the corresponding variation in full PL spectrum. The model is developed with a central emphasis on Fickian diffusion, derivation of potential profiles and solution of the Schrödinger equation. We establish a quantitative correlation with our experimental PL spectra, and thereby attempt to provide a useful solution to engineer the optical emission of QD materials subjected to thermal annealing.

II. EXPERIMENTAL METHODS

To correlate with our theoretical interpretation, we have grown single-layer InAs/GaAs QDs by solid source molecular beam epitaxy (MBE) on a (100) oriented GaAs substrate. An EPI MOD GEN II system, equipped with Ga, In, Al, Si, and Be effusion cells and an As cracker was used. The
structure of the samples grown is depicted schematically in Fig. 1(a). After initial oxide desorption, the GaAs buffer layer was grown at about 590 °C, and then the substrate temperature was slowly reduced to 520 °C to grow the InAs QD layer. A slow growth rate of 0.032 ML s\(^{-1}\) was chosen to deposit a 2.7 ML InAs layer. The QD layer was subsequently covered with relatively thick (1000 Å) GaAs capping. The heterostructure was then terminated with an uncapped 2.7 ML InAs QD layer grown under identical conditions as the previous ones for atomic force microscopy (AFM) measurements. Samples cut from the central region of the as-grown wafer were subjected to \textit{ex situ} RTA anneal in an Argon atmosphere at different annealing temperatures between 650 and 850 °C. All the samples treated in this way exhibited highly reflecting surfaces like that of the as-grown samples. The annealing was done under GaAs proximity capping in order to prevent degradation of sample quality due to arsenic out-diffusion from the sample surface.\(^{14}\) PL experiments are carried with a closed cycle He cryostat operating at 8 K using a 405 nm solid state blue laser at 40 mW excitation power. Experimental PL spectra from samples annealed at various temperatures are shown in Fig. 1(c). We observe a sharp decrease in PL full intensity in samples annealed at temperatures exceeding 800 °C. Although annealing has the beneficial effect of full width at half maximum (FWHM) reduction, it is to be borne in mind that annealing at very high temperatures may lead to excessive interdiffusion, and thereby complete degradation of QD structure.

III. THEORETICAL MODEL AND SIMULATIONS

A. Annealing induced interdiffusion

High angle annular dark field-scanning tunneling electron microscopy (HAADF-STEM) data from our as-grown sample\(^{22}\) indicate a truncated pyramid type QD structure as shown in Fig. 1(b). The exact QD dimensions, which we incorporate in our simulations, are arrived at considering both TEM results and a good correlation with PL data from the as-grown sample. The dimensions predicted from as-grown PL are slightly larger than those from TEM data, and this is likely due to presence of some Ga in the outer layers of the QD.

We carry out interdiffusion simulations on this single QD in the barrier. The system is taken in a cuboidal box of dimensions \(2w_{\text{bot}} \times 2w_{\text{bot}} \times 8h_{\text{QD}}\). These dimensions are chosen in such a way as to reduce spurious errors arising due to abrupt boundary conditions, while at the same time, bearing in mind time complexity of the computation. It is widely established that RTA of InAs/GaAs QD heterostructures leads to In/Ga interdiffusion between QD and barrier material.\(^{12,13,23-25}\) We model this diffusion process for indium using 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 In\(_x\)Ga\(_{1-x}\) 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 Eq. (1):

![Fig. 1. (Color online) (a) Schematic of MBE grown InAs/GaAs QD heterostructure. (b) Truncated pyramid type QD structure as obtained from the HAADF-STEM image with the dimensions which are incorporated in simulations. (c) Experimental PL spectra from samples annealed at various temperatures between 650 and 850 °C.](image-url)
We then solve Eq. (1) 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 account for the variation in 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 $D_0 = 8.5 \times 10^{-14}$ m$^2$ s$^{-1}$ and $E_a = 1.23$ eV, respectively.

Results from our simulations (Fig. 2) show appreciable change in indium concentration profile of the QD structure with increase in annealing temperature. Gradual desorption of indium from the QD with gallium in-diffusion is clearly seen commencing at an annealing temperature of 650 °C and total dissolution of the QD in the wetting layer (WL) is observable at 850 °C.

**B. Variation in carrier confinement potentials**

A single-band assumption is used to calculate the carrier confinement potentials and effective masses, which are necessary to solve the Schrödinger equation for carrier energy states. We use the modified concentration profile of the annealed heterostructure and bulk band parameters of InAs and GaAs to obtain the electron and hole confinement potentials. The position-dependent bulk band gap after interdiffusion is obtained from the following empirical relation [Eq. (3)] (Ref. 26) involving indium content $x$ in In$_x$Ga$_{1-x}$As:

$$E_g(r) = 1.519 - 1.584x + 0.475x^2.$$  

To calculate the electron and hole confinement potentials, it is assumed that bulk CB and VB offsets, $\Delta E_e$ and $\Delta E_h$ bear the constant ratio 76/34. However, crystal strain arising due to lattice mismatch between InAs and GaAs considerably affects the band profiles. A simplified model, which enables us to recalculate the confinement potentials, is adopted to account for the effect of strain. In the case of the as-grown QD, it is assumed that the energy shifts in the calculated CB and VB due to strain in the dot material are constant. This is justified since the variation in strain inside the dot material is small. We take these shifts to be $\Delta E_e = -450$ meV and $\Delta E_h = 90$ meV. In case of an annealed QD, the strain is assumed to vary in a linear fashion with the mole fraction of indium, thereby resulting in $\Delta E_e$ and $\Delta E_h$ varying in space. Effectively, these strain corrections cause the portion of the calculated CB inside the QD to move closer to the bulk GaAs CB, and the calculated VB inside to move farther above the bulk GaAs VB. Variation in effective mass is taken care of by a linear interpolation of electron and hole effective masses in InAs and GaAs using Eqs. (4) and (5)

$$m_e^*(r) = 0.0465[1-x(r)] + 0.044x(r).$$

FIG. 2. (Color online) (a) Indium concentration profile of the as-grown QD. (b) QD annealed at 650 °C, (c) 750 °C, and (d) 850 °C along the vertical symmetry plane.
$m_0^2(r) = 0.2774[1 - x(r)] + 0.241x(r)$. 

(5)

It can be seen from the results of our band profile calculations (Fig. 3) that annealing leads to a decrease in carrier confinement potentials inside the QD. The reason for the same may be understood by considering two effects. First, interdiffusion causes an overall increase in QD Ga content, which leads to a greater difference between both the calculated bands inside the QD, and hence reduced band offsets. Second, the strain effect, which is directly related to $x$ in our simulations, also becomes more uniform and decreases in magnitude with annealing. As the correction due to the strain energy distribution decreases, it is expected that the band profiles deviate lesser from the originally calculated profiles, thereby maintaining the confinement potential for electrons at a greater value but for holes at a lower value. Both these effects, that is interdiffusion induced decrease in band offsets and variation in strain appear to favor a decrease in hole confinement potential. In case of electrons, the former effect dominates, ultimately causing their confinement potential to reduce too. Thus, both potential profiles become observably smoother and shallower with an increase in annealing temperature. Such a variation in confinement potential is likely to lead to an increase in ground-state carrier energy.

C. Schrödinger solver and calculation of ground state PL peaks

The three-dimensional Schrödinger equation [Eq. (6)] is solved to obtain the energy states of an electron and a hole in the QD.

$$-\frac{\hbar^2}{2} \nabla \cdot \left( \frac{1}{m^*} \nabla \psi \right) + V\psi = E\psi.$$  

(6)

Here simple finite difference approximation is used, thereby resulting in a discretization of the QD in barrier system described earlier. We impose $\psi=0$ on the boundaries of the cube, under the assumption that QDs in the structure are spaced sufficiently enough to neglect mutual interaction. The discretized Schrödinger equation is a large-scale matrix eigenvalue problem, in which the energies of the system are given by the eigenvalues of a large ($10^5 \times 10^5$ order) sparse matrix. The open-source MATLAB program EIGIFP.M (Ref. 32) is used to compute the first few eigenvalues of $H$, in which lies our interest. It is noticed that this program, which uses a preconditioned Krylov subspace method, is especially efficient in our context when compared to conventional large-scale eigenvalue estimators based on Arnoldi iteration methods.

Electrostatic interaction between electron and hole charge densities in the QD is accounted for by addition of the interaction energy $E_{\text{coul}}$. Here a full self-consistent Schrödinger–Poisson method is not adopted, since it is observed that $E_{\text{coul}}$ is itself small compared to the initially calculated confinement potentials.

To determine the Coulomb potential due to the electron (hole) charge density, we solve the Poisson equation, given by
The electrostatic interaction energy is given by

\[ E_{\text{Coul}} = \int \rho_h \varepsilon V_{e,h} d\tau. \]  

In the above equations, \( \rho_e = -e \psi_e^2 \) and \( \rho_h = e \psi_h^2 \), \( \psi_e \) and \( \psi_h \) being the ground state electron and hole wave functions which are obtained from the Schrödinger solver. Note that in case of an annealed QD, the permittivity \( \varepsilon \) is itself varying in space, which we approximate by a linear interpolation between \( \varepsilon_{\text{InAs}} \) and \( \varepsilon_{\text{GaAs}} \).

PL peak energy \( E_{\text{PL}} \) is calculated by

\[ E_{\text{PL}} = E^e_{\text{conf}} + E^h_{\text{conf}} + E_{\text{Coul}} \]

\( E^e_{\text{conf}} \) and \( E^h_{\text{conf}} \) are the electron and hole energy states, calculated with a common reference, in our case, the bottom of the conduction band in the barrier material.

D. Correlation with experimental PL peaks

Figure 4 shows the comparison between calculated ground state PL peak energies and our experimental results. The theoretically calculated values are in very good agreement with the experimental data, with a standard deviation of 8 nm, and a maximum deviation of 20 nm at 700 °C. This variation in PL peak energy may be explained in terms of the change in confinement energies of the carriers, as shown in Fig. 5. The decrease in carrier confinement potentials, which occurs as elucidated earlier, causes the respective confinement energies to increase with annealing, thereby blueshifting the PL peak. Further, our earlier observation that variation in strain due to annealing aids the decrease in hole confinement potential but opposes the decrease in electron confinement potential is reflected in the rate of change in electron and hole energy states with annealing temperature. It can be observed that the ground state energy of holes increases at a faster rate than that of electrons.

E. Calculation of the full PL spectrum

So far, we have described the calculation of PL energy from a single QD and studied its variation with annealing temperature. To calculate the PL emission from the ensemble of QDs of varying size in the heterostructure, we use the QD size distribution to calculate the intensity distribution as a function of PL energy, which is essentially the PL spectrum. AFM data from the surface layer of QDs in the sample reveal a distribution of QD heights as shown in Fig. 6(a). We observe that the data is best fitted with a lognormal distribution given by

FIG. 4. (Color online) Comparison between model and experimental variation in PL peak energy with annealing temperature.

FIG. 5. (Color online) Variation in electron and hole confinement energies \( E_{\text{Conf,e}} \) and \( E_{\text{Conf,h}} \) and corresponding variation in the PL peak, \( E_{\text{PL}} \), with reference to the bulk GaAs conduction and valence bands.

FIG. 6. (Color online) (a) Distribution of QD heights in the uncapped layer of the heterostructure as extracted from AFM observations. A lognormal distribution fits the data more closely than a Gaussian. (b) Shell-like formation of an InAs/GaAs QD. An \( \epsilon \) variation in QD base width causes an equal variation in QD height, and corresponding variations along other dimensions.
Our study quantitatively reproducing the variation in PL spectra, our studies allow us to make simple qualitative observations. From the results in Fig. 8, we observe that smaller QDs undergo a more rapid blueshift at lower annealing temperatures than larger QDs. When an as-grown QD is subjected to annealing, indium present in the outer layer of the QD diffuses into the barrier due to a greater concentration gradient at the boundary. In the case of small QDs, the QD core is thereby exposed to the barrier at low annealing temperatures leading to rapid indium out-diffusion. Indeed, with very small QDs (around 5 nm), we observe from our results that such an effect causes the PL emission energy to increase rapidly and saturate to the bulk GaAs band gap. This QD size-dependent blueshift causes different portions of the PL spectrum from the as-grown heterostructure to respond differently to annealing. The tail at the lower wavelength (smaller QD size) end undergoes a larger blueshift than the higher wavelength (larger QDs) end. This results in an effective broadening of the PL spectrum with an increase in annealing temperature. However, at around 750 °C, the blueshifts from large and small QDs become more comparable, reducing the significance of this effect. Beyond this temperature, it is likely that the effect of an overall size homogenization in the ensemble causes a reduction in FWHM as the QDs begin to merge into the WL.

IV. CONCLUSION

We have presented a model for the effect of thermal annealing on the PL properties of single-layer InAs/GaAs QDs, and followed it up with an experimental correlation. We initiated our study with computation of chemical composition of the annealed heterostructure. 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. The close experimental correlation achieved by the model represents an advance in predicting annealing effects on QD heterostructures and specifically addresses the necessity for a design tool for optical properties of QD materials. A detailed calculation of strain effects on confinement potentials may help offer a richer picture of the effect of interdiffusion on band profiles and also perhaps obtain a better correlation with experimental results.

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