Evaluation of strain balancing layer thickness for InAs/GaAs quantum dot arrays using high resolution x-ray diffraction and photoluminescence

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The impact of strain-balancing quantum dot superlattice arrays is critical to device performance. InAs/GaAs/GaP strain-balanced quantum dot arrays embedded in p-i-n diodes were investigated via high resolution x-ray diffraction (HRXRD) and photoluminescence (PL) as a function of the GaP thickness. A three-dimensional modification of the continuum elasticity theory was proposed and an optimal thickness was determined to be 3.8 ML. HRXRD-determined in-plane strain in superlattices with this range of GaP thickness gave an empirical value for the GaP thickness to be 4.5 ML. Optical characterization indicated the highest integrated PL intensity for the sample at the optimal strain balanced condition. © 2009 American Institute of Physics. [doi:10.1063/1.3264967]

Epitaxial quantum dots (QDs) have generated much interest from the III–V semiconductor device field for their potential to enhance performance in particular device characteristics. For example, semiconductor lasers can exhibit improved threshold current densities using QDs,1,2 QD infrared photodetectors have also shown incident absorption enhancements over quantum well (QW) detectors3,4 and a number of approaches either have been proposed or were demonstrated for improvement in photovoltaic conversion efficiency.5–8 The use of epitaxial QDs have been proposed as the most probable candidate for the realization of the intermediate band solar cell.5 Recently, Stranski–Krástinow (SK) grown InAs/GaAs QDs have demonstrated improved single junction short-circuit currents.6 Due to the strain-driven nature of the SK growth mechanism of epitaxial QDs, correct strain-balancing is essential to growing the significant numbers of QD layers necessary for these devices. With greater numbers of layers, designs which neglect strain can lead to dislocations and poor QD uniformity which can ultimately degrade photovoltaic parameters such as open circuit voltage7,8 and laser operation.9

Strain-balancing, first shown to increase critical thickness by Katsuyama et al.,10 has since advanced in application and has been shown useful in decreasing misfit and threading defects in many superlattice (SL) structures, improving various optical, mechanical, and device properties.7,11–14 Alternating layers of compressively strained and lattice matched epitaxial material on a substrate have inherent individual layer thickness limits imposed by the Matthews and Blakeslee formulation.15 Miller et al.11 and Ekins–Daukes et al.12 have suggested means of relieving strain in a QW SL by introducing an alternating tensilely strained material to balance the compressively strained layer. Consideration of these approaches has lead to the present work in which they are applied to a multiple-layer array (SL) of InAs QDs in a GaAs host with GaP strain-balancing layers.

Five test structures with 10× layer stacks of InAs (wetting layer + QD)/GaAs/GaP/GaAs were grown on (100) GaAs substrates using an organometallic vapor-phase epitaxy reactor using traditional III–V metal-organic and hydride gases. Further details of growth are described in Ref. 16. InAs is compressively strained to GaAs by 7.2%, and GaP has a tensile lattice mismatch of 3.6%. The individual layer thicknesses of the GaP grown for this study were within the calculated critical thicknesses of a strained epilayer on a GaAs substrate (72 Å). Pseudomorphic growth was then assumed with no relaxation of atomic lattice constants.

It has been shown that strain-balancing can be extremely effective in QW solar cells using the thickness of the first strained layer to determine subsequent balancing layers.12 However, the assignment of a thickness for a layer of discontinuous islands is difficult, a modified version of this method was used here to take into account this thickness nonuniformity inherent in nanostructures grown by S-K. For QW strain balancing theory, the continuum elasticity theory (CET) can be used to approximate the appropriate thickness of the strain balancing GaP layer. Equation (1) illustrates the relationship between layer thickness and relevant material parameters.

\[
t_b = t_{sl} \left[ \frac{A_1 a_i^2 (a_0 - a_{ld})}{A_2 a_i^2 (a_0 - a_{ld})} \right].
\]

The subscripts denote strained layer, balancing layer, and substrate, as sl, b, and 0, respectively, with \( t_{sl} = 2.15 \text{ ML} \) of InAs for a QD approximation derived from growth conditions. This theory includes both the material lattice constants (\( a_i \)) and their stiffness coefficients (contained within the constant \( A_i \)), of the alternating materials. This constant \( A \) is shown in Eq. (2), and is a common ratio of the stiffness coefficients.12

\[
A_i = C_{1i,j} + C_{12,j} - \frac{2C_{12,j}^2}{C_{1i,j}}.
\]

In this equation, \( C \) represents stiffness coefficients of the \( j^{th} \) layer material. This method predicts a value of 2.0 ML for \( t_b \) in the InAs/GaAs/GaP system. In this work, a modification to the CET method was used. This modification allows a prediction of balancing layer thickness to be assessed independently for two separate unit cells with one cell as a SL with only a wetting layer, and another to be assessed for a SL with only a QD.

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\[ t_{\text{b,weighted}} = \rho \sigma t_{b,\text{qd}} + (1 - \rho \sigma) t_{b,\text{wl}}. \]

Equation (3) introduces a weighting method for such modification of the CET theory, where \( \rho \) is denoted as the two-dimensional density of QDs, and \( \sigma \) represents the cross-sectional area of the base of a single QD. The product \( \rho \sigma \) represents a fractional areal density \( QD \) base area per unit area and is between zero and one. Representative QD heights and density were determined by AFM to be 6 nm and \( 5 \times 10^{10} \text{ cm}^{-2} \), respectively. Using the areal densities of both QDs and the wetting layer (QD areal density subtracted from unity), a standard weighting was used to determine an intermediate GaP thickness value as shown in Eq. (3). This gave a value of 3.8 ML. This value was then used as the center-point in the series of samples with varying strain balancing layer thicknesses.

The GaP thicknesses were centered on the modified-CET-method predicted thickness, while two samples were grown with thinner layers, and two were grown with thicker layers, for a range of 3.1 to 5.0 ML of GaP. As discussed in Ref. 17, homogenous strain compensation can be clearly evaluated using high-resolution x-ray diffractometry (HRXRD). \( \omega/2\theta \) scans along the [004] reflections were used to determine the out-of-plane strain in the QD SL for these samples [Fig. 1(a)]. Here, the zeroth order SL peak [SL(0), arrows] can be seen on the left of the substrate Bragg peak for the 3.1 ML GaP sample, indicating the compressive nature of the SL. For the 4.2 ML GaP sample, the zeroth order SL peak is nearly coincident with the Bragg peak, indicating the least amount of out-of-plane strain of the five samples studied. The out-of-plane strain was determined from the experiment by the use of a differentiated formulation of Bragg’s law shown in Eq. (4), while the in-plane strain was determined using these values and a modified Poisson’s ratio.

\[ \frac{\Delta a}{a} = \Delta \theta_{sl} \cot \theta_b. \]

In this equation, \( \Delta \theta_{sl} \) is the difference in angle between the substrate Bragg peak and the zeroth order SL peak, while \( \theta_b \) is the value of the substrate Bragg angle. \( \Delta a/a \) is the fractional lattice mismatch representing the out-of-plane strain of the SL.

A comparison of the in-plane strain and that predicted by the models is shown in Fig. 1(b). The CET method is plotted using the above equations giving the value of 2.0
ML. The modified CET data used the three-dimensional (3D)-modified version of these equations, gave the zero in-plane strain value at 3.8 ML of GaP. This model correlates better with the HRXRD data, in that a linear fit to this experimental data predicts approximately 4.5 ML. Using similar GaP strain balancing, a five-layer QD p-i-n solar cell structure was achieved an approximate 4% increase in short circuit current value over a baseline cell.6

Cross-sectional bright field TEM images were obtained with the [001] zone-axis aligned parallel to the beam direction, as shown in Fig. 2. QD regions are imaged (a) with and (c) without strain-balancing layers. In both images, the layers are clearly visible and the dark regions are the InAs QDs. Figure 2(a) shows a vertical stack of ten QDs is clearly aligned and a 20 nm diameter is maintained. Figure 2(b) shows a zoomed in detail of the layer structure of the SL. Here, the elemental contrast is clear with the lightest layers indicating GaP. In Fig. 2(c), alignment is maintained, but QD size expands in diameter to four to five times near the top of the stack due to the loss of the fractional lattice mismatch between InAs and GaAs.

While HRXRD can provide a means to determine structural information and a low homogeneous strain condition, measurements of radiative recombination intensity provide a very sensitive means to evaluate the optical quality of the QDs. Photoluminescence (PL) spectra were taken from these structures as a function of the GaP strain balancing layer thickness in order to verify the optical quality of the strain balanced QDs. Experiments were performed using a focused 30 mW HeNe laser and an Ocean Optics NIR512 infrared spectrometer. All samples showed a single PL peak at 1.07 eV ± 5 meV, typical for InAs QDs.19 The FWHM for all of the samples ranged from 90–95 meV. Figure 3 shows the values of the integrated intensity of the PL signal from each sample as a function of GaP thickness. For this recipe and reactor, PL intensity variation was calculated to be ±1.5%. This data peaks at the sample with 4.2 ML indicating the highest radiative recombination efficiency of excited carriers occurring in the strain neutral sample. This is a clear indication that the calculated strain neutral condition using the modified CET theory results in the growth of both higher optical and material quality QD arrays than using the CET method alone. Not shown is the PL FWHM variation indicating no significant QD size trend with changing strain balancing layer thickness.

In conclusion, we introduced a three-dimensionally modified version of CET theory for the prediction of GaP thickness intended for the compensation of the strain induced by multiple stacks of SK-grown InAs QD on GaAs. The HRXRD technique was used to experimentally verify the appropriate strain balancing predicted by the modified theory. PL was used to provide optical characterization of the InAs structures as a function of GaP thickness and was found to support the optimal strain balanced condition suggested by the model. Using only the Matthews and Blakeslee’s original formulation for critical thickness underestimates the critical QD SL thickness, since it can only be applied individually to a region with a QD and a region without. Considering that these two unit cells are constrained to the same balancing layer material and thickness, clearly one will be under- and one will be over-strain-compensated. Complex atomistic models may account for second-order effects and provide some improved accuracy; however, using the method presented, an effective, first-order approximation for strain-balancing layer thickness can be determined.


FIG. 3. PL integrated intensity values as a function of GaP thickness indicating a peak in integrated PL value between 3.7 and 4.7 ML with the highest value from the sample with 4.2 ML. Inset shows PL spectrum of 4.2 ML sample.