Three-dimensional measurement of composition changes in InAs/GaAs quantum dots

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Abstract. We present a transmission electron microscope (TEM) analysis of InAs/GaAs quantum dots (QDs) which have been subject to thermal annealing. Annealing produces a significant shift in infrared detector response to longer wavelengths, indicating changes in QD size, composition, or both. A three-dimensional reconstruction of an ‘average’ QD is obtained by combining compositionally-sensitive dark field 002 TEM images of many QDs, followed by fitting to a structural model assuming cylindrical symmetry. Errors in compositional measurements are estimated, and the validity of the model is assessed by TEM image simulations using 2-beam dynamical electron diffraction theory. As-grown material exhibits an increasing concentration of In towards the top of the QDs, whereas annealed material shows diffusion of indium from the upper part of the QD towards the sides and base. There is no measurable change in the position of the outer interface of the QD.

1. Introduction
The properties of InAs/GaAs quantum-dot (QD) structures are of great interest for many optoelectronic devices such as lasers for telecommunications [1], optical amplifiers and detectors [2,3]. Indium incorporation during growth, and redistribution during thermal treatment, plays a significant role in determining their optical and electronic properties. Annealing leads to a blue shift and a narrowing in optical emission, and has been shown to alter the size, shape and the chemical composition of QDs [4-6]. A variety of transmission electron microscopy (TEM) techniques have been used to evaluate the composition in QDs (e.g. [7-9]); however, a simple method of three-dimensional compositional analysis does not yet exist since all TEM images are a 2D projection of the 3D structure [10]. Significant changes in QD shape, size and composition are known to occur during encapsulation by overlying material [11]; uncapped dots are likely to be significantly different to those in bulk material, leading to the requirement for characterisation of QDs fully inside a matrix of different material. Here, we assess the possibility of using 002 dark-field (DF) diffraction contrast images to obtain quantitative 3D composition measurements using a simple structural model. Quantum dot infrared photodetector (QDIP) structures were grown on (001) GaAs by molecular beam epitaxy; 50nm thick upper and lower cladding layers of Al₀.₁Ga₀.₉As surrounded a 30-repeat QD structure, in which nominally 2.4ML InAs QDs were deposited at 510°C between 1nm In₀.₁₅Ga₀.₈₅ layers separated by 40nm GaAs spacers. Modulation doping was employed in the spacer layer at an equivalent value of 2 electrons/dot. QD densities were 3 x 10¹⁰ cm⁻² and exhibited room temperature
photoluminescence at 1260 nm. Post-growth annealing was carried out at 800°C for 2 minutes. As-grown samples exhibited peak photoresponse at 6.75 µm with an applied bias of -14V which red shifted to almost 10 µm after annealing (Fig. 1), caused by a large change in bandgap (i.e. intermixing). Cross-section specimens were prepared using standard techniques (mechanical thinning followed by ion milling using Ar⁺ at 6 and 3kV) and examined in a JEOL 2000FX TEM at 200kV.

2. Results

Figure 2 shows dark field 002 TEM images of (a) as-grown and (b) annealed QDs. These images are an average of several QDs with imposed mirror symmetry in order to reduce noise in the data. The InAs QD appears as bright central region (high In content) surrounded by a dark halo. Although the annealed QD appears larger, the position of the outer dark line is essentially unchanged; a more accurate description is that In and Ga are redistributed inside the dot during annealing to give a more uniform internal composition.

Figure 1. Photoresponse of as-grown and annealed QDIP structures.

3. Analysis

Previous studies of InAs QDs have shown that they appear almost identical when viewed from any viewpoint perpendicular to the growth direction [12], i.e. their symmetry is close to cylindrical. This suggests that a structural model with cylindrical symmetry can be used, which greatly reduces the computational effort required to extract compositional data from images such as Fig. 2. Furthermore, since the 002 diffracted beam is relatively weak, close to kinematic electron diffraction conditions apply and the image may be regarded as a simple 2D projection $I_{2D}$ of a 3D structure $I_{3D}$. Under the condition of cylindrical symmetry, we may represent any smoothly varying 3D structure using a series of $n$ Gaussian functions, i.e.

$$I_{2D} = \int_{-\varepsilon / 2}^{\varepsilon / 2} I_{3D} \, dz$$

$$I_{3D} = \sum_{i=1}^{n} a_i \exp \left[ -\frac{(x-x_0)^2+z^2}{2\sigma_i^2} \right] + C$$

where the projection direction is along the $z$ direction, $a_i$, and $\sigma_i$ are parameters describing the $i^{th}$ Gaussian function and $C$ is a constant (background) value. In this analytical approach, the 3D model can be obtained directly from the 2D image since the relationship between $I_{2D}$ and $I_{3D}$ is exact. The specimen thickness is an unknown parameter and thus must be supplied by other measurements or by obtaining the best fit between the model and experiment. Thus, by fitting each horizontal line in the
image to a series of Gaussian functions + constant background it is possible to produce a ‘3D intensity model’ for a specimen of thickness \( t \). In practice, we find that the series can be truncated at \( n = 2 \) while still giving a satisfactory fit to the data. A 3D composition distribution \( X_{3D} \) may be obtained from \( I_{3D} \) using the kinematic relationship between intensity and composition as shown in Fig. 3. For the In\(_x\)Ga\(_{1-x}\)As system this is double valued for compositions below \( x \approx 0.47 \); a choice must thus be made between the two solutions. Here, since the QD has a GaAs substrate and capping layer we may propagate the lower composition value (from outside the QD towards its centre) to the point at which the gradient of intensity reverses. This results in an artificially sharp boundary between the QD and surrounding material in the composition maps.

In order to evaluate this procedure, the 3D composition distribution \( X_{3D} \) was used as the input to a fully dynamical image simulation as shown in Fig. 4 for both the as-grown and annealed structures for a range of specimen thicknesses. It can be seen that, for a given image, as the specimen thickness increases the amount of indium in the dot must also increase to maintain the bright core at the same level relative to the GaAs. The central row of images in Fig. 4 shows the difference between the dynamical simulation and the experimental image (Fig. 2). Although all of the simulated images are in reasonable agreement with the experiment, it can be seen that the model tends to overestimate In content in very thin specimens (the dot is too bright, giving a dark region in the difference image) and underestimate the In content in thicker specimens (the dot is too dark, giving a bright region in the difference image). The actual specimen thickness \( t \) is unknown for the images of Fig. 2 but is probably 50 < \( t \) < 100 nm.

Figure 4. Bottom row: slices through the 3D composition distribution \( X_{3D} \) obtained using a model of cylindrically symmetric Gaussian functions for different specimen thicknesses. Top row: dynamical simulations of dark field 002 images using \( X_{3D} \). Changes in lattice parameter as a function of composition \( x \).
composition were included but shear strains were ignored. Centre row: difference between the experimental and simulated images.

4. Discussion and Summary
These results imply that it may be possible to use a simple model of QD structure to obtain accurate 3D compositional data. However, some problems still remain. First, the need for an accurate measurement of specimen thickness is essential, since it is possible to fit the experimental data to a wide composition range while maintaining a good fit for all reasonable specimen thicknesses. Second, although the contrast passes through a minimum between the bright QD centre and the surrounding GaAs, the intensity does not reach zero. This is presumably due to the effects of finite resolution, internal strain and/or inelastic scattering; the use of an ‘average’ image, obtained by summing images from several QDs, will also increase this effect. This leads to an artificially sharp boundary between the QD and the surrounding material, and a poor estimate of In content close to the minimum of Fig. 3 (0.15 < x < 0.3). Finally, the effects of strain contrast are also visible in the compositional model; the darker area above the QD is interpreted as a change in In content outside the QD.

Despite these limitations, the 3D compositional data in the as-grown sample clearly shows a concentration of In towards the top of the dot and the V-shaped region of high In content [1]. The maximum In concentration in the QD for a specimen thickness of 87nm is x = 0.7. The annealed sample shows a redistribution downwards and outwards from the region of high In content, leading to a cone-shaped region of high In content and a lowered maximum of x = 0.6 for a specimen thickness of 87nm.

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