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P. A. Crozier, M. Catalano, R. Cingolani, and A. Passaseo

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Direct quantitative measurement of compositional enrichment and variations in $In_yGa_{1-y}As$ quantum dots

P. A. Crozier[a)]
Center for Solid State Science, Arizona State University, Tempe, Arizona 85287

M. Catalano
IME–CNR, Via Arnesano, 73100 Lecce, Italy

R. Cingolani and A. Passaseo
Unità INFM di Lecce, Dipartimento Ingegneria dell'Innovazione–Università di Lecce, Via Arnesano, 73100 Lecce, Italy

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Assessment of the composition of quantum dots on the nanoscale is crucial for a deeper understanding of both the growth mechanisms and the properties of these materials. In this letter, we discuss a direct method to obtain a quantitative evaluation of the In variation across nanometer-sized InGaAs quantum dots embedded in a GaAs matrix, by means of electron energy-loss spectroscopy in a scanning transmission electron microscope. © *2001 American Institute of Physics.*
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Quantum dots (QDs) are the subject of intense investigation because of their potential applications in optoelectronics.[1–6] The ability to fully exploit the innate characteristics of these structures depends on being able to understand and control the island formation process responsible for producing the QDs. Detailed characterization of dot structures and properties is critical to developing improved device performance. Correlating structure and composition at the nanometer level with optical and electrical measurements is an essential step for improved understanding. In particular, the presence of compositional disorder in QD structures, gives rise to a strong variation of their optical and electronic properties. The assessment of compositional variation in low-dimensional ternary alloy systems is difficult and has not been adequately addressed so far.[7–9]

In this letter, we outline a method to quantitatively measure the spatial variation of the In content across nanometer-sized $In_yGa_{1-y}As$ quantum dots. We employ electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) to measure the compositional profiles across the dot. The advantage of this method is that the measured composition is not strongly influenced by strain. The adjacent wetting layer (WL) is used to estimate a spatial response function under conditions identical to those employed for the dot measurement. This spatial response function together with a compositional model of the dot are used to simulate compositional line profiles from the dot and wetting layers. By varying the parameters of the model we can optimize the fit to experimental data and thus determine the variations in the In/As concentration across the center of the dot.

$In_yGa_{(1-y)}As$/GaAs QDs were grown by low-pressure metal–organic chemical-vapor deposition (LP-MOCVD) on a 100-nm-thick (100) GaAs substrate. The growth was performed in a horizontal LP-MOCVD system (AIXTRON 200 AIX). Trimethyl–gallium and trimethyl-indium and pure AsH_3 were used as the source metals. Pd-purified H_2 was used as a carrier gas and the growth temperature was 550 °C. Four monolayers of $In_{0.5}Ga_{0.5}As$ were deposited on the GaAs substrate giving a nominal WL thickness of 1.2 nm and a nominal concentration of $y=0.5$. After a 60 s growth interruption, a 30 nm GaAs capping layer was deposited. Additional details of the dot synthesis can be found elsewhere.[10] Conventional transmission electron microscopy (TEM) showed that the dots have a narrow size distribution peaked around (14 ± 2) nm and a dot density of about $1.9\times10^{10}\,cm^{-2}$.

Compositional analysis was carried out on a Vacuum Generator's HB501 STEM. This instrument is capable of forming an intense nanometer-sized electron probe and is equipped with a GATAN energy-loss spectrometer and an ES Vision data acquisition system for acquiring position-resolved EELS. A series of 50–100 spectra was acquired from lines across both the WL and the center of dots (see Fig. 1). The ionization edge intensity was extracted using standard methods[11] and the In/As concentration ratio calculated from the integrated signal intensities. A sample of pure InAs was used as a reference standard for the EELS quantification. Typical In/As concentration profiles are shown in Fig. 2.

To extract absolute composition information from the experimental concentration profiles it is necessary to correct for:

(1) the effect of the spatial response function arising from the electron probe size, probe instabilities, and beam spreading in the sample, and
(2) the projection problem because the dot is embedded in a GaAs matrix. Both of these effects are addressed in this letter.

For one-dimensional interface analysis, the measured elemental profile, $M(x)$, and the projected elemental profile, $E(x)$, will be functions of only one coordinate (because of symmetry) and can be expressed as

a)Electronic mail: crozier@asu.edu

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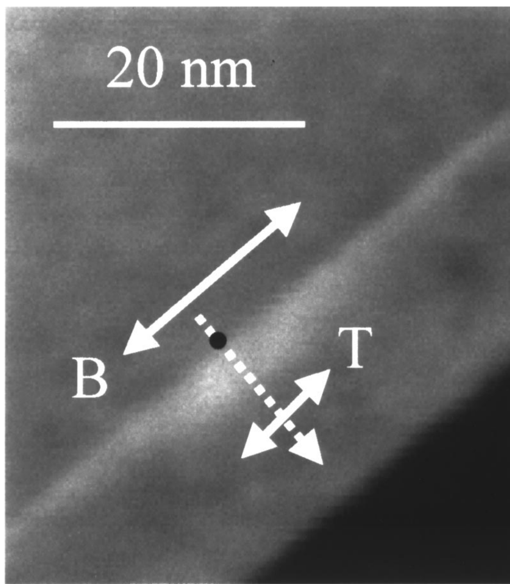

FIG. 1. High-angle annular dark-field image used to estimate the base width B and top width T of the dot. The dotted line shows the path traversed by the electron probe to obtain the experimental profiles shown in Fig. 2. The circle shows the approximate full width at half maximum of the probe.

$$M(x) = E(x) * \mathrm{PP}(x), \tag{1}$$

where* signifies a convolution and the function $\mathrm{PP}(x)$ is a projection of the cylindrically symmetric probe current distribution $P(r)$ onto a line perpendicular to the interface.[12] To a good approximation we find that the projected probe $\mathrm{PP}(x)$ can be simply described as a Lorentzian function $[\approx 1/(x^2+\rho^2)]$.

In practice, the electron probe will be broadened by instabilities in the beam position and beam spreading in the sample during spectral acquisition. The simplest way to incorporate both instabilities and beam spreading is to broaden the function $\mathrm{PP}(x)$ by increasing the value of the Lorentzian parameter ρ. This spatial response function was determined by simulating the experimental profiles from the WL. Typically, we find that the best match between the experimental data and the simulated profiles is obtained with the probe parameter $\rho = 0.55$ nm [full width half maxima (FWHM) $= 2\rho = 1.1$ nm], the well width of about 1.2 nm, and the In/As concentration = 0.30. The In/As concentration is about 30%–40% lower than the photoluminescence data would suggest. The reason for this discrepancy is that some of the In is lost from the upper and lower surfaces of the WL during TEM sample preparation by ion milling.[13]

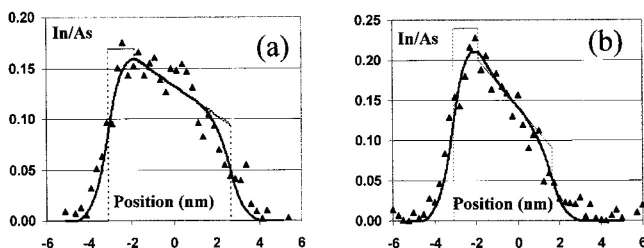

FIG. 2. In/As profiles derived from the model overlaid with the experimental profiles for dots 1 (a) and 4 (b) of Table I (triangles, experiment; solid line, simulation convolved profile; and light dotted line, projected In/As profile).

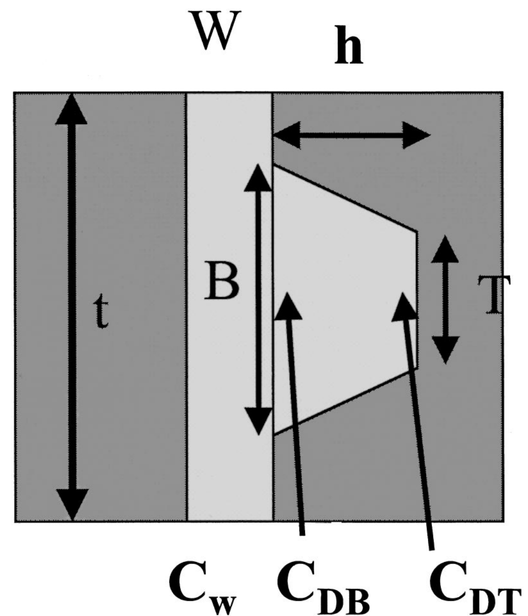

FIG. 3. Truncated cone model for the QD. The model can be characterized with a number of parameters: sample thickness t, WL width W, WL In/As ratio C_w, In/As ratio at base of dot C_{DB}, In/As ratio at top of dot C_{DT}, base diameter of the cone B, top diameter of the cone T, and the dot height h.

We can use the same response function to interpret the data from the quantum dots because the elemental profiles were performed through the dot center where the radius of curvature is large compared to the probe diameter. Determination of the absolute composition of the quantum dots is complicated because the measured In/As are projected concentration ratios from the entire sample thickness. To proceed we assume that the dot can be modeled as a truncated cone defined in Fig. 3. We assume that the In/As concentration in the well is constant C_w and that the In/As concentration along a line through the middle of the dot varies in a linear manner and is C_{DB} and C_{DT} at the base B and top T, respectively.

High-angle annular dark-field images are relatively free of strain contrast and can be used to estimate the base width B and the top width T (Fig. 1). The well width was assumed to be 1.2 nm and the probe FWHM = 1.1 nm. The low-loss region of the electron energy-loss spectrum can be used to estimate the local total foil thickness t because the mean-free path for inelastic electron scattering from GaAs is well known.[14,15] This effectively means that the truncated cone model has four free parameters: C_w, C_{DB}, C_{DT}, and h.

Figure 2 shows the results of fitting the truncated cone model to the experimental In/As line scans. The convolved projected concentrations give good fits to the experimental profiles showing that the projected cone model is reasonable for the dots. Table I summarizes the model parameters for four quantum dots including the two shown in Fig. 1. The

TABLE I. Characteristic parameters for the truncated cone.

Dot No.	h (nm)	B (nm)	T (nm)	C_w	C_{DB}	C_{DT}
1	4.5	21±2	15±3	0.17	0.5±0.1	0.4±0.15
2	3.2	18±1	10±2	0.23	0.8±0.15	0.9±0.2
3	3.2	17±1	14±2	0.14	0.7±0.15	0.6±0.2
4	3.5	18±1	10±2	0.24	0.8±0.2	0.65±0.2

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dots are found to have In/As base concentrations between 0.5 and 0.8 showing that substantial In enrichment has occurred in the dots. A detailed error analysis shows that the In/As concentration ratio in the dot can be determined to within 20%.[12] The dot width h is between 3.2 and 4.5 nm with the larger dot giving significantly lower In concentrations. The observation that the dots are enriched in In is in good agreement with theoretical predictions for compositional enrichment of dots relative to the WL.[16] Tersoff's analysis shows that when interface mixing is negligible, the concentration y' of the straining alloy phase in a nucleated island can be expressed as

$$y' = y/(1-\alpha), \quad \text{when} \quad y \leqslant 1-\alpha,$$

$$y' = 1 \quad \text{when} \quad y \geqslant 1-\alpha,$$

where y is the nominal concentration in the WL and α is a factor that depends on the shape of the island and usually lies in the range 0.2–0.6. For our experiments, $y=0.5$ and the resulting compositional enrichments are in the range 0.6–1, which agrees with our experimental measurements. This implies that interface mixing due to capping may not have a big influence on the In profile measured here.

Our data show only slight evidence for depletion of In at the top of the dots. We do not see any evidence for the inverted triangle profile reported in Ref. 9. According to Tersoff,[16] large compositional variations within the dot may occur if the growing dot depletes a significant fraction of the In from the WL. From knowledge of the dot size, density, and composition, and the WL thickness and composition, it is possible to calculate the reduction of In content in the WL resulting from dot formation. Assuming that the dots are all In rich with a value of $y'=0.9$ yields a reduction in the nominal value of the WL of only 2.5% (i.e., $y=0.485$ for the WL). This would imply that there should not be a significant variation in composition between the base and the top of the dot as we find in our measurements. Dots formed on much thinner wetting layers or layers with smaller values of y would be expected to show greater compositional variation. The In concentrations at the WLs at the base of the dots were found to be 30% lower on average than the In concentrations away from the dot showing that local In depletion has occurred in the immediate vicinity of the dot.

In summary, we have made quantitative measurements of the composition of the In/As ratio in nanometer-sized quantum dots capped with GaAs. Care must be taken to reduce TEM sample preparation artifacts. However, the method is not strongly affected by strain and yields compositions that are accurate to within 20%. We find evidence for strong enrichment of In in the dots.

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