

Composition and strain relaxation of $\text{In}_x\text{Ga}_{1-x}\text{N}$ graded core shell-nanorods

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Two $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanorod samples with graded In compositions of $x = 0.5 - 0$ (Ga-rich) and $x = 0.5 - 1$ (In-rich) grown by molecular beam epitaxy were studied using transmission electron microscopy. The nanorods had wurtzite crystal structure with growth along [0001] and core-shell structures with In-rich core and Ga-rich shell. Energy-dispersive X-ray analysis confirmed grading over the entire compositional range and showed that the axial growth rate was primarily determined by the In flux, and the radial growth rate by the Ga flux. There was no evidence of misfit dislocations due to grading, but the strain due to the lattice mismatch between the In-rich core and Ga-rich shell was relaxed by edge dislocations at the core-shell interface with Burgers vectors $b = a\langle 11\bar{2}0 \rangle$ and $b = c\langle 0001 \rangle$.

Keywords: InGaN nanorods, transmission electron microscopy, EDX mapping, core-shell structures, strain

I. Introduction

The great success of making III-nitrides optoelectronic devices in the blue range has led to interest in extending devices to longer wavelengths for light emitting diodes and lasers working in the green range [1]–[4], and for solar cell applications [5]. $\text{In}_x\text{Ga}_{1-x}\text{N}$ has a direct band gap, the energy of which may be varied [6] by changing the In content (x). However the growth of high quality $\text{In}_x\text{Ga}_{1-x}\text{N}$ with high In-content is difficult as the lattice mismatch between InN and GaN is 11%, therefore growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ with high In-content on a GaN base introduces dislocations and strain fields [7]. These defects are generally charged and can act as non-radiative recombination centres, a detrimental quality for LED and photovoltaic devices. Strain generated by lattice mismatch between two compositions induces piezoelectric polarization and high electric fields which leads to carrier separation and a reduced recombination efficiency in light emitting devices [8]. Furthermore, InN requires a low growth temperature (compared to GaN) at around 400-500 °C due to its higher volatility at elevated growth temperatures that leads to spinodal decomposition and In clustering.

These challenges are potentially resolved in the growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanorods by molecular beam epitaxy (MBE). The MBE allows low temperature growth with precise control over the growth parameters that enables more efficient In incorporation. The geometry of the nanorods should also allow misfit strain arising from lattice mismatch with the substrate to be accommodated by permitting elastic relaxation at the lateral free surfaces [9], [10]. The growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanorods under N-rich conditions has been studied for over a decade [11] and growth of nanorods over the whole compositional range of $x = 0 - 1$ has also been demonstrated [12]. The spontaneous growth of core-shell nanorod structures is commonly

reported for $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{Al}_x\text{In}_{1-x}\text{N}$ nanorods grown both by MBE and Magnetron Sputtering techniques [13]–[16]. However, composition grading has been studied less intensively, and the investigation of graded nanorods that cover the entire range of composition was introduced for the first time by our group [17]. Two $\text{In}_x\text{Ga}_{1-x}\text{N}$ samples graded to cover the entire compositional range of $x = 0 - 1$ grown by plasma-assisted MBE (PA-MBE) are studied in this paper and the compositional and structural changes during grading are analysed.

II. Experiment

Graded $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanorods with $x = 0.5 - 0$ and $x = 0.5 - 1$ were grown directly on p-type Si(111) substrates under strong N-rich condition for five hours in a Varian ModGen II MBE system. Activated Nitrogen was supplied by HD25 RF plasma source. The samples were grown at $\sim 450^\circ\text{C}$ with the In and Ga sources inclined at $\sim 35^\circ$ normal to the substrate which was rotated at 10 rpm. The growth process has been started by growing a uniform composition of $x = 0.5$ for the first three hours followed by a stepwise grading of In/Ga for two hours by just changing Ga/In beam pressures as shown in Table 1. Cross sectional TEM samples were prepared by mechanical polishing followed by Ar^+ beam thinning or by scraping off the nanorods into ethanol and drop-cast onto holey carbon films. The nanorods were studied in cross-sectional orientation (with the growth axis nearly perpendicular to the beam) and in plan-view orientation (growth axis parallel to the beam) by JEOL 2010 and ARM 200F transmission electron microscopes operated at 160 kV and 200 kV respectively. The composition and strain relaxation of the nanorods were studied using EDX and selected area electron diffraction methods.

Table 1: The Ga and In beam equivalent pressure sequence for the two $\text{In}_x\text{Ga}_{1-x}\text{N}$ samples.

$\text{In}_x\text{Ga}_{1-x}\text{N}$ graded from $x=0.5-0$ (Ga-rich)		$\text{In}_x\text{Ga}_{1-x}\text{N}$ graded from $x=0.5-1$ (In-rich)		Time duration (hours)
In BEP (Torr)	Ga BEP (Torr)	In BEP (Torr)	Ga BEP (Torr)	
$\sim 3.0 \cdot 10^{-8}$	$\sim 2.2 \cdot 10^{-8}$	$\sim 3.0 \cdot 10^{-8}$	$\sim 2.2 \cdot 10^{-8}$	3
$\sim 2.25 \cdot 10^{-8}$	$\sim 2.2 \cdot 10^{-8}$	$\sim 3.0 \cdot 10^{-8}$	$\sim 1.65 \cdot 10^{-8}$	0.5
$\sim 1.5 \cdot 10^{-8}$	$\sim 2.2 \cdot 10^{-8}$	$\sim 3.0 \cdot 10^{-8}$	$\sim 1.1 \cdot 10^{-8}$	0.5
$\sim 0.75 \cdot 10^{-8}$	$\sim 2.2 \cdot 10^{-8}$	$\sim 3.0 \cdot 10^{-8}$	$\sim 0.55 \cdot 10^{-8}$	0.5
~ 0	$\sim 2.2 \cdot 10^{-8}$	$\sim 3.0 \cdot 10^{-8}$	~ 0	0.5

III. Results and discussion

Nanorods of both graded samples have wurtzite structure with growth along [0001]; the cross sectional TEM images and corresponding selected area electron diffraction (SAED) patterns

taken close to the $[11\bar{2}0]$ zone axis using JEOL 2010 TEM are shown in Figure 1. The Ga-rich nanorods are about 700 ± 100 nm long and 100 ± 20 nm wide and the In-rich nanorods are about 1000 ± 200 nm long and 60 ± 20 nm wide. Examination on the nanorods under two beam conditions showed bend contours as well as finer contrast features which will be discussed below.

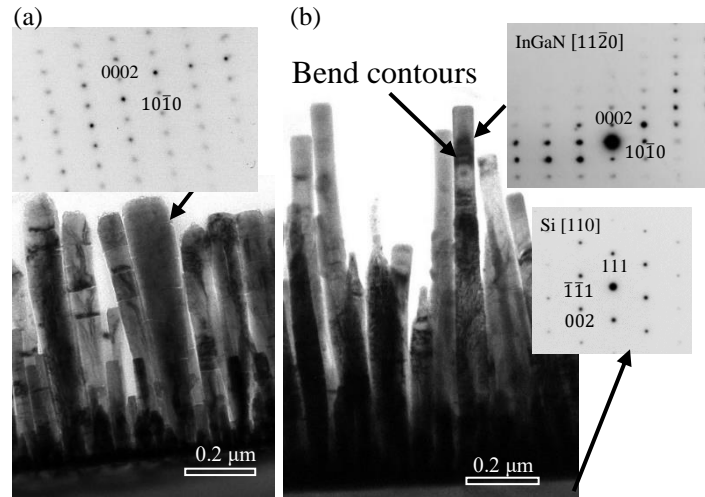


Figure 1: Cross sectional TEM images of (a) Ga-rich and (b) In-rich graded samples and the corresponding SAED patterns taken close to $[11\bar{2}0]$ zone axis using JEOL 2010 TEM.

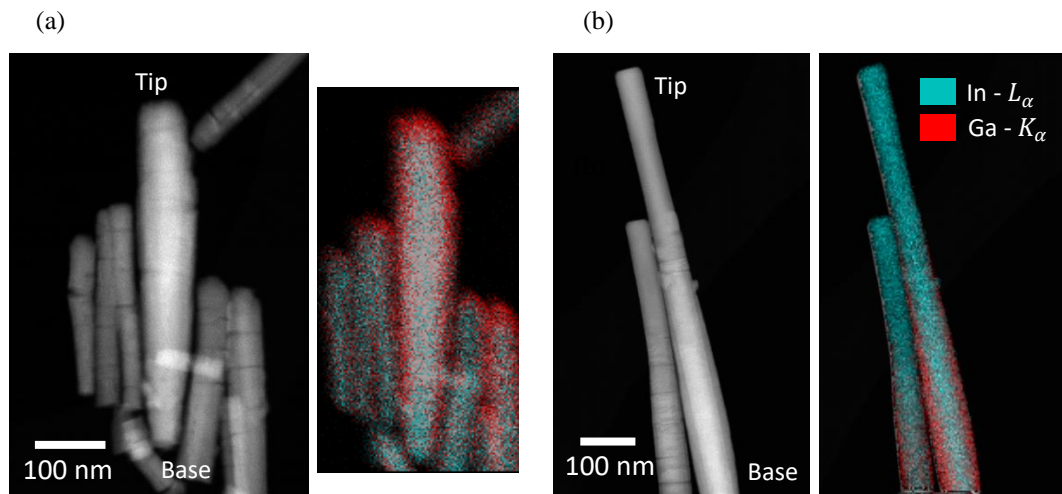


Figure 2: HAADF images and EDX elemental maps of $\text{In}_x\text{Ga}_{1-x}\text{N}$ with (a) $x = 0.5 - 0$ and (b) $x = 0.5 - 1$.

Figure 2 shows high angle annular dark field (HAADF) images and energy dispersive X-ray (EDX) elemental maps taken using the ARM 200F operating at 200 kV equipped with a 100 mm^2 windowless EDX detector. The EDX mapping confirmed the core-shell structure, with In-rich core and Ga-rich shell in the nanorods consistent with nanorods grown with a nominal composition of $x = 0.5$ [13], [17]. Figure 2a shows that the Ga-rich sample has an In-rich core which tapers towards the very end of growth with an increase in thickness of the Ga-rich shell (Fig. 2a). In contrast, figure 2b has a Ga-rich shell which tapers along the growth direction with no significant changes in the In-rich core thickness observed. Moreover, the Ga-rich nanorods are both shorter and broader than the In-rich nanorods. Both samples show no evidence of abrupt composition changes corresponding to the discrete steps in beam pressures during

growth (Table 1). This suggests some significant diffusion of both Ga and In adatoms on the growth surfaces to enhance composition gradients in the growth direction.

Figure 3 shows EDX line scans along the growth direction for both samples. Figure 3a and c shows the grading to GaN ($x=0.5$ to 0). The composition of this rod is about $x=0.4$ which is constant until about 600 nm of its growth from the substrate. This is consistent with our previous studies on nominal $x=0.5$ nanorods [13]. Notably, there is an increase in Ga content (to $x=0$) towards the tip in the final 100 nm of growth. This result suggests that the initial 3hrs of growth corresponds to a nanorod length of approximately 600 nm and the final two hours of graded growth ($x=0.5-0$) corresponds to a length of 100 nm. The Ga-rich graded sample, therefore, has a growth rate of about 200 nm hr^{-1} which is then reduced to an average of $\sim 60 \text{ nm hr}^{-1}$ for the graded growth. This shows that the growth rate along $[0001]$ direction is primarily dependent on the In pressure which reduces during grading while the Ga pressure remains constant.

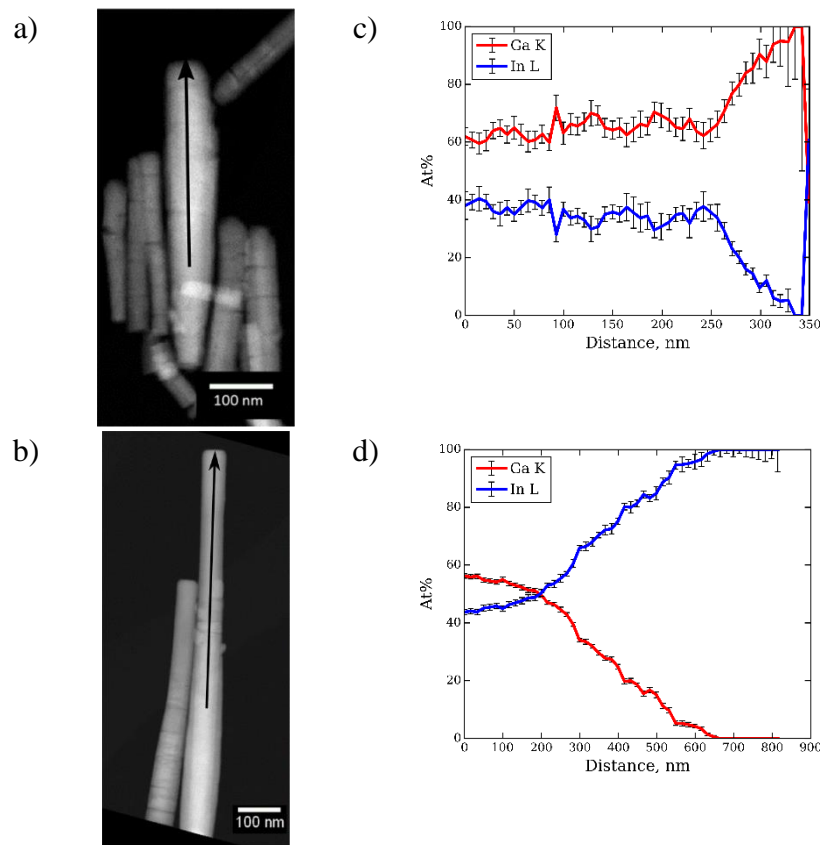


Figure 3: HAADF-STEM images and the elemental EDX line scans of Ga-K and In-L taken along the indicated arrows in (a, c) Ga-rich and (b, d) In-rich graded $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanorods. The distance is measured in the growth direction, along the arrows indicated in (a) and (b).

The In-rich graded sample ($x = 0.5 - 1$), in figure 3b) and d) on the other hand shows a gradual increase of In content along the growth direction. The growth rate along $[0001]$ direction during grading is 230 nm hr^{-1} . This is comparable to that during the first 3 hours of $x=0.5$ growth (200 nm hr^{-1}). This again suggests that this axial growth rate is controlled by the In flux which was constant throughout growth and not by the Ga flux which was decreased during grading. The increased In concentration in the core compared to the expected

composition ($x = 0.5$) suggests that In diffusion from the sidewalls to the (0001) surface during growth is a significant factor, and the slight increase in the axial growth rate during grading may indicate that this contribution is enhanced, suggesting that the Ga adatom flux plays a role in binding In to the sidewalls. However, the results are not conclusive on this point.

The tapering of the shell in the In-rich sample shows that the lateral growth is reduced as the Ga flux is decreased consistent with the assumption that all the Ga adatoms arriving on the side walls are absorbed with low diffusion or re-evaporation rates, and that lateral growth is much less sensitive to the In flux. This also implies that the nanorod radius should be roughly constant for the Ga-rich samples where the Ga flux stays the same while the In flux is reduced. This is also consistent with the observations in figures 1 and 2.

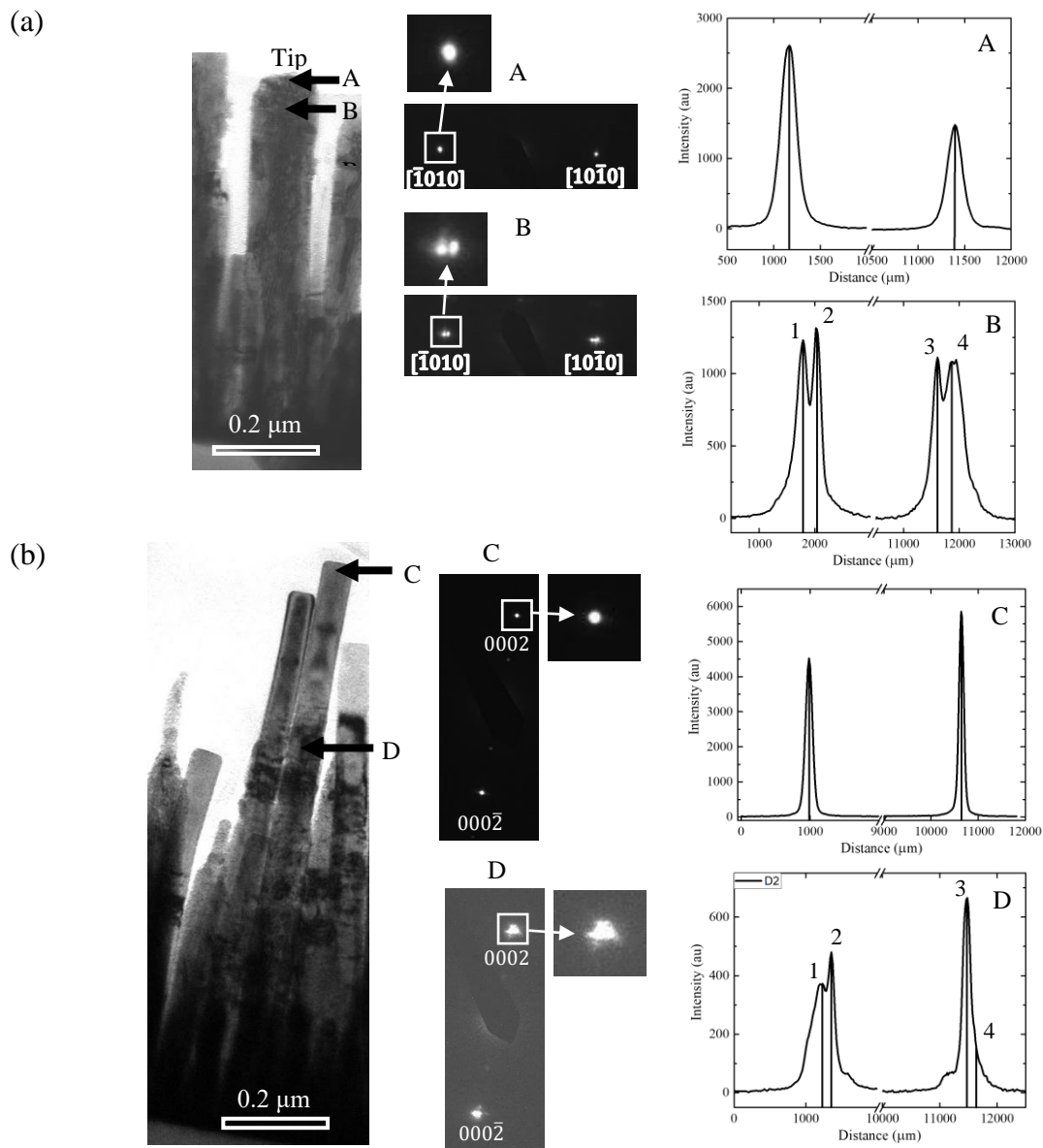


Figure 4: (a) Ga-rich graded sample and (b) In-rich graded sample showing the SAED positions and corresponding SAED taken on $[10\bar{1}0]$ and $[000\bar{2}]$ systematic rows respectively with intensity line profiles taken across the spots with $300\mu\text{m}$ window along both directions. The peaks are indicated by straight lines.

From the elemental EDX mapping of the In-rich sample, the compositions in the core and shell during the first 3 hours of growth were determined to be $x=0.68\pm 0.04$ and $x=0.34\pm 0.02$ respectively, corresponding to a difference in lattice parameters between the core and shell of about 0.012 ± 0.002 nm equivalent to a lattice misfit of 0.04 ± 0.005 . If the core-shell interface is coherent (matched in-plane lattice parameter), the core should be under isotropic compression. On the other hand the Ga-rich shell is under compensative tensile stress along the c axis and is free to relax in all other directions. In such geometries, strain energy should be reduced and relaxed when the core radii and the shell thickness exceed the critical thickness, by forming dislocations, or by surface roughening. The critical core radii and the shell thickness are previously reported for various InGaN core-shell nanorod structures [18] where the critical shell thickness is dependent on the core radius. During the first 3 hours of growth, the In-rich graded sample has core radii about 50 ± 10 nm and shell thickness about 25 ± 5 nm and the Ga-rich sample has core radii about 65 ± 5 nm and shell thickness about 30 ± 10 nm which exceed the critical core radii and shell thickness which should be < 10 nm [19]. The surfaces are smooth and therefore it is expected that the samples of this study should have dislocations produced to accommodate the lattice mismatch. This was investigated firstly by selected area electron diffraction (SAED) using both $[10\bar{1}0]$ and $[0002]$ systematic rows of reflections using a long camera length (50 and 80 cm calibrated with Si substrate) with an area of illumination ~ 125 nm covered by the SAED aperture.

The SAED patterns taken on the graded rods show split spots (labelled by B and D in figure 4) in both directions along $[10\bar{1}0]$ and $[0002]$ below the tip of the rods indicating a lattice mismatch between the core and shell. There are single sharp spots only at the tip (labelled by A and C) consistent with the single composition. The lattice parameter estimations using $[0002]$ and $[10\bar{1}0]$ systematic rows reflections, along the growth direction of the rods are plotted below in figures 5 for the Ga-rich and In-rich samples.

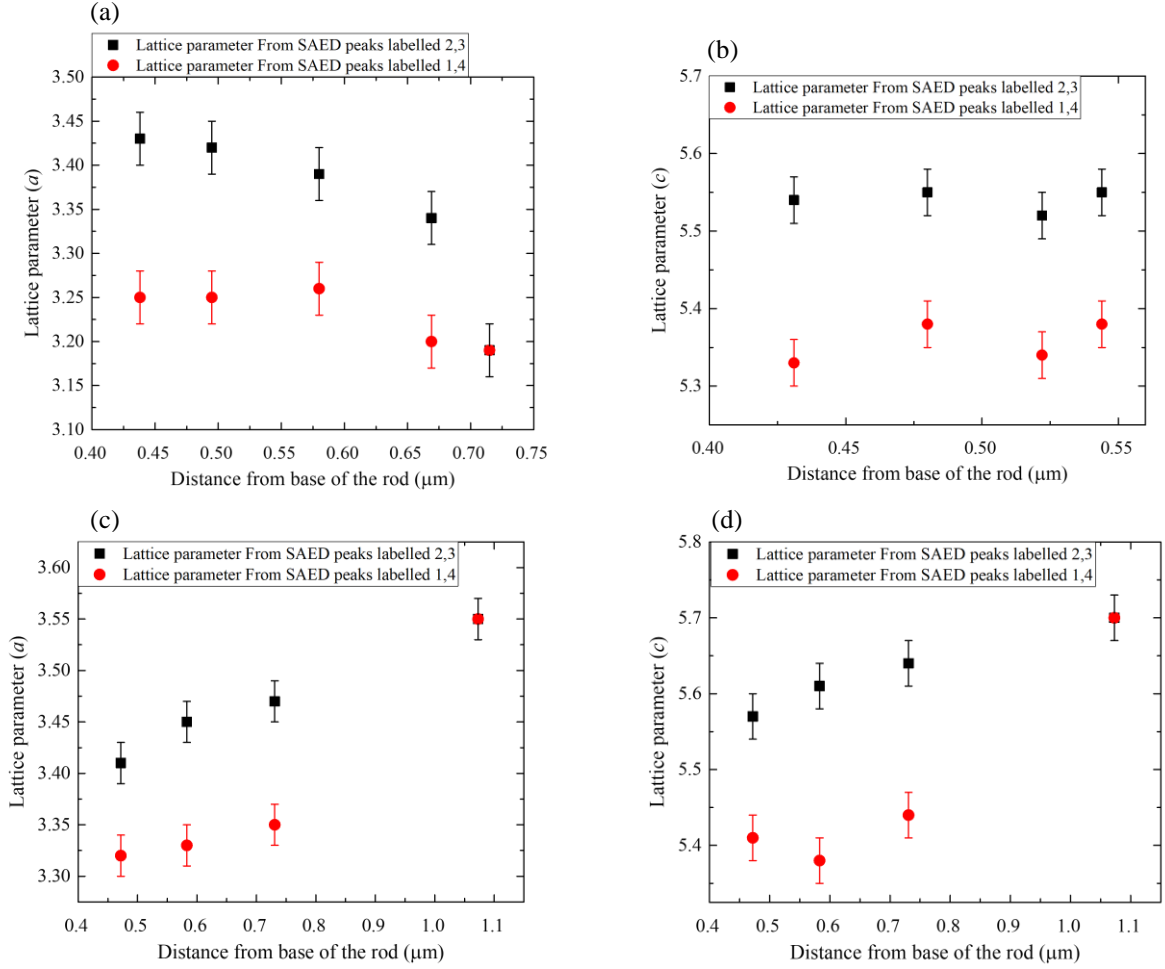


Figure 5: (a, b) Ga-rich graded sample and (c, d) In-rich graded sample: Lattice parameters calculated using (a, c) $[10\bar{1}0]$ and (b, d) $[0002]$ systematic rows reflections.

The inner spots specified by 2 and 3 in the intensity profiles in fig. 4 correspond to the In-rich (core) region and the outer spots (specified by 1 and 4) to the Ga-rich (shell) region. The lattice parameters generally decrease with growth for Ga-rich samples and increase with growth for In-rich samples consistent with the grading. We expect that the system will be fully relaxed if the estimated mismatch from Figure 5 is equal to the equilibrium lattice mismatch calculated for the core and shell compositions from the EDX data, and is partially relaxed when it is less than that [9], [10]. From Figure 5, the average lattice misfit between core and shell for the In-rich graded nanorods during the first 3 hours of growth was calculated to be $\sim 0.030 \pm 0.005$ along $[10\bar{1}0]$ and $[0002]$ directions and for Ga-rich graded nanorods it is about 0.05 ± 0.01 along $[10\bar{1}0]$ and 0.032 ± 0.006 along $[0002]$. The lattice mismatch is estimated from the measured compositions to be about 4% along both directions indicating fairly a complete strain relaxation along both $[10\bar{1}0]$ and $[0002]$ directions in the two graded samples.

Figure 6 shows a bright field image of an In-rich nanorod taken using JEOL 2010 TEM with $\{0002\}$ systematic row reflections operating. It shows periodic contrast features, as arrowed in the inset, which would be consistent with a set of edge dislocations at the core-shell interface that has a periodicity of 11-13 nm. If we assume these are edge dislocation loops lying in the shell around the core diameter with Burgers vector $b = c[0001]$, the spacing between the

dislocation cores corresponds to a misfit of $4\pm 1\%$, consistent with full relaxation of mismatch strain in the c-direction.

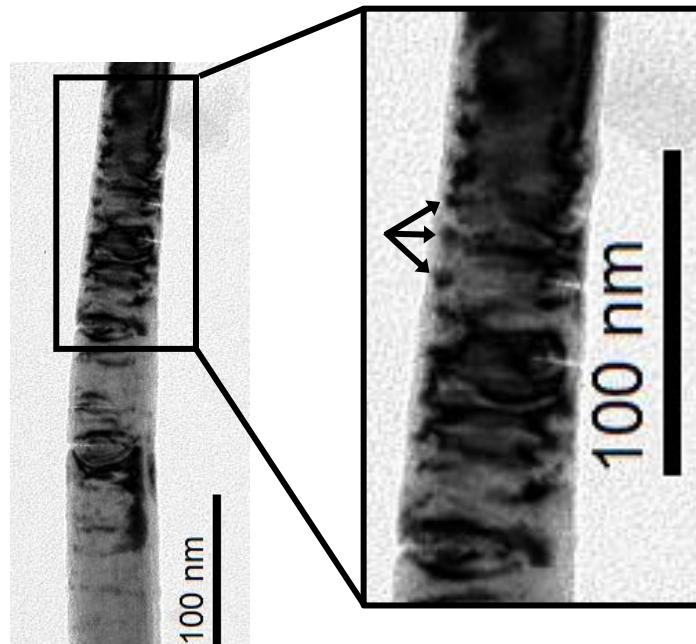


Figure 6: Bright field TEM images of an In-rich graded sample taken at $[0002]$ systematic row with a section magnified in the inset that shows dislocation cores and Moiré fringes.

The general contrast across the central region of the nanorod in Figure 6 is relatively complicated, but can be partially described as moiré fringes. These arise owing to the overlap of the misfitting core and shell lattices. The spacing of the Moiré fringes (D) can be related to the d-spacings of the two lattices [9], [10] through $D = \frac{d_1 d_2}{(d_1 - d_2)}$ where d_1 and d_2 refer to the main diffracting planes for the core and shell which are the (0002) planes. The spacing of Moiré fringes observed in this region is approximately $D=6.3$ nm, i.e. around half the dislocation spacing, giving a misfit of $4.4\pm 0.4\%$, consistent with the equilibrium misfit of $4.0\pm 0.5\%$ estimated earlier from the EDX data.

Misfit dislocations running parallel to the nanorod axis can be seen in plan-view cross sections. A high resolution HAADF image of an ungraded plan view sample of $x=0.5$ taken at the core-shell interface is shown in figure 7. The Bragg filtered image using $[10\bar{1}0]$ reflections shows that there are edge-on dislocations at the core-shell interface with a spacing of about 5 nm. These dislocations have Burgers vector $b = a[11\bar{2}0]$ as seen in the Burgers circuit. The spacing between the dislocation cores corresponds to 15 lattice planes that has a misfit of $6\pm 1\%$, which is comparable to the misfit of the relaxed lattice which is about 4%.

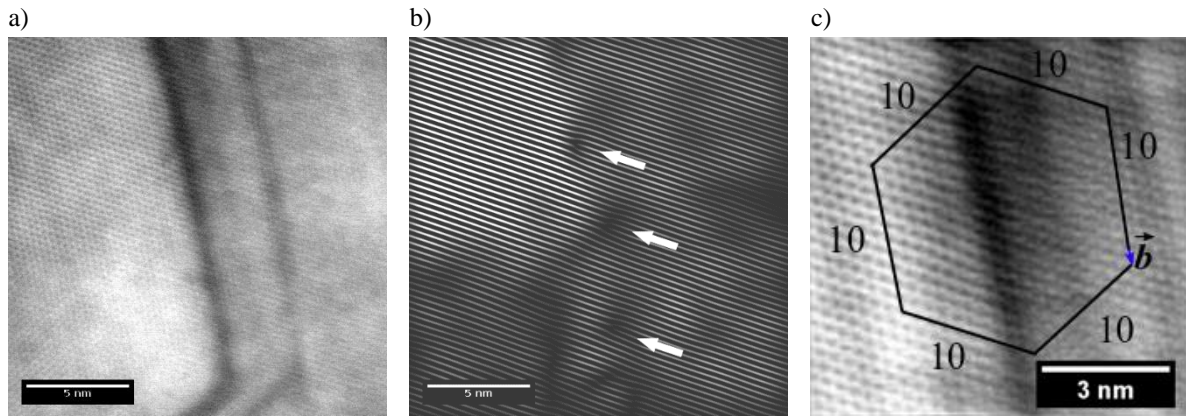


Figure 7: (a) HAADF image of a core-shell interface of a plan-view cross section, (b) Bragg filtered image of (a) using $g = 10\bar{1}0$ reflections and the edge dislocation cores are indicated by white arrows. (c) a Burgers circuit used to characterise the dislocation type and the blue arrow indicates the Burgers vector is to be $\langle 11\bar{2}0 \rangle$.

Thus the results in Figures 6 and 7 clearly show that the line and loop edge dislocations are formed to relieve the radial and axial strain in the nanorods due to the core-shell geometry.

IV. Conclusions

The $\text{In}_x\text{Ga}_{1-x}\text{N}$ graded samples which were grown by PA-MBE under N rich condition have nanorods with single crystalline hexagonal wurtzite structure grown along $[0001]$ direction. These nanorods intrinsically grow with core-shell structures with In-rich core and Ga-rich shell.

The entire range of composition of $x = 0 - 1$ has been achieved by grading and confirmed by the EDX analysis. The growth rates and the aspect ratio of the nanorods strongly depend on their composition. The In-rich sample demonstrates a higher axial growth rate with taller and tapering nanorods and the Ga-rich sample shows a higher radial growth rate with relatively larger diameters. From the measured growth rates, the results suggest strongly that the axial growth rate is controlled by the In flux and the radial growth rate by the Ga flux.

The core-shell structures are also manifested in the SAED patterns by the splitting of diffraction spots observed along both the $[0001]$ and $[10\bar{1}0]$ directions. The mismatches between the diffraction spots agree with the equilibrium lattice mismatches estimated from the measured core and shell compositions both in the radial and axial direction, suggesting a near-complete strain relaxation occurs in the nanorods. There is evidence for dislocations with Burgers vector $b = c[0001]$ present as loops surrounding the core and edge dislocations with Burgers vector $b = a \langle 11\bar{2}0 \rangle$ which run parallel to the nanorod axis but confined at the core-shell interface. These results also affirmed that the strain is mainly due to the core-shell geometry and not due to grading.

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