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Does In form In-rich clusters in InGaN quantum wells?

C J Humphreys*

Department of Materials Science and Metallurgy,

University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK

The reason the InGaN/GaN quantum well system emits intense light even though the dislocation density is high is assessed. First, the evidence from electron microscopy for nanometre-scale In-rich clusters in InGaN quantum wells is presented. Such clusters would localise the excitons away from the dislocations and hence the dislocations would not quench the light emission, consistent with observations. However, it is then shown that InGaN damages extremely rapidly under an electron beam, and that the damage causes In-rich clusters to form. No evidence is found of gross indium clustering at low beam currents and short exposure times in the electron microscope. However, at such low electron doses the image is noisy, and low-level indium clustering in InGaN quantum wells could possibly exist, but be masked by the noise. A different technique, 3-dimensional atom probe field ion microscopy, has therefore been used to image the InGaN quantum wells. This reveals that InGaN is a random alloy, with the local statistical fluctuations in indium content expected in a random alloy, but with no indium clustering. Since In-rich clusters are clearly not necessary for bright light emission from InGaN quantum wells, another mechanism must be responsible for the exciton localisation observed. It is shown that thickness fluctuations in the InGaN quantum wells of only one monolayer, observed in electron microscopy, result in an exciton confinement energy of 58 meV, sufficient to localise the carriers at room temperature. An alternative localisation mechanism due to randomly formed In-N-In chains proposed by others is discussed. It is concluded that In-rich clusters in InGaN quantum wells do not exist in the specimens we have studied, and in any case they are not necessary to localise the excitons and for bright light emission.

1. Introduction

A remarkable feature of InGaN/GaN quantum well LEDs is that they emit intense light, even though the dislocation density is typically 10^9cm^{-2}. In all other light-emitting semiconductors the light emission is quenched if the dislocation density exceeds about 10^3cm^{-2}. Yet InGaN quantum wells emit strong blue and green light (depending on the In concentration) when the dislocation density is one million times higher than that in other light-emitting

* email: colin.humphreys@msm.cam.ac.uk

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semiconductors, even though it is known that dislocations in InGaN are non-radiative recombination centres.

The widely-believed solution to the above problem, up to a few years ago, was that InGaN was an unstable alloy and the In in the InGaN quantum wells formed In-rich clusters. Since the band-gap of InN is less than that of GaN, the bandgap of these In-rich clusters is reduced, and hence the electrons and holes are spatially localised in these clusters. At room temperature (and below) in InGaN, an electron and hole form a bound exciton, hence the In-rich clusters localise the excitons. The clusters were believed to be small, on a nanometre scale. Statistically, most threading dislocations would not pass through these nanometre-scale In-rich clusters, even for a dislocation density of $10^9 cm^{-2}$ at which the average dislocation spacing is about 300 nm. Hence it was almost universally believed that the In-rich clusters localised the excitons away from most of the dislocations so that they did not quench the light emission. Thus it was believed that the intense light emission observed from InGaN quantum wells with a high dislocation density was due to In-rich clusters.

In this paper we first present evidence to support this argument. We then show that In-rich clusters are produced in InGaN in the electron microscope due to electron beam damage. However, careful low-dose electron microscopy reveals no gross In clustering, but it cannot rule out small In fluctuations. We then report that three-dimensional atom probe analysis of InGaN quantum wells yields that InGaN is a random alloy, with no In fluctuations other than would be expected of any random alloy. This is consistent with our electron microscopy results. Finally, we return to the question of why InGaN emits intense light despite having a high dislocation density.

2. The evidence for exciton localisation in InGaN

There is clear evidence that, at low temperature, the dominant emission from InGaN/GaN quantum-well structures involves the recombination of strongly localised excitons (see, for example [1-3]). Graham *et al.*[3] studied the low temperature (T = 6 K) optical properties of a series of $In_xGa_{1-x}N$/GaN single-quantum-well structures where the indium fraction x varied from sample to sample over the range 0.05 – 0.25. The structures were grown by Metal Organic Vapour Phase Epitaxy (MOVPE), and the InGaN quantum well was 2.5 nm thick. By comparing the strengths of the phonon-accompanied recombination with those obtained from a theoretical model, the spatial extent of the carrier wavefunctions in the plane of the quantum well was estimated. This localisation length was found to range from 1 nm for the InGaN quantum well containing 25% indium, to 3 nm for the 5% indium alloy. Thus the

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exciton localisation length in the plane of the quantum well is typically about 2 nm. The key question is what causes this localisation.

3. The case for gross In-rich clusters in InGaN

3.1 Thermodynamics

It has long been recognised that InGaN epilayers could separate into indium-rich and indium-poor phases during prolonged annealing [4]. Thermodynamic calculations then showed that there is a miscibility gap in the $In_xGa_{1-x}N$ system and that for typical compositions (x~0.1 for blue emission, x~0.2 for green) and typical InGaN growth temperatures (600-800 deg C) the unstrained homogeneous alloy is unstable, leading to decomposition into In-rich and In-poor regions [5]. It is not clear how applicable these equilibrium thermodynamic calculations are to the InGaN layers grown by MOVPE or Molecular Beam Epitaxy (MBE)(see later), but Ponce *et al.*[6] have reported phase separation in MOVPE grown thick (200 nm) epilayers of InGaN with In fractions of 0.1 and above.

3.2 The evidence from electron microscopy for indium-rich clusters

Bright-field transmission electron microscopy (TEM) images of InGaN/GaN quantum well structures were reported to show dark dot-like features with a size of about 3 nm in the InGaN quantum wells [7,8]. Since an indium atom is much larger than a gallium atom, fluctuations in InGaN compositions will cause variations in lattice strain and hence strain contrast in TEM images. The dot-like features were therefore attributed to strain contrast. Energy-dispersive X-ray analysis in the TEM suggested a correlation between the dark spots and higher indium content [8]. This was confirmed by Cho *et al.*[9] who used energy-filtered transmission electron microscopy (EFTEM) to analyse the regions of strain contrast observed in InGaN quantum wells. EFTEM images clearly revealed these strained regions to be indium-rich clusters with a size of 2-3 nm.

A popular method for studying these indium-rich clusters has been lattice parameter mapping. In this technique, high-resolution TEM lattice images are taken of InGaN/GaN quantum well structures. The indium-rich clusters give rise to localised strain, and by measuring the local lattice fringe spacings a two-dimensional lattice parameter map can be plotted, which shows the size of the indium-rich clusters to be typically a few nm. Strains of the order of 10% are found in these clusters. By using Vegard's law, the lattice parameter map can be converted to a composition map. For InGaN quantum wells grown with 10-20% indium, the indium-rich clusters are typically found to contain at least 80% indium [10-13], although the projection problem in TEM makes it difficult to quantify the indium content. We will call such clusters

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"gross indium-rich clusters". It was reported that such gross indium-rich clusters may, in fact, be pure InN [11], and pure InN regions with a 1-3 nm size were reported in InGaN quantum wells grown by both MOVPE and MBE, as measured using high resolution TEM lattice parameter mapping of samples with mean composition of 16% In in the InGaN quantum wells [14].

3.3 The argument for gross In-rich clusters

The argument for gross indium clustering in InGaN quantum wells appears to be strong. We know from optical measurements that the excitons in InGaN are localised on a 1-3 nm scale. Thermodynamic calculations show that InGaN is unstable and should decompose into In-rich and In-poor regions. TEM shows gross In-rich clusters in InGaN quantum wells on a nanometre scale, similar to the scale on which the excitons are localised.

Because of the apparently strong and convincing arguments given above, many hundreds of papers have been published stating that InGaN quantum wells contain gross In-rich clusters, and that these clusters are responsible for the exciton localisation. The Cambridge GaN research group has observed such clusters in the TEM many times, and indeed they are among the authors of a paper demonstrating that those clusters are indium-rich [9]. However, this work necessarily used high electron doses for the EFTEM images which revealed the In-rich clusters. We will now demonstrate that in the wide range of InGaN materials we have examined, such gross indium-rich clusters do not exist, and they are produced by electron beam damage in the TEM.

4 The effect of electron beam damage on InGaN in the TEM

4.1 Growth and sample preparation

InGaN/GaN quantum well structures were grown by MOVPE in a Thomas Swan 6x2 inch close coupled showerhead reactor. Trimethyl gallium, trimethyl indium and ammonia were used as precursors, and hydrogen and nitrogen as carrier gases. Thin GaN nucleation layers were established at 530 deg C on c-plane sapphire substrates prior to growth of GaN epilayers at 1030 deg C with nominal thickness of 2 μm. $In_xGa_{1-x}N$ wells and GaN barriers, all having the hexagonal crystal structure, were grown on these epilayers without growth interrupts and at a single temperature. The single quantum well (SQW) with a composition of $In_{0.22}Ga_{0.78}N$ in figures 1 and 2 was grown at a nominal temperature of 710 deg C and had a well thickness of 3.0nm. The SQW with a composition of $In_{0.18}Ga_{0.82}N$ in figure 2 was grown at a nominal temperature of 730 deg C. The quantum well thicknesses were measured using high

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resolution TEM, and the compositions measured using X-ray reflectivity and high resolution X-ray diffraction as described elsewhere [15,16].

Wedge-shaped cross-sectional TEM specimens were prepared by tripod polishing on diamond lapping mats. Using a wedge angle of ~3 deg, the InGaN/GaN at the thin end was reduced to electron transparency. To remove surface damage associated with mechanical polishing, the samples were ion milled for a few minutes (Gatan PIPS; Ar+ ions) at 3.2 keV with ion guns at angles of 4 deg relative to each of the wedge surfaces. This ion polishing was performed under "single modulation" (each ion gun active for about 3 out of every 10 seconds) to minimise any heating of the sample.

4.2 Transmission electron microscopy

We have found that InGaN quantum wells damage extremely rapidly in the electron beam of a TEM at the beam currents normally used for imaging. The damage causes indium-rich clusters to form. Figure 1 shows (0002) lattice fringe images of an $In_{0.22}Ga_{0.78}N$ quantum well using high-resolution TEM(HRTEM). The lattice fringe images were obtained with the specimen tilted about 6-7 deg away from a $<11\bar{2}0>$ axis towards the adjacent $<10\bar{1}0>$ pole. At this orientation a systematic row of reflections are excited with (0002) and $(000\bar{2})$ under equal excitation. The images in figures 1 and 2 were recorded using 400 keV incident electrons in a JEOL4000EX. Figure 1a was recorded within 20 seconds of first exposing this part of the quantum well to the electron beam, figure 1b is the same area after a few minutes of exposure. We have analysed these images to produce lattice parameter maps [16,17] using a process similar to the DALI technique [11]. After only a few minutes exposure to the electron beam we found nanometre-size indium clusters formed which caused local strains of up to 10%, corresponding to an indium fraction x of 60%. These cluster sizes, strains and compositions are typical of those found by others using TEM (for example [10,11]). However, we have found no evidence at all of gross indium clustering if low electron beam currents are used. At low electron dose, the lattice fringe image of the quantum well and the lattice parameter map are both reasonably uniform (figure 1a, 1c), [16,17]. We have studied the effect of 200, 300, and 400 keV incident electrons. For the 200 keV electrons we used a FEI Tecnai F20-G2. We reduced the electron beam current substantially below the maximum available, so that the current density incident on the sample was $35 Acm^{-2}$. Electron beam damage of the InGaN QWs was already strong after less than 30 seconds of exposure to 200 keV electrons at this current density.

Insert Fig.1

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Since publishing the Smeeton *et al.* [16,17] papers it has been suggested to us that our results may apply only to InGaN grown on MOVPE equipment at Cambridge, or may be related to our TEM specimen preparation procedures, rather than being a general effect. We have therefore purchased a very bright blue commercial LED and examined the InGaN quantum wells it contains by TEM. Again, we found no evidence of gross indium clustering at low electron beam currents and short exposure times in the TEM. However, as the electron dose increased, indium-rich clusters formed, just as in the Cambridge grown samples [18]. O'Neill *et al.* [19] also reported that In-rich clusters formed as a result of electron beam damage in their specimens. We also prepared TEM specimens using only mechanical polishing instead of using a combination of mechanical polishing followed by ion beam thinning. We observed no differences in the behaviour of both specimens in the TEM, suggesting that the susceptibility of InGaN to electron beam damage is intrinsic to the InGaN/GaN system and not a consequence of our ion milling procedures [18]. We have also studied MBE grown InGaN/GaN structures. In *all* the samples we have studied, we observe no gross indium clustering in the TEM at low beam currents and short exposure times. Indium-rich clusters *only* appear at higher electron doses.

5. Does TEM give any evidence for genuine In clustering?

Slight fluctuations in the TEM image contrast of InGaN quantum wells can be observed in low-dose images. This could be due to genuine low-level compositional fluctuations or to the noise which is inherently present in low-dose images. In addition, the initial stages of damage may already have occurred in low-dose images, since significant radiation damage can occur in orienting the specimen in the electron microscope before recording the image. Hence even the lowest dose images should not be treated as a faithful representation of the original specimen.

We have analysed the fluctuation in lattice parameter in lattice parameter maps of low-dose high-resolution TEM images of InGaN quantum wells of various compositions. A typical result is that for an $In_xG_{1-x}N$ quantum well with x = 0.18, as measured by X-ray reflectivity and high-resolution X-ray diffraction. In our low-dose lattice parameter maps (figure 2) the maximum measured fluctuation in the strain (defined as d(InGaN)/d(GaN) for the 0002 lattice fringes) is ±0.01. This could be due to noise or it could correspond to a maximum fluctuation in indium content x of ±0.06, using Vegard's law. Hence, an $In_xGa_{1-x}N$ alloy with x=0.18 has possible indium fluctuations in the range 0.12 to 0.24, averaged through the specimen because of the projection problem.

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Insert Fig.2

The noise in our low-dose lattice parameter maps is at a similar level to the fluctuations observed above. We therefore conclude that small-scale indium fluctuations may genuinely exist in InGaN quantum wells, but be masked by the noise in our TEM images. We note that these compositional fluctuations, if they do exist, are significantly smaller than the gross fluctuations reported in the literature.

In the light of the Smeeton *et al.* [16,17] papers, which suggested that the gross indium-rich clusters in InGaN quantum wells reported by many researchers might be due to electron beam damage, the Gerthsen group revised their earlier conclusions [11,12]. They observed that the indium concentration in the clusters increased with increasing irradiation time in the electron microscope. However, because they found In-rich clusters already in their first HRTEM images taken after only 20s of exposure to the electron beam they concluded that In-rich clusters genuinely existed in their InGaN quantum wells, but that the In concentration was significantly lower than they had previous stated [20].

The Kisielowski group has recently made detailed studies of indium clustering in InGaN, following their earlier work [10]. They claim that InGaN quantum wells can be imaged in HRTEM with negligible electron beam damage and that indium-rich clusters genuinely exist [21]. They have found that no measurable alteration of the initial element distribution occurs for electron irradiation times of up to 2 minutes and current densities of 20-40 Acm^{-2} [22]. They report that green $In_xGa_{1-x}N$ quantum wells (with average indium fraction x about 0.2) have genuine indium-rich clusters, 1-3 nm wide with In content up to 0.40 [23]. This disagrees with our findings reported above (see figure 2).

A key question is whether the electron micrographs carefully recorded and reported in the above papers [20-23] are, in fact, damage free. Electron-beam damage of inorganic materials in an electron microscope can be a complex process and the damage mechanism for strained thin layers of InGaN is not yet known. In some inorganic materials, there appears to be a threshold electron beam current density for damage to occur, below which there appears to be little or no damage [24,25]. If InGaN behaves in this way then Gerthsen and Kisielowski may be correct that damage-free electron micrographs of this material can be recorded. However, for other inorganic materials there appears to be no lower threshold electron beam current density for damage, which can also occur for incident electron energies as low as 40 keV [26].

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If InGaN behaves in this way then damage-free microscopy is impossible. Until more is known about the mechanism(s) by which strained thin layers of InGaN damage, we cannot be sure that it is possible to record high resolution electron micrographs in which the damage is negligible.

6. 3-D Atom Probe studies of indium clustering

Our low-dose TEM studies have revealed that gross indium clustering does not exist in the many InGaN quantum wells we have studied. However, we cannot rule out lower level indium clustering for the reasons given above, namely the fact that such genuine clustering, if it exists, may be masked by the noise in low-dose images, and genuine clusters cannot be distinguished from indium-rich clusters already created by the electron beam in even low-dose images. In addition, since the electron-beam damage mechanism in strained layers of InGaN is not yet known, we do not know if it is possible to record damage-free electron micrographs of this material. In order to assess whether low-level indium clustering genuinely exists we therefore need a different technique from electron microscopy. The method should not involve exposure to high-energy electrons, and it should preferably provide direct information, at the atomic level, of the distribution of indium in InGaN quantum wells. In addition, the technique should preferably avoid the projection problem in TEM.

It is well known that the three-dimensional atom probe (3DAP) can provide nanometre-scale information about composition variations in a variety of materials [27]. We have recently applied this technique to InGaN quantum wells. The InGaN/GaN multiple quantum well (MQW) sample used was grown by MOVPE under similar conditions to the samples used for TEM described above, except that approximately 6 μm of GaN was grown on c-plane sapphire at 1020 deg C, following deposition of a 30 nm GaN buffer at 540 deg C. The QWs and barriers were grown at a single temperature of 740 deg C. High resolution X-ray diffraction gave the thickness of the $In_xGa_{1-x}N$ layers as 2.38 ±0.10 nm, and the indium fraction x=0.18. Room temperature PL showed bright blue emission at 454 nm.

Needle-shaped 3DAP specimens were prepared in a FEI Dualbeam Quanta FIB/SEM. All SEM imaging was performed at 5 kV and exposure times and currents were minimised in order to limit the risk of damage to the InGaN quantum wells. The 3DAP images were obtained using an Oxford nanoScience instrument fitted with a prototype laser module.

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Figure 3 shows reconstructions of the InGaN/GaN structure with the indium and gallium atoms displayed. Four indium-containing quantum wells are clearly visible, and we have analysed in detail the indium distribution in the bottom three of these since the top well may have been damaged by sample preparation. We have compared the indium distribution with the expected distribution from a random alloy. No significant deviations were found from that expected in a random alloy for all three of the quantum wells (for further details see [28]). We therefore conclude that there is no evidence of indium clustering in this sample.

Insert Fig.3

Two independent direct imaging techniques, TEM and 3DAP, have therefore found no evidence for indium clustering in InGaN quantum wells. The 3DAP results indicate that the distribution of In in the InGaN sample studied is that of a random alloy. Local compositional fluctuations statistically exist of course in a random alloy, but there is no atomic clustering.

7. Localisation Mechanisms

The evidence for exciton localisation on a nanometre scale in InGaN quantum wells is strong (see Section 2). This is consistent with InGaN quantum well structures emitting intense light with high quantum efficiency, despite having a high dislocation density. In this section we discuss possible mechanisms for the carrier localisation, having ruled out gross indium clustering.

7.1 Quantum well thickness fluctuations

At low temperature, excitons are known to be localised in GaAs/AlGaAs quantum wells by well-width fluctuations. The localisation energy is typically only a few meV, and so localisation by this mechanism only occurs at low temperature in GaAs/AlGaAs [29]. However, the localising effects of well-width fluctuations are much greater in the InGaN/GaN quantum-well system, both because the InGaN is more highly strained and because the piezoelectric effect is much stronger than in GaAs/AlGaAs.

High-resolution electron micrographs show that in the InGaN/GaN quantum well system, the lower quantum well interface appears to be atomically abrupt, whereas the upper interface is atomically rough [3]. The in-plane extent of these well-width fluctuations is small, typically 1-2 nm. The thickness variation is typically one monolayer (= 0.259 nm). Calculations show that for an InGaN/GaN quantum well system with an indium fraction of 0.25, and well widths of 3.3 nm and 3.3 nm + 1 monolayer, the quantum well bandgap for the n = 1 electron and

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hole confined states decreases by 58 meV. Since kT at room temperature is 25 meV, a monolayer change in quantum well thickness, consistent with electron micrographs, is sufficient to localise the carriers [3].

7.2 In-localised hole wave functions

Bellaiche *et al*. [30] have suggested from theoretical calculations of cubic InGaN that even for a perfectly homogeneous InGaN material the carriers could be localised. The calculations predict localisation of the hole wave functions around In in InGaN along randomly formed In-N-In chains. Hole localisation leads to exciton localisation because of the small effective Bohr radius of excitons in GaN (= 3.4 nm). Chichibu *et al.* [31] have recently explained their positron annihilation results in InGaN in terms of such In-N-In chains. Unfortunately there is no theoretical calculation of the carrier localisation energy due to In-N-In chains in a random hexagonal InGaN alloy.

8. Thermodynamics of strained InGaN

The thermodynamic calculations reported earlier [5] which predicted the decomposition of InGaN were for bulk material. However Karpov [32] has calculated the phase diagram for an InGaN layer epitaxially matched to a GaN layer, which puts the InGaN into biaxial compression. The effect of the strain is to stabilise the InGaN, and no decomposition is predicted for normal growth conditions.

Electron microscopy of the InGaN quantum wells we have studied in this paper reveals no misfit dislocations. We are aware that the measured critical thickness for the introduction of misfit dislocations depends on the resolution of the experimental technique used to detect the dislocations [33] and that electron microscopy, because of the limited volume of specimen sampled, may over-estimate the critical thickness. However, electron microscopy indicates that, at least locally, our InGaN quantum wells are fully strained, and this is confirmed by our X-ray diffraction measurements.

Hence we would not expect indium-rich clusters to form in our strained InGaN quantum wells, and this is precisely what our TEM and 3DAP results reveal.

9. Conclusions

1. Low-dose TEM shows no evidence of gross indium clusters in InGaN quantum wells.
2. 3DAP shows that InGaN is a homogeneous random alloy, consistent with TEM results and with thermodynamic calculations that take strain into account.

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3. Indium-rich clusters in InGaN are not necessary to localise the excitons. Excitons can be localised by atomic scale well-width fluctuations and by In atoms in In-N-In chains forming statistically in a homogeneous InGaN alloy.
4. Calculated localisation energies at In atoms in In-N-In chains in hexagonal InGaN are not yet available. However, the localisation energy provided by a monolayer well-width fluctuation of an InGaN quantum well is about 60 meV, sufficient to localise excitons at room temperature.
5. We therefore have a consistent story that in the InGaN/GaN quantum-well system, the InGaN is a random alloy. Localisation of the excitons may be due to monolayer thickness variations of the quantum wells, which TEM shows occur on a 1-2 nm in-plane length scale, consistent with the PL evidence of the in-plane localisation length of the excitons of 1-2 nm. The 60 meV localisation energy strongly localises the excitons at room temperature. Additionally, excitons may be localised around In atoms in InGaN, but the localisation energy for this in hexagonal InGaN is not yet known.

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Figure Captions

Figure 1. A pair of HRTEM lattice fringe images demonstrating the electron-beam induced damage to an $In_{0.22}Ga_{0.78}N$ quantum well. The (0002) lattice fringe images were obtained using a JEOL 4000 EX operating at 400kV. (a) shows the image after minimal exposure to the beam, and (b) the same region after only a few minutes of exposure. (c) is a lattice parameter map of (a), and (d) is a lattice parameter map of (b).

Figure 2. Lattice parameter maps of two different $In_xGa_{1-x}N$ quantum wells, with x = 0.18 and 0.22, taken from HRTEM (0002) lattice fringe images using a low electron dose. Note that the colour scale is different here from that used in figure 1. Any possible In fluctuations are of a similar magnitude to the noise in the lattice parameter maps and significantly smaller than those usually reported in the literature for InGaN quantum wells.

Figure 3. Three-dimensional Atom Probe Field Ion Microscope (3DAP) image of InGaN/GaN multi quantum wells. Each dot represents a single atom: light blue is gallium and orange is indium. Statistical analysis shows that the indium distribution is as expected in a random alloy.

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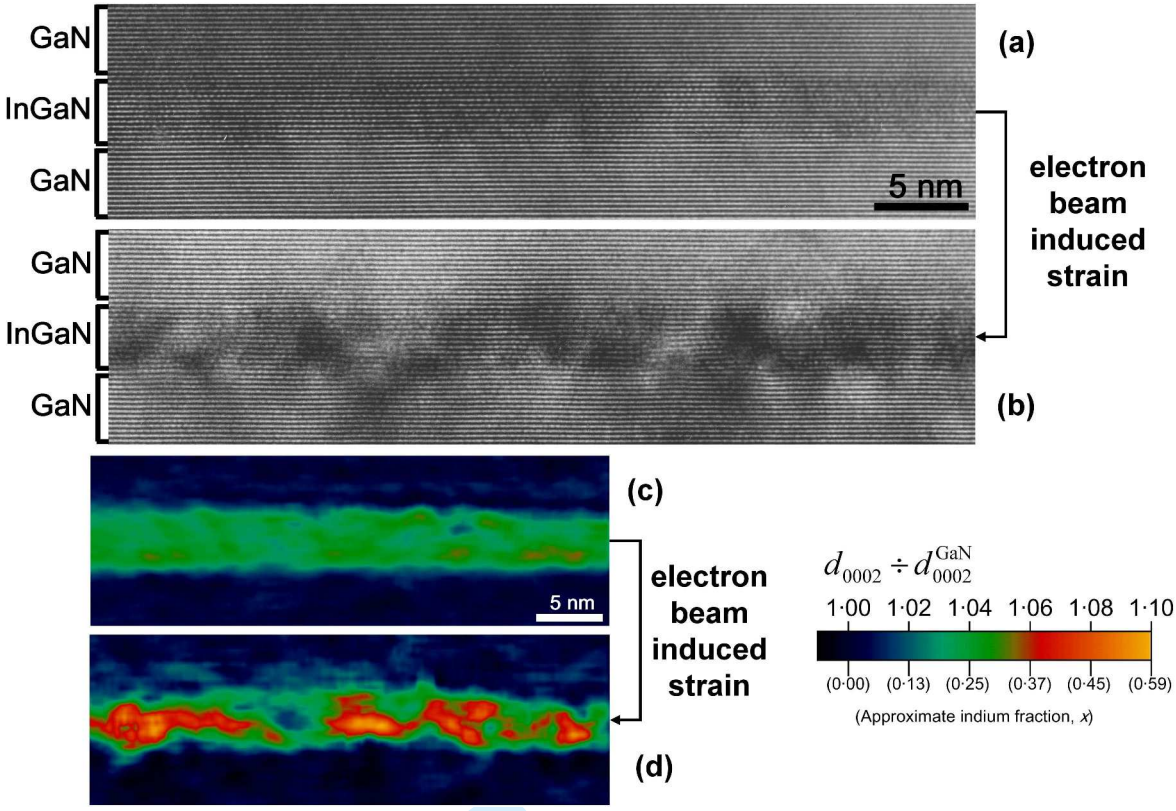

Figure 1

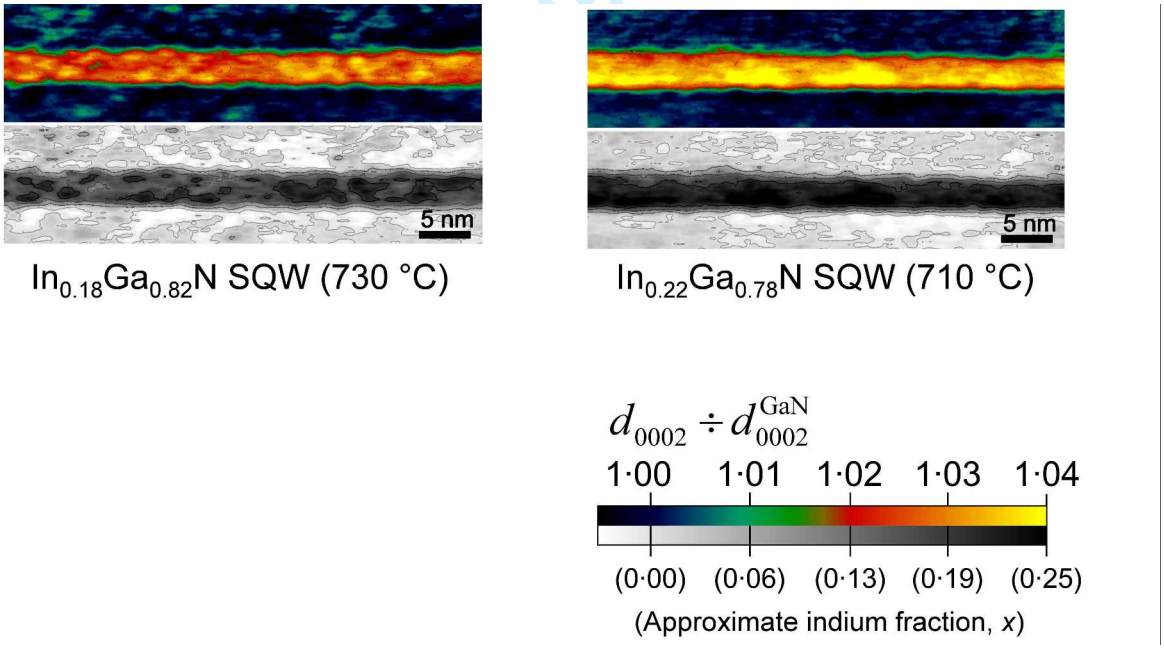

Figure 2

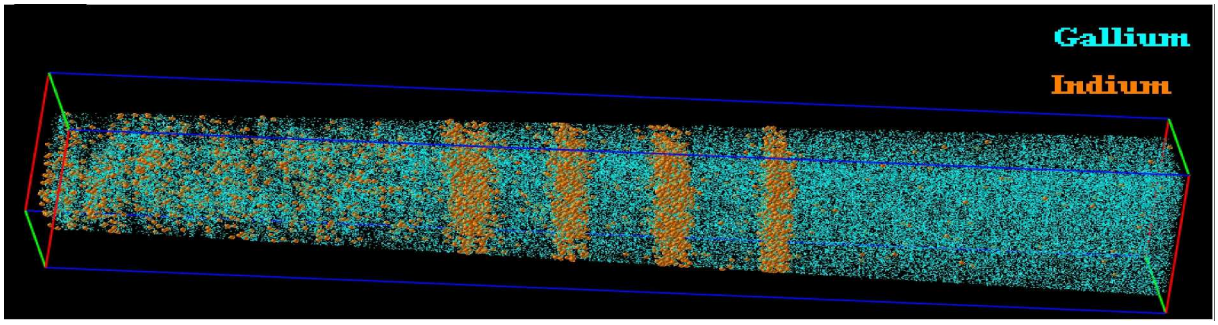

Figure 3

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