Structure and composition of non-polar (11-20) InGaN nano-rings grown by Modified Droplet Epitaxy

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Droplets grown by modified droplet epitaxy on non-polar (11-20) surfaces of InGaN epilayers on GaN have been associated with underlying ring-like structures. This work discusses droplet etching as a possible mechanism for ring formation, and droplet creeping as a possible explanation for the droplets sitting askew of the ring centre. Transmission electron microscopy (TEM) analysis shows the droplets to move along the <0001> *c*-axis, and indicates that they have a very high In content.
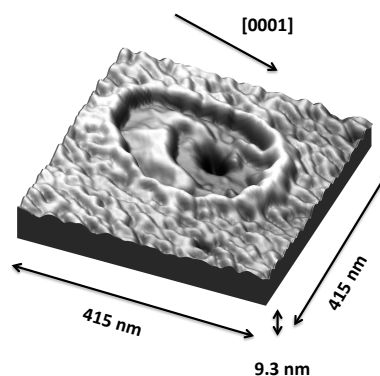
Atomic Force Microscopy (AFM) data of double-ring structure, rendered in 3D.

1 Introduction

Nitride-based quantum dots (QDs) show promise as sources for single photon emission, enabling comparably high temperature emission [1] and access to the blue and green spectral region [2]. The wurtzite structure of gallium nitride (GaN) results in significant electric fields across strained QDs grown in the *c*-plane orientation due to the very large piezoelectric constants. This reduces the radiative recombination efficiency due to the spatial separation of the electron and hole via the quantum confined Stark effect (QCSE). Thus, non-polar structures are of interest as this internal electric field can be largely reduced, as has been demonstrated by Zhu *et al.* [3].

Modified Droplet Epitaxy (MDE) is a QD growth technique in which an InGaN epilayer is made to undergo partial decomposition, resulting in the formation of nanoscale surface metallic droplets. Subsequent GaN overgrowth has been shown to result in the formation of QDs [4]. When performed on non-polar (11-20) planes of InGaN/GaN systems, a bimodal distribution of droplets has been observed in some samples [5]. The smaller droplets

are typical of MDE growth on the *c*-plane [4], and it is our understanding that these evolve into QDs upon capping. However, Atomic Force Microscopy (AFM) data reveals the presence of larger droplets and associated ring structures. These are under investigation to ascertain how they relate to the QD formation process, and also how they themselves might be exploited as confinement centres.

2 Experimental Methods

2.1 Growth

Samples were grown by Metal Organic Vapour Phase Epitaxy (MOVPE) in a 6 × 2 in. Thomas Swan close-coupled showerhead reactor on *r*-plane (1-102) sapphire substrates. Initially, a 30 nm GaN nucleation layer was grown at 500 °C and 500 Torr, followed by a 1 μm buffer layer grown at 1050 °C, using a V/III ratio of approximately 60. After a discontinuous SiN_x layer was formed by passing 90 standard cubic metres per minute (sccm) of SiH_4 for 600 s, a three dimensional growth step was carried

out at a pressure of 300 Torr using a V/III ratio of 1900, and then followed by a 2D growth with a V/III ratio of 60 at 100 Torr. This resulted in an approximate threading dislocation density of 3 x 10^8 cm^{-2} and basal stacking fault density of 2.6 x 10^5 cm^{-2} [5]. The InGaN epilayer was grown at 695 °C and 300 Torr using trimethylgallium, trimethylindium and ammonia as precursors, and N_2 as the carrier gas. InGaN epilayer deposition was carried out for 120 s, resulting in a thickness of 10 monolayers (ML). The flow of ammonia was reduced down to 500 sccm for 60 s. This is known as the ramp stage, and is intended to achieve a smooth transition to the stage in the absence of ammonia. The samples were immediately annealed in an N_2 atmosphere at the same temperature and pressure to achieve partial decomposition of the epilayer, resulting in the formation of metallic droplets. (Capping of the droplet in order to form QDs can be carried out at 695 °C to deposit 10 nm of GaN using N_2 as the carrier gas. Further GaN is deposited at 1050 °C using H_2 as the carrier gas.)
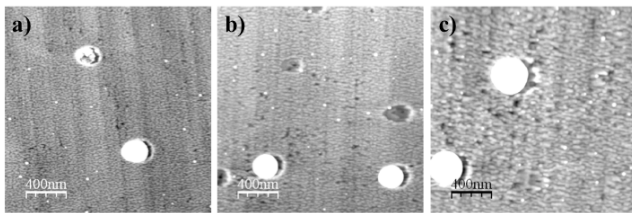
3 Results

3.1 Atomic Force Microscopy

Figure 1 AFM images of uncapped surfaces of the epilayers, after an anneal time of a) 15, b) 30, and c) 60 seconds, data height 10 nm. Small droplets can be observed, as is typical of MDE growth, and large droplets can be seen to be associated with ring structures. Some ring structures are observed to be no longer associated with a droplet; is it not clear why this is the case.

Figure 1 shows Atomic Force Microscopy (AFM) images of InGaN epilayer samples after anneal times of 15, 30 and 60 seconds. Firstly, it can be observed that a bimodal droplet size distribution has evolved. The smaller droplets (typically of the order of 30 nm in width and 7 nm in height) are characteristic of MDE and are also present after *c*-plane MDE growth. It is our understanding that these smaller droplets form QDs upon capping, supported by a correlation of the density of such droplets measured by AFM, and the density of bright Cathodoluminescence (CL) features in the Scanning Electron Microscope (SEM) [3]. More unusually, larger droplets are also present, typically 250 – 500 nm in width, and 60 – 100 nm in height depending on the anneal time. These sit in a skewed position atop underlying ring structures. This skewing appears to occur in a consistent direction for all samples studied. Not all the ring structures are observed to be associated with a remaining droplet, implying the droplet has been lost in some

manner. The mechanism by which this occurs is not yet understood. The surface roughness of the surrounding epilayer film is also perceived to increase with increasing anneal time. The RMS roughness has been measured as 0.71 ± 0.03 nm, 0.75 ± 0.06 and 1.17 ± 0.08 nm for samples annealed for 15, 30 and 60 s, respectively.

The skewed droplet position was confirmed to be inherent in the growth stage, rather than a result of the AFM measurement. This was achieved by performing a downward scan, imposing an offset, and then performing an upward scan. The position of the droplet with respect to the ring was unchanged.
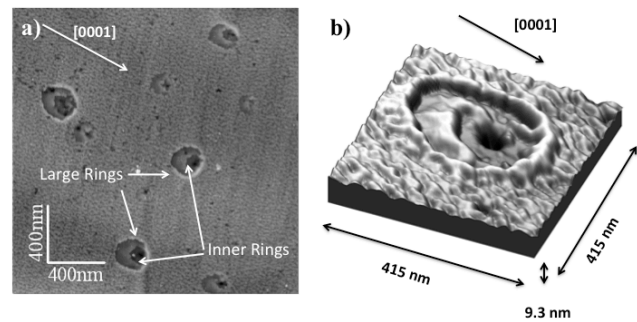

Figure 2 AFM a) image of etched epilayers, data height 9.3 nm, and b) one ring rendered in 3D. The double-ring structure can be observed.

AFM was carried out after etching in 16 % HCl for 1 minute, as shown in Figure 2. The droplets can be seen to have been removed during the etching process, which indicates they are metallic in nature, as expected. However, not only do we now see the larger rings more clearly, but we can observe that smaller, inner ring structures lie within the larger ones. These also lie in an off-centre position within the larger rings, but in an anti-parallel direction to the droplet position. Furthermore, it was found that the rings are formed of discrete hillocks, rather than a single continuous toroid. This may indicate that the individual hillocks should act as QDs themselves.
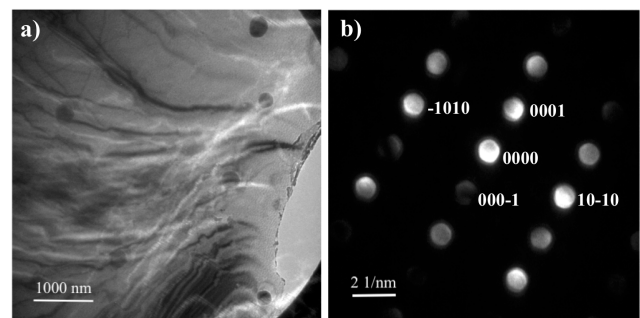
3.2 Transmission Electron Microscopy

Figure 3 a) Ronchigram and b) CBED pattern measured in an FEI Tecnai F20 FEGTEM. This proves the movement of the

droplets to be along the c-axis, and is tentatively used to assign the movement to the [000-1] direction.

Convergent Beam Electron Diffraction (CBED) analysis was carried out in an FEI Tecnai F20 FEGTEM in order to ascertain in which direction the droplets sit askew. The defocussed Ronchigram can be seen in Figure 3 a) and the corresponding diffraction pattern in Figure 3 b). As can be seen from the indexed diffraction pattern, the offsets of the inner ring and droplet with regards to the large rings are along the *c*-axis. Upon comparison with simulated Ronchigrams in a manner analogous to Ponce *et al.* [6], it is tentatively suggested that the droplet sits in a position displaced in the [000-1] direction from the centre of the outer ring.
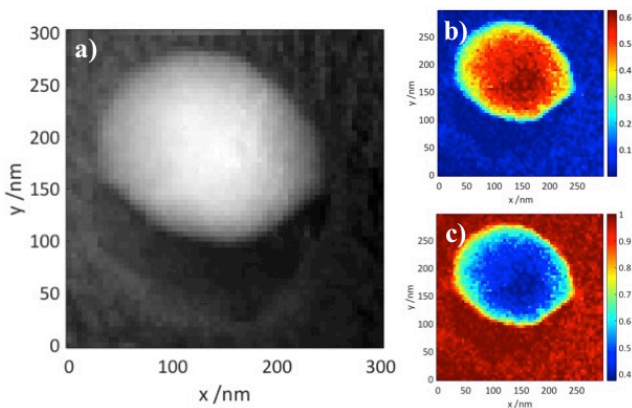

Figure 4 a) HAADF-STEM, and EDX analysis of a droplet, taken with an FEI Tecnai Osiris FEGTEM. The EDXS analysis shows the atomic percentage of b) Indium, and c) Gallium. This indicates a very high In content.

A sample which had undergone a 15 s anneal was investigated in an FEI Tecnai Osiris FEGTEM as a plan-view sample in STEM, and compositional analysis carried out via EDX. Figure 4 shows the High-Angle Annular Dark-field Scanning Transmission Microscopy (HAADF-STEM) image of a droplet and corresponding In and Ga atomic percentages, as determined by Energy Dispersive X-ray Spectroscopy (EDXS) analysis. As expected, the In content is greater within the droplet. It should be noted that as the X-ray count is averaged through the thickness of the TEM foil and therefore includes the count from the underlying GaN film: this has the effect of underestimating the In percentage for the droplet. Figure 5 shows the HAADF-STEM image of a ring without a droplet from the same TEM foil, and the corresponding EDX analysis of the atomic In and Ga percentages.

Due to the noise in the data, it is difficult to make definitive conclusions, but it would appear that no marked difference in the composition of the ring could be observed compared to the surrounding film. CL studies at room temperature indicate that the wavelength of emission from
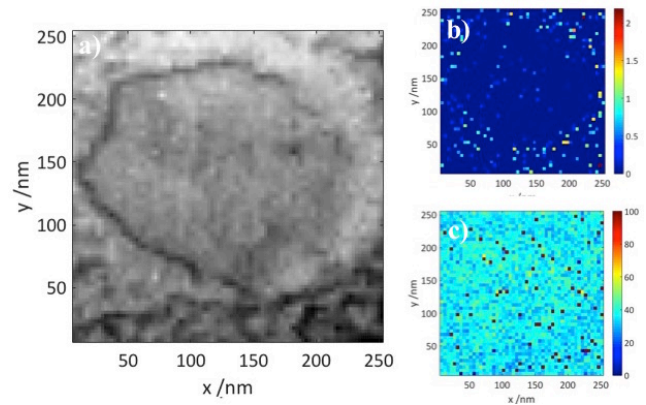

Figure 5 a) HAADF-STEM image and b) EDX analysis of a ring in the absence of a droplet, taken with an FEI Tecnai Osiris FEGTEM. The EDXS analysis shows atomic percentage of In and Ga No difference in In content can be determined between the ring and the surrounding InGaN film.

the epilayer is highly position-dependent but is in the range 400 – 550 nm, consistent with our expectation that InGaN is present. AFM reveals the ring to have a thickness in the order of a few nanometers. If our interpretation of the data is correct and the rings are indeed of the same composition as the surrounding film, they will act as confinement centres, unless a change occurs upon capping. They may behave as quantum rings, or, as is perhaps more likely due to their uneven and discontinuous topography, a cluster of quantum dots.

4 Discussion

A schematic of the proposed mechanism is displayed in Figure 6. It is hypothesized that the rings form via a droplet etching mechanism (Fig. 6 a)). Li *et al.* [7] observe such a mechanism during growth of QDs via droplet epitaxy in the GaAs system, and Heyn et al. [8] discuss such a mechanism on AlGaAs substrates. We propose that the Ga/In metallic droplet precipitates decomposition of the InGaN film immediately below it, leading to a recession below the droplet. In and Ga atoms are incorporated into the droplet, and diffuse to the edge where recrystallization leads to the formation of the InGaN ring.

We propose that the skewed double ring structure is the result of the droplets 'creeping' (Fig. 6 b)). This phenomenon has been observed in the GaAs system by Wu *et al.* [9]. The direction of movement appears to be determined the crystallographic anisotropy in both cases. Furthermore, Wu *et al.* also discuss the formation mechanism of stepping nanostructure 'footprints' in the surface of the samples. This correlates with the double ring structures we observe. This is referred to as a 'stick-slip' mechanism: during the 'stick' stage the droplet remains stationary and grows due to incorporation of atoms from the underlying layer. Then, once the driving force is sufficiently high, the 'slip' stage, or movement of the droplet, occurs. This is
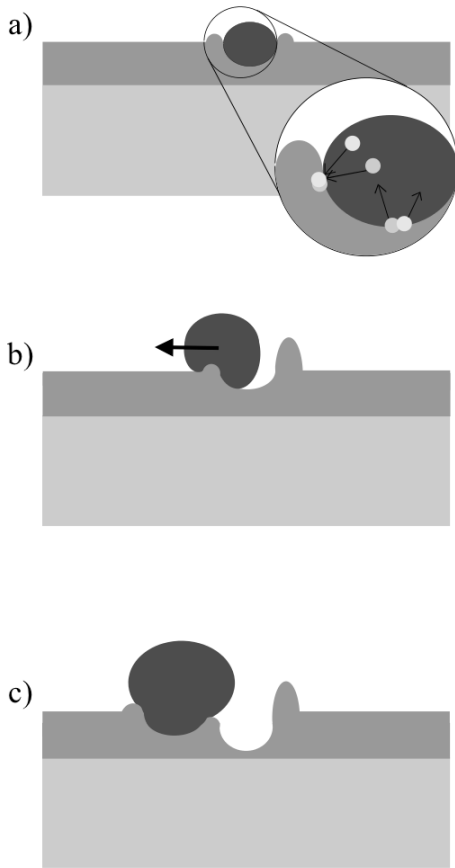
Figure 6 Schematic of droplet etching and creeping mechanisms, leading to double-ring structures. a) The droplet etches the underlying InGaN film. Ga and In atoms diffuse to the edges of the droplet, where recrystallization leads to the formation of a ring. b) The droplets creep in a direction determined by the crystallographic anisotropy when favourable to do so. c) The droplet movement halts, and further etching of the underlying layer continues. The resulting structure consists of a double-ring enclosing recessions.

halted due to frictional forces, and the process repeats (Fig. 6 c)). If the lateral growth of the metallic droplet is sufficiently large, and the movement sufficiently small, this could lead to the double ring structure observed. This would provide an explanation as to why the droplet sits in an antiparallel direction to the inner droplet. An indication that droplet creeping is occurring can be seen from AFM images of a sample grown under slightly altered conditions (120 s growth, 0 s ramp, 30 s anneal), which shows elongated tails characteristic of droplet creeping (Fig. 7).

The driving force for the droplet movement is as of yet unclear. In their discussion, Wu *et al.* suggest that the direction of the movement observed in the Ga on GaAs droplets is determined by random thermal fluctuations, after which it is more favourable for movement to continue in that direction. This is due to the difference in the surface energy of the freshly exposed surface, $\gamma_{vs(L)}$, in comparison

to the rest of the exposed film, $\gamma_{vs(s)}$, [10]. The net force on a droplet of diameter d will therefore be:

$$F_{tot} = (\gamma_{vs(s)} - \gamma_{vs(L)})d \qquad (1)$$

So if $\gamma_{vs(s)} > \gamma_{vs(L)}$ there is a driving force for droplet motion to continue in the same direction. If, however, $\gamma_{vs(s)} < \gamma_{vs(L)}$, the droplet will remain stationary. The value of $\gamma_{vs(L)}$ is temperature dependent. Another possibility is that surface ordering provides the driving force for movement of the droplet [11]. As observed in Figure 7, the tail region is smoother than the surrounding, rougher film surface. Therefore surface smoothing takes place underneath the droplet during movement. It is not yet understood why the growth procedure of this particular sample led to such extensive creeping; determining this would assist in ascertaining the driving force for creeping in all samples.
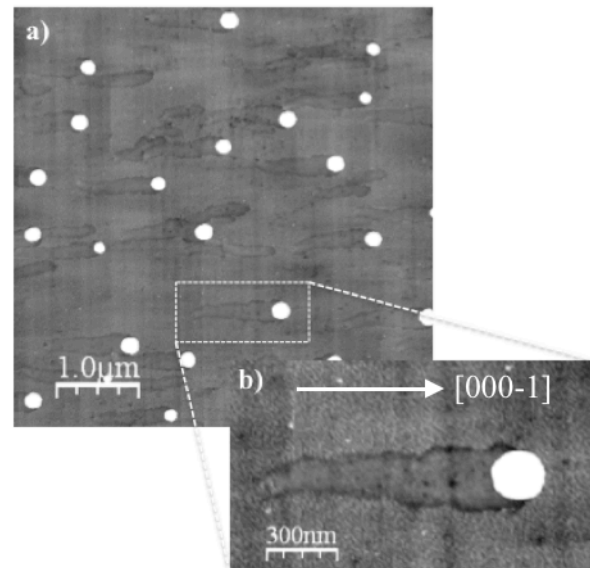

Figure 7 AFM image of a sample which has undergone 120 s growth, 0 s ramp, and 30 s anneal, a) 15 nm data scale, b) and enlarged droplet and tail, data scale 7 nm. Elongated 'tails' of the droplets can be seen, indicative of a droplet creeping mechanism.

5 Conclusions

It has been observed that two sizes of metallic droplets form during MDE. The larger droplets sit within a raised 'ring' structure, and it is hypothesized that these are formed via a droplet etching mechanism analogous to that observed in the GaAs system. The droplets sit to one side of this ring, and a smaller ring sits in an anti-parallel direction. A mechanism is proposed to explain this whereby a droplet etches the underlying film then creeps to a new position when it reaches a critical size. It is then halted by frictional forces and begins to etch the underlying layer again, forming the larger, outer ring. CBED analysis in the TEM confirms the direction of movement to be along the

c-axis, and tentatively suggests it to be along the [000-1] direction. STEM-EDXS analysis indicates a high In content within the droplet, but no change in In content within the ring relative to the surrounding epilayer. The rings will therefore act as confinement centres, but the exact nature of their emission properties is not yet understood. Further work is ongoing to attempt to gain insight into this and the effect that capping has on the evolution of the observed droplets and the formation of quantum dots.

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