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Nucleation of InN quantum dots on GaN by metalorganic vapor phase epitaxy

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InN quantum dots (QDs) on GaN (0001) grown by metalorganic vapor phase epitaxy onto a sapphire substrate were studied by transmission electron microscopy (TEM). We found that the nucleation of InN QDs on GaN is directly related to the presence of threading dislocations (TDs) in the center of the QDs. The TEM analysis revealed that the TDs finish at the InN/GaN interface and they are pure edge dislocations. Therefore, spiral growth models cannot explain nucleation of these QDs. Although controlling edge TDs constitute a possible approach to determine the QD density, a better approach may be an increase in the material growth rate in order to enter the diffusion-limited growth mode, where growth is not sensitive to surface heterogeneities. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2152110]

Over the past decade, the epitaxial growth of quantum dot (QD) semiconductor nanostructures has attracted much research due to its significant potential in the manufacture of optoelectronic devices. Self-assembled growth, based on control of strain in the epilayers, leads to homogeneity in the size and shape of the dots, which determines the optical and electrical properties of the nanostructures. Furthermore, QD structures are especially promising because they act as electron localization centers so increasing emission efficiency, and may have uses in single-photon emitters.[1] Simultaneously, research activity in III-N semiconductor materials continues to be very intense due to the wide range of applications in optical and electronic devices. Recently, among the III-N compounds, InN is receiving attention, since its small band-gap energy, 0.7 eV (Ref. 2), is well adapted to applications in telecommunications. The optimization of III-N materials (including InN and InGaN alloys) may lead to coverage of the entire spectral range from near infrared to deep ultraviolet. Most of the recent research in III-N materials has been focused on InGaN alloys.[3,4] Phase separation has been commonly observed in this alloy[5,6] since the miscibility between GaN and InN at the typical growth temperatures is relatively poor.

Despite this level of research in InGaN, the epitaxial growth of binary InN on GaN is not as developed as other III-N materials, and there are very few groups that can obtain InN QDs (Refs. 7–9). It is well known that the growth of GaN QDs on AlN follows the Stranski–Krastanov growth mode[10–12] and despite the high GaN/AlN mismatch, $\sim$2.47%, coherent GaN QDs on AlN are generally obtained.[13] However, it is not clear if InN grows on GaN three dimensionally via the Stranski-Krastanov mode, because the (compressive) lattice mismatch ($\sim$10%) is very high. Therefore, it has been proposed that the strain in epitaxial InN is initially relieved by dislocations rather than by surface islanding.[14] The InN islands emerge after strain relief, thus they are dislocated and strain free.[14] Recently, we obtained data on the nanoscale strain state of InN nanostructures using synchrotron radiation diffraction, which clearly demonstrates that the QDs are mostly relaxed with a residual strain smaller than 0.6% of the lattice mismatch, a small part of which is elastic relaxation.[15] Unfortunately, the growth of good quality InN heterostructures is difficult and thus this semiconductor is currently an important technological challenge.

Transmission electron microscopy (TEM) techniques allow imaging of most crystalline materials, giving information about the structure of defects at the atomic level and also chemical composition at subnanometer levels.[16–18] Nevertheless, while extended defects in GaN, AlN, and ternary alloys InGaN and AlGaN, have been extensively analyzed using electron-beam techniques, only a few works on InN heteroepitaxy have been reported.[19–21]

The goal of this letter is to discuss the nucleation process of InN QDs on GaN grown by metalorganic vapor phase epitaxy (MOVPE). Preferential nucleation of the InN dots in GaN containing dislocations will be demonstrated. The focal point in our research is the relationship between the GaN threading dislocations (TDs) and the InN QDs.

The structural characterization of InN QDs on GaN has been carried out using high-resolution transmission electron microscopy (HRTEM) and conventional transmission electron microscopy (CTEM). These observations were carried out in JEOL 2011 and JEOL 1200EX electron microscopes working at 200 and 120 kV, respectively. InN QDs were grown onto GaN by MOVPE. First, a buffer layer of GaN was grown using the classical two-step process on (0001) sapphire at a temperature close to 1000 °C; then the InN QDs were deposited in the same growth run at a temperature of

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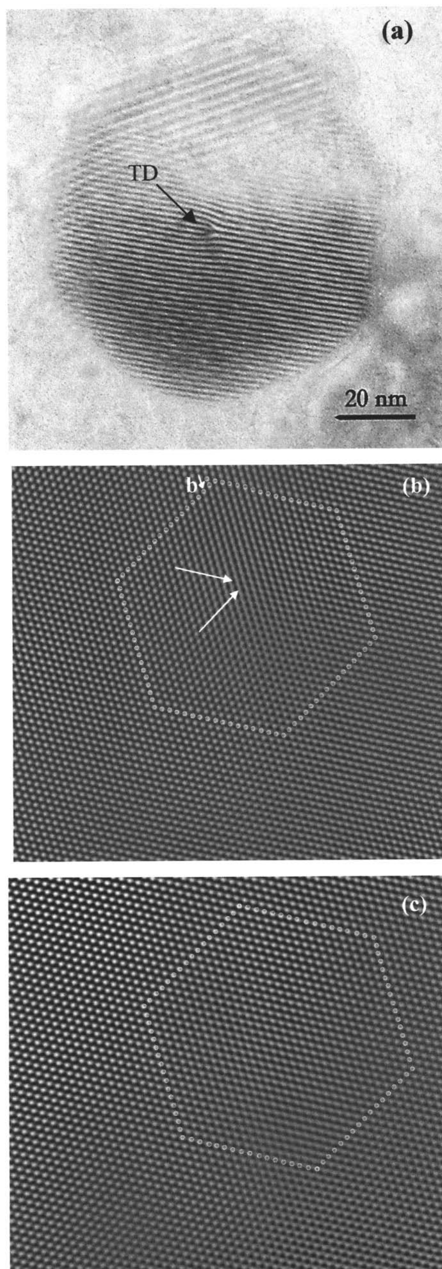

FIG. 1. (a) Moiré fringes revealing the presence of a TD. Fourier filtered image revealing solely (b) the GaN and (c) InN. In (b) two extra $\{1\bar{1}00\}$ half planes and the edge component of the Burgers vector $b=1/3\langle 11\bar{2}0\rangle$ have been indicated in the GaN.

550 °C, under a V/III molar ratio of 15 000, using ammonia (NH_3) as a nitrogen precursor. A thermodynamic analysis was performed by analyzing the dot size versus reciprocal temperature. This revealed that the growth is kinetically controlled[22] (usually diffusion-limited processes are expected in MOVPE growth), and therefore the growth is sensitive to surface inhomogeneities which can nucleate the QDs. This is clearly related to the inefficient decomposition of ammonia at the low growth temperature (550 °C) required for InN.

Large areas containing InN QDs were analyzed, revealing a truncated hexagonal pyramid shape in the QDs. They also exhibit a well-defined moiré fringes pattern in planar view specimens, as can be observed in Fig. 1(a). The moiré fringes pattern arises from the interference between electron beams diffracted by two materials with different lattice parameters. Diffraction patterns showed perfect alignment between InN and GaN crystals indicating that these moiré fringes are of the translational type. In our case, the fringes are produced by overlapping a single set of parallel $\{1\bar{1}00\}$ planes in the InN/GaN heterostructure. These moiré fringes suggest at least partial InN relaxation, i.e., different in-plane lattice parameters of InN and GaN. These patterns can also be used to locate and obtain information about dislocations.[23] In Fig. 1(a) two terminating moiré fringes can be clearly observed, indicating the position of a TD in the area corresponding to the InN QD (marked with an arrow in the picture). This TD is placed approximately in the center of the quantum dot. We have been able to characterize this TD in more detail by determining its location and Burgers vector. In order to determine the location (GaN and/or InN), planar view HREM images were recorded along the [0001] zone axis, in areas of the QD containing a TD. Fourier filtered images, revealing solely the GaN [Fig. 1(b)] and InN [Fig. 1(c)], were obtained. In Fig. 1(b) the projection of two extra $\{1\bar{1}00\}$ half planes can be observed in the GaN (white arrows). The Burgers circuit drawn around the area containing the half planes shows a closure failure, therefore the TD has an edge component of the Burgers vector, $b=1/3\langle 11\bar{2}0\rangle$. The same procedure was carried out in Fig. 1(c), i.e., in the InN. As can be observed no closure failure is shown in the Burgers circuit. From this analysis, we can conclude that the TDs observed in areas of the InN QDs have an edge component (either pure edge or mixed character is possible, since any Burgers vector component along the electron beam does not affect the moiré fringes). Furthermore, they are located in the GaN substrate and do not propagate through the InN QD.

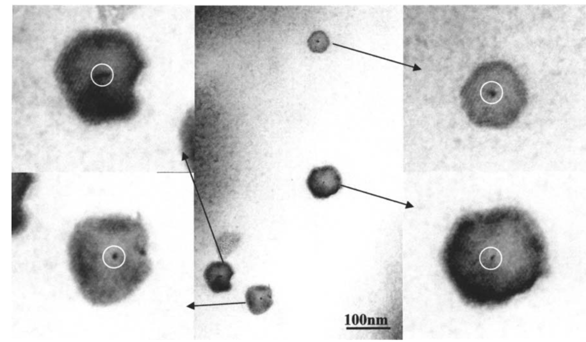

FIG. 2. General view of the InN/GaN QDs along the $\langle 0001\rangle$ zone axis. The white circles in the magnified images show clearly TDs placed in the middle of the InN QDs.

This TD in the center of a QD was not an isolated observation, but a general feature. Using CTEM in planar view specimens, a technique that allows the analysis of large areas of the heterostructure, we found that the TDs were placed almost in the center of the QDs. Figure 2 shows a general view of the InN/GaN heterostructure in a planar view specimen. As can be observed in the magnified images, each InN QD is associated with a central TD (marked with a white circle), thus these dislocations seem to be correlated with the nucleation process of the QDs.

To determine if the TDs are a type or $a+c$ type, images were recorded in two beam conditions with $g=0002$ and $g=\bar{2}110$ near the $\langle 01\bar{1}0\rangle$ zone axis [Figs. 3(a) and 3(b), respectively] in cross-section specimens. Applying the $g\cdot b$ invisibility criterion, it can be concluded that the TD in the GaN

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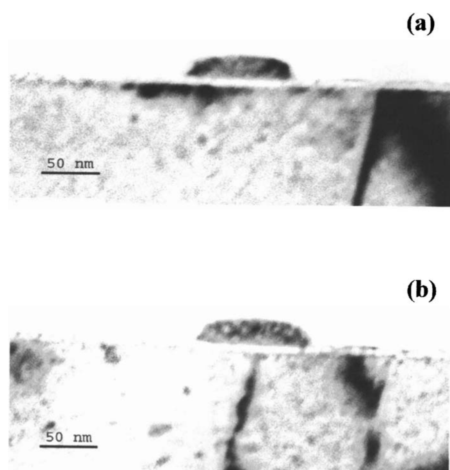

FIG. 3. (a) Bright-field XTEM images recorded under two beam conditions for (a) $g=0002$ and (b) $g=\bar{2}110$ near the $\langle 01\bar{1}0\rangle$ zone axis showing the pure edge character of the TD.

is a pure edge dislocation ($b=1/3\langle 11\bar{2}0\rangle$). Figure 3(b) shows that the dislocation can be clearly detected in the GaN, but not in the InN. The TD stops at the interface between the GaN and InN QD, confirming the previous result about the TDs obtained by moiré fringes. It seems than the misfit relaxation begins with the bending of an edge threading dislocation ($b=1/3\langle 11\bar{2}0\rangle$) pre-existing in the material growing on and continues with the generation of new dislocations.

To summarize, it has been observed that the InN QDs are associated with GaN pure edge TDs. Therefore, these TDs have to be closely related to the nucleation process. Previous works[24,25] have reported that the morphology of III-N films and hillock growth follow predictions based on Burton, Cabrera, and Frank's model (BCF),[26] demonstrating that the spiral growth is related to TDs with *c* components.[27] In this material even though InN QD nucleation is associated with TDs, the *c* component of the Burgers vector is not present. Therefore the BCF model is not sufficient to describe the nucleation of InN QDs on GaN. It seems that the strain field originating from the edge TDs at the surface of GaN is the process that governs the location of the InN QDs. A similar mechanism of QD nucleation was observed in GaN on AlN (Ref. 13), but in that case QDs nucleated adjacent to edge TDs that propagated in the AlN barrier and it is not the generally accepted mechanism for GaN QD nucleation. A possible mechanism to increase and control InN QD density may be through control of the surface morphology and defect population of the substrate material (including the pure edge TDs). However, in the present case this is clearly related to the low growth rate of InN, linked to the poor dissociation of NH_3 at low temperature. As a result, the available chemical-potential difference, which is the driving force for growth, is low, and nucleation occurs on sites where local conditions lower the energy barrier for nucleation. Clearly, the TDs we have observed fulfill these conditions. This indicates that an improvement of InN QDs quality may be realized through the increase of InN growth rate, i.e., by operating in the gas diffusion-limited growth mode in MOVPE. In this respect, the use of alternative precursors, decomposing at lower temperatures, is promising. This study is underway in our group.

In conclusion, we have demonstrated that InN QDs grow preferentially centered on regions of GaN where TDs become a misfit relaxation segment. The TEM analysis has shown that TDs do not propagate through InN QDs and they are pure edge dislocations. The nucleation of the InN QDs does not follow the BCF model, i.e., associated with the presence of TDs with a screw Burgers vector component. The strain field around the TD with a pure edge component in the GaN may be the main factor that governs the nucleation of InN/GaN QDs. The optimization of the density of these dislocations and the homogeneity and density of QDs should be closely related, constituting a challenge in future optoelectronic devices. To switch to the gas diffusion-limited growth mode in MOVPE or the use of alternative precursors, is in hand in our laboratory, in order to attain this goal.

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