Observation of V Defects in Multiple InGaN/GaN Quantum Well Layers

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Multiple In₀.₁₈Ga₀.₈₂N (4 nm)/GaN (40 nm) quantum well (QW) layers in a green laser diode were observed by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and conventional transmission electron microscopy. HAADF-STEM provided undoubted evidence that V defects in the multiple QW have the thin six-walled structure with InGaN/GaN {1011} layers. The detailed structure of the observed V defects is discussed on the basis of the formation mechanism of V defects which was proposed taking into account the growth kinetics of the GaN crystal and a masking effect of In atoms segregated around the threading dislocation (Shiojiri et al. J. Appl. Phys. 99, (2006) 073505). [doi:10.2320/matertrans.48.894]

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1. Introduction

The lifetime of GaN-based violet or purple light emitting diodes (LEDs) and laser diodes (LDs) can exceed 10000 h,¹ and they have been widely manufactured for commercial use. Such structures can be produced by epitaxial lateral overgrowth (ELOG) of the GaN layer on a sapphire substrate,²,³ followed by deposition of AlGaN/GaN strained-layer superlattice (SLS) claddings.⁴–⁶ The ELOG and SLS prevent dislocations from forming due to mismatch between the Al₂O₃ and GaN lattices, and between the GaN and AlGaN lattices, respectively, thereby reducing the density of threading dislocations (TDs) that propagate to the multiple InGaN/GaN quantum well (QW) active layer through the substructures. Shiojiri et al.,⁷ who performed high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) that clearly distinguished between Al₀.₁₄Ga₀.₈₆N (2.2 nm) and GaN (2.3 nm) layers in an n-SLS cladding, observed that the SLS significantly reduces the number of TDs reaching the multiple QW (MQW) layer. In spite of these advances, defect-free multiple InGaN/GaN MQW layers have not yet been obtained.

The most troublesome defects in the MQW are V defects or inverted hexagonal pyramid (IHP) defects. They cause undesirable long-wavelength small emissions in addition to the main emission.⁸–¹⁰ These names originate from the fact that empty pyramidal pits, with hexagonal openings at the growth surface and sidewalls parallel to the {1011} planes, are formed during the MQW growth.¹¹ These are subsequently filled during growth of the p-type GaN capping layer to form an IHP.¹² The V defects often nucleate on TDs crossed with the InGaN QW just above the underlying layer. They have the thin six-walled structure with InGaN/GaN {1011} QWs which was proposed by Wu et al.¹³ This structure was first found in the In₀.₂Ga₀.₈N (2.5 nm)/GaN (8 nm) MQWs in a violet LD by HAADF-STEM¹⁴ and confirmed in back-scattering electron images by field-emission gun (FEG) scanning electron microscopy (SEM).¹⁵ Although some researchers have conjectured no InGaN/GaN sidewall layers,¹⁶,¹¹,¹²,¹³,¹⁰ Recently, Shiojiri et al.⁸ have discussed the formation mechanism of V defects. They explained the formation of the V defects taking into account the growth kinetics of the GaN crystal¹⁷ and a masking effect of In atoms by analogy with ELOG.²,³ The growth rate of the {1011} surfaces of the GaN crystal decreases with decreasing temperature while the growth rate of the {0001} surface increases.¹⁷ Then, if a mask disturbing the {0001} layer growth is formed at a low temperature, then the growing crystal terminates on the {1011} planes, exhibiting the {1011} facets. The deposition of the InGaN/GaN MQW layer is usually performed at a reactor temperature as low as 800~850°C because of the low sticking coefficient of In atoms at high growth temperature. Indium atoms which are trapped and segregated in the strained field (Cottrell atmosphere) around the core of a TD play a role as a small mask, hindering Ga atoms from migrating on the {0001} layer to make a smooth monolayer. Once the poor surface diffusion of Ga atoms, and particularly In atoms, impedes the layer-by-layer growth on the {0001} surface with this masking effect, the InGaN and GaN crystals successively grown at the low temperature exhibit the {1011} facets, which become the six side-walls of the V-shape pit. Thus, the generation of the V defects is ascribed to the low reactor temperature. This suggests that no V defects are generated in structures grown at high temperature. In fact, V defects were not observed in an n-SLS cladding⁷ and a p-SLS cladding¹⁸ grown at a temperature as high as 1150°C.
It is the aim of the present paper to show undoubtedly evidential images of the V defects that have the thin six-walled structure with InGaN/GaN \{1011\} QWs. Details of the shape of the V defects observed are discussed on the basis of the formation mechanism of V defects.\(^8\)

2. Experimental Procedure

Conventional metalorganic chemical vapor-phase deposition (MOCVD), using trimethylgallium (TMGa), trimethylindium (TMIn) and ammonia (NH\(_3\)) as precursors, was used to grow the MQW active layer which comprised five 4-nm InGaN QWs spaced with 40-nm GaN barriers, as schematically shown in Fig. 1. The MQW layer was directly deposited onto the HT-GaN layer in a thickness of 2\(\mu\)m and at a reactor temperature of 800°C. The HT-GaN layer was grown at 1020°C on the LT-GaN buffer layer that was previously deposited on the (0001) sapphire substrate at a low temperature (520°C). The MQW was covered with the \(p\)-AlGaN layer. This specimen was a prototype wafer of the green emission LD. Since it was prepared to investigate details of the MQW, some structures including \(n\)-and \(p\)-SLS cladding layers were not deposited. The average indium content in InGaN QWs was estimated to be 18%.

The specimen for HAADF-STEM and conventional transmission electron microscopy (CTEM) was prepared by mechanical polishing, followed by ion milling. HAADF-STEM and CTEM observations were performed in a Tecnai 30, equipped with a lens of \(Cs = 1.2\) mm, operated at 300 keV. The HAADF-STEM images were recorded in a detector range of \(D = 36\sim 181\) mrad using a convergent electron probe with a semiangle of \(\alpha = 15\) mrad. All the HAADF-STEM and CTEM images presented in this paper are original images free of image-processing.

3. Results and Discussion

Figures 2(a) and 2(b) show cross-sectional HAADF-STEM and CTEM images of the In\(_{0.18}\)Ga\(_{0.82}\)N/GaN MQW, respectively, taken in the \(b\) axis. The nominal thicknesses of the In\(_{0.18}\)Ga\(_{0.82}\)N QWs and GaN barrier layers were 4 and 40 nm, respectively. For the analysis of the structure details of V defects, the present specimen with the thick QWs and barriers compares favorably with the In\(_{0.2}\)Ga\(_{0.8}\)N (2.5 nm)/GaN (8 nm) MQW that was used in a previous experiments.\(^8,14\) HAADF-STEM images give rise to strong contrast dependence on the atomic number so-called Z-contrast, unlike CTEM images.\(^19\) The HAADF-STEM images are mainly formed by thermal diffuse scattering of electrons or incoherent imaging of elastically scattered electrons.\(^19,20\) According to the high thermal diffuse scattering cross-section of In atoms, the intensities of In\(_{0.18}\)Ga\(_{0.82}\)N layers are stronger than that of GaN layers. If HAADF-STEM
contrast is described as the Z-contrast proportional to the square of the atomic number, the intensity ratio of $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$ and GaN is 100 : 85. Therefore, the thin bright bands parallel to the basal plane in Fig. 2(a) correspond to the $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$ QWs and the thick dark bands between the QWs correspond to the GaN barriers, whose thicknesses are as expected for the preparation. The HAADF-STEM image gives directly the composition information as well as spatial information. In contrast to the HAADF-STEM image, the $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$ QWs in a bright-field CTEM image of Fig. 2(b) appear as dark contours, which were caused by strong diffraction ascribed to the large elastic scattering factor of In atom.

Typical images of the V defect are shown in Figs. 3(a) and 3(b). A HAADF-STEM in Fig. 3(a) reveals that the V defect starts on the first QW crossed with a TD, which runs from the HT-GaN layer to the capping layer through the MQW. The inclined brighter thin stripes terminate on horizontal InGaN QWs, successively decreasing the number of the sidewall stripes with increasing height of the V, and the apical angle of the V-shape (see Fig. 4(a)) nearly agrees with the angle between the \{1011\} and \{1011\} planes, 56°. Thus, it is clear that the side walls are formed with thin InGaN layers and GaN layers. The structure of the side walls was quite definitely imaged in Figs. 4(a) and (b). These images support very strongly the previous observations,\textsuperscript{8,14,15} the images for which were somewhat obscure, and completely deny the model\textsuperscript{11,12,16} that the main InGaN QWs end abruptly at the surfaces of the pits and the pits are then filled by the GaN capping layer with no InGaN/GaN sidewall layers. The InGaN and GaN sidewall layers were epitaxially grown successively on the six \{1011\} planes during the MWQ deposition, each of them forming by the layer-by-layer growth similar to the growth on the \{0001\} planes. Since the thin InGaN layers were spaced with the thin GaN layers, having the same composition with the main $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$ QWs, they might also work as another MQW, emitting undesirable long-wavelength weak extra lights.\textsuperscript{8}

In the CTEM image in Fig. 3(b), the thin $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$ layers are observed parallel to the \{1011\} planes, as shown by arrowheads. It may be noted that these thin layers are identified on the basis of the results from HAADF-STEM images. The contrast along the main QWs in the CTEM image deserves our attention. Dots on the QWs emphatically indicate local lattice-strained spots as diffraction contrast. Watanabe et al.\textsuperscript{21} found In-rich spots, considered as quantum dots,\textsuperscript{22,23} in the $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$ (2.5) nm/GaN (8 nm) MQW. The In rich spots were distributed on the QWs and agreed to the areas with lattice expansion along the c direction. This was obtained by high-resolution HAADF-STEM which provided both precise atom column positions and clear Z-contrast, thereby allowing us to map both the strain field and the In atom distribution in the MQW. Hence, the observed dots in Fig. 3(b) can be regarded as evidence of In-rich spots or quantum dots. At the apex or starting point of the V defect, we can see strong diffraction contrast in CTEM image in Fig. 3(b) and also a brighter spot in the HAADF-STEM images of Figs. 3(a), 4(a) and 4(b). This area can be considered as the In-rich mask assumed in the formation mechanism of the V defects.\textsuperscript{8}

The capping layer in the present specimen was so thin that the top area of the V defect was empty. A part of the main MQW in the front (or back) of the V defect remained in the specimen prepared for EM. The CTEM image in Fig. 3(b) reveals this part by the fifth QW appearing in the V-shape. In any case, the TDs did not terminate at the apexes of the V defects but survived within the V defects and then propagated to the free surface through the capping layer. This reveals and supports the conclusion that the InGaN QWs and GaN barriers were connected in good lattice coherence with each other on the \{1011\} interfaces, to make the cellurally same structure as a whole.\textsuperscript{8}
As described above, the mask induces a V defect where the QWs and barriers grow exposing the \{10\textbar C22\textbar 11\} surfaces as the natural habit at the low temperature. The (0001) growth is still kept on the surface without the masking effect. Thus, the whole MQW has the (0001) surface as well as the \{10\textbar C22\textbar 11\} surfaces during the MQW deposition. The corners connecting the (10\textbar 11) interface (or the (10\textbar 11) interface) with the (0001) interface are not sharp (making an angle of \(\sim 118^\circ\) but curved, as seen in Figs. 4(a) and 4(b). The InGaN and GaN crystals were formed by the layer-by-layer growth on the (0001) and \{10\textbar C22\textbar 11\} surfaces, where each monolayer on these surfaces would extend from the remote nucleation site toward the edge by supply of atoms stuck and migrating on the surfaces. As the monolayers are grown, a shortage in the supply of atoms might have occurred gradually on both the (0001) and \{10\textbar C22\textbar 11\} surfaces, and particularly in the InGaN whose growth rate is smaller than that of the GaN. Then, the monolayers on the (0001) and \{10\textbar C22\textbar 11\} surfaces cease from growing before they meet with each other. This might be ascribed to the low growth rate at the low temperature of 800°C. As a result of successive growth of these monolayers, a surface with step-wise lattices was formed near the corner. In the low-magnified HAADF-STEM images the corner interfaces are observed as if they were curved. These curved corners, thus, can be explained on the proposed formation mechanism of V defects.8)

4. Conclusion

We observed an InGaN/GaN multiple quantum well (MQW) layer by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and conventional transmission electron microscopy (CTEM), and established the structure of V defects, confirming the formation mechanism of the V defects which was previously proposed by Shiojiri et al.8)

(1) Specimen used in this experiment comprised five 4-nm In\(_{0.18}\)Ga\(_{0.82}\)N QWs spaced with 40-nm GaN barriers, which were deposited at a reactor temperature of 800°C on the 2-μm GaN layer. The MQW was covered with the 50-nm \(p\)-AlGaN capping layer. In HAADF-STEM images the In\(_{0.18}\)Ga\(_{0.82}\)N QWs appeared as thin bright bands and the GaN barriers appeared as thick dark bands between the QWs.

(2) In the MQW, V defects were observed nucleating on a threading dislocation (TD) crossed with the InGaN QW just above the underlying GaN layer. HAADF-STEM gave undoubted evidence that the V defects have a thin six-walled structure with InGaN/GaN \{10\textbar C22\textbar 11\} QWs.

(3) The segregation of In atoms was observed at the starting points of the V defects, by CTEM and HAADF-STEM. This might work as the In-rich mask which induced the \{10\textbar C22\textbar 11\} facets on the GaN crystal grown at the low temperature, as proposed in the formation mechanism of the V defects.8)

(4) The TD incorporated with the V defect propagated to the free surface through the V defect buried with the cap layer. This provides evidence for the fact that the InGaN QWs and GaN barriers were connected in good lattice coherence with each other on the \{10\textbar 11\} interfaces, to make the cellurally same structure as a whole.8)

(5) The corners connecting the \{10\textbar 11\} interfaces on the walls of a V defect with the (0001) interfaces in the main MQWs were curved. This is explained as a result of the layer-by-layer growth on the (0001) and \{10\textbar 11\} surfaces where each monolayer did not cover over its under-monolayer for lack of atom. The successive growth of these monolayers formed an interface with step-wise lattices near the corner, which is observed as the curved corner of the QW in the low-magnified HAADF-STEM images.
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