STRUCTURAL PROPERTIES OF NITRIDES GROWN BY OMVPE ON SAPPHIRE SUBSTRATE

H. AMANO, T. TAKEUCHI, S. YAMAGUCHI, S. NITTA, M. KARIYA, M. IWAYA, C. WETZEL, I. AKASAKI
Department of Electrical and Electronic Engineering, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468 Japan

ABSTRACT

Crystalline quality of nitrides on sapphire by OMVPE has been investigated. First, in-situ observations of the crystallization process of the low temperature deposited AlN buffer layer or GaN buffer layer on sapphire substrate have been performed. Small hexagonal mesas were formed from the sapphire to the surface and finally they formed a stacked structure. Secondly, a low temperature deposited buffer layer located between the high temperature grown GaN was found to reduce the etch pit density of GaN films. Thirdly, structural properties of Ga$_{1-x}$In$_x$N ($0 \leq x \leq 0.21$, and $x=1$) on GaN and GaInN/GaN MQWs on GaN have been characterized by X-ray diffraction. Coherently grown GaInN showed almost the same twisting as the underlying GaN layer, while free standing InN showed large twisting. Thickness of the well layers in MQWs has been controlled within one monolayer preciseness, and the fluctuation of alloy composition has been controlled to within 2%.

INTRODUCTION

The first demonstration of stimulated emission from GaN was reported by Dingle et al. [1], who succeeded in optically pumped lasing at 2K. Since then, it took about a quarter century to realize stimulated emission [2] and lasing [3] by current injection. Nowadays, room temperature pulsed lasing by current injection in the emission wavelength from 376nm to 440nm have been realized [3-11]. Continuous wave lasing near 400nm has also been succeeded [12].

The group III nitride based laser diode (LD) is the first LD composed of the hexagonal wurtzite crystals. Therefore, it is interesting to clarify whether the mechanism of lasing in nitrides is the same as in other III-V compounds or not. It should be also noticed that group III nitride based LDs were grown on dissimilar substrates, that is sapphire [3-5, 8-12], Mg-spinel [13] or 6H-SiC [6,7]. Therefore, it is important to clarify the structural properties of nitrides on such dissimilar substrates.

The aim of this paper is, first, to clarify the growth process of GaN on dissimilar substrates, especially on sapphire, and second, to characterize its structural properties. In addition, structural properties of nitride based heterostructures and laser structures are also characterized.

EXPERIMENTS

Crystallization Process of The Low Temperature Deposited Buffer Layer And The Following Growth of Nitrides on Sapphire by OMVPE

Difficulty in growing large size bulk crystals and the lack of substrate materials with lattice constants and thermal expansion coefficient close to those of nitrides have long prevented the use of nitrides. The use of low temperature deposited thin AlN buffer layer has changed the situation drastically [14]. Although there is a large lattice mismatch between GaN and sapphire substrate, device quality GaN and nitride alloys have been achieved. The growth process of GaN films on sapphire substrates covered with the AlN buffer layer has been observed in ex-situ SEM [15,16]. Later on, it was reported that low temperature deposited GaN buffer layer [17] has the same effect as that of an AlN buffer layer. The growth mode of GaN using the GaN buffer layer was also reported [18], and was similar to that using the AlN buffer layer.

Nowadays, LDs emitting coherent light in the UV and violet region have been realized. It was pointed out [19], however, that GaN films grown on sapphire with low temperature
Fig. 1 In-situ observation of the crystallization and decomposition process of the low temperature deposited AlN buffer layer on sapphire by OMVPE.
deposited buffer layers contain large amount of dislocations on the order of $10^8 \sim 10^{10} \text{cm}^{-2}$, which might affect performance of the nitride based device. In order to realize low dislocation density GaN on highly mismatched substrate such as sapphire, it is essential to understand the mechanism of the growth of GaN using low temperature deposited buffer layers.

In situ observation of the solid phase crystallization process of the low temperature deposited amorphous buffer layer by organometallic vapor phase epitaxy (OMVPE) has been performed using transmission electron microscopy (TEM) with a high temperature sample stage [20, 21]. Either an AlN buffer layer or a GaN buffer layer was deposited on sapphire (0001) substrate at 500°C. The average thickness of each buffer layer was about 50nm when deposited. During heating, the crystallization process of the buffer layer was observed by TV screen and was simultaneously stored by video tape. Fig. 1 shows the cross sectional TEM images of the AlN buffer layer at different temperatures. Nucleation and growth occurred at around 760°C (figs.1(a) and (b)). As the temperature was raised to around 800°C, a single domain covered large portion of the area. Then truncated hexagonal mesas covered with (0001) and \{10\overline{1}1\} facets, about 10nm thick and about 13nm wide were gradually formed starting at the sapphire side and progressing to the surface (fig.1 (c)). Finally, the entire AlN buffer layer became a stacked structure of the above mentioned small mesa islands. When the temperature was raised to 840°C, AlN dissolved into Al and nitrogen (figs.1 (d) and (e)).

In the case of a GaN buffer layer, the process is quite similar, but each event occurred at about 100°C lower than that of the AlN buffer layer. The size of each mesa is also somewhat different. They are about a factor of two or three larger than those of the AlN buffer layer.

These stacked structures composed of small truncated hexagonal mesas relieve the large lattice mismatch between sapphire and the upper high temperature grown GaN to a great extent. At the same time, however, they act as the source of threading dislocations. Many threading dislocations are generated at the edges of the mesas [16].

Insertion of a second low temperature deposited buffer layer between the high temperature grown GaN was found to reduce the etch pit density [22]. Deposition conditions were just the same as the first GaN buffer layer on the sapphire substrate. Figs. 2 (a) and (b) show the SEM images of the surface morphology of the etched surface of GaN. The sample shown in fig. 2 (a) (Sample (a)) was grown by the conventional method, i.e., GaN was grown by OMVPE on sapphire substrate using a single low temperature deposited GaN buffer layer. The Total thickness is 2 μm. The structure of the sample shown in fig. 2 (b) (Sample (b)) is almost the same. In addition, in the sample (b), a second low temperature deposited buffer layer was inserted between the high temperature grown GaN. Etching was done with a mixture of H₃PO₄ and H₂SO₄, with a ratio of 1:3 at 250°C for 30 min. Etch pit density of sample (a) is $10^7$−$10^8$ cm². In contrast, we could not see any etch pits over a entire area of 1 cm² in sample (b).

It is natural to think that the origin of the etch pit is the nanopipe [23, 24], because if there are nanopipes at the surface, they will become wide by etching with hot phosphoric acid, and they become as observable etch pit in the microscope. The origin of the nanopipe is thought to be screw dislocations [23]. Therefore, we conclude that insertion of the low temperature deposited buffer layer might stop the threading of screw dislocations.

### Structural Properties of GaInN on GaN

For the fabrication of LDs or other novel devices, heteroepitaxial growth of ternary alloys are indispensable. Realization of high quality heterostructures and quantum structures free of dislocations is one of the critical issues because there is a large lattice mismatch between GaN, InN and AlN.

Single heterostructures of ternary GaInN alloys with various molar fraction and also binary InN on GaN were fabricated by OMVPE. Thickness of all the InN containing layers was around 40 nm. The underlying GaN layer, about 2.5μm in thickness, has been grown on sapphire (0001) substrate using low temperature deposited AlN buffer layer. Strain and relaxation of ternary heterostructured alloys were analyzed by reciprocal space mapping (RSM) of X-ray diffraction intensity around the asymmetrical diffraction spot of nitrides.
Fig. 2. SEM image of the etched surface of the undoped GaN 2 \( \mu \text{m} \) thick grown by conventional one buffer layer sequence (fig.2 (a)) and newly developed two buffer layer sequence(fig.2 (b)). Etching was done with a mixture of \( \text{H}_3\text{PO}_4 \) and \( \text{H}_2\text{SO}_4 \) with a ratio of 1:3 at 250 °C for 30 min.

By measuring the RSM of the asymmetrical diffraction, it is possible to measure independently both the lattice constants \( a \) and \( c \) of ternary alloy and GaN. For the samples with InN molar fraction up to 0.21, the lattice constant \( a \) of underlying GaN layer and that of GaInN were both 3.182±0.001Å [25]. This result shows that ternary GaInN was coherently grown on GaN, in other words, GaInN was biaxially compressed. InN molar fractions were calculated from the lattice constant assuming Hook's law. Details have been reported previously [25]. A slight difference of the lattice constant \( a \) from that of the bulk value (3.188±0.001Å) [26, 27] is caused by the thermal stress originating from the difference in the thermal expansion coefficients between GaN and sapphire. On the contrary, however, binary InN on GaN showed almost perfect relaxation as shown in fig.3. The lattice constant \( a \) of InN obtained in this study is 3.540 Å, which is in good agreement with other literature [28].

Fig. 3 RSM around the (024) diffraction of InN on GaN. Horizontal scale shows \( \lambda/a \), and vertical scale shows \( \lambda/c \), where \( \lambda=1.540562 \). Scales are written in units of [1/\( \mu \text{m} \)].
2θ/ω–scan profiles of the symmetrical (0002) diffraction from the single heterostructure calculated within the dynamical theory coincide very well with experimental profiles. Therefore, any fluctuation of alloy composition and that of strain relaxation is negligibly small, at least in GaInN films about 50 nm thick with InN molar fraction less than 0.21.

The GaInN film is so thin that the X-ray diffraction profile becomes wide irrespective of the crystal perfection [29]. Therefore, it is difficult to measure the crystalline quality of thin GaInN on GaN by symmetrical X-ray diffraction. In order to characterize the crystalline quality of GaInN on GaN, grazing incidence X-ray diffraction (GIXD) has been performed. By using GIXD, the equivalent thickness becomes large, and we can characterize the crystalline quality of the thin film. In this study, (1010) diffraction was used. We used vicinal (0001) sapphire substrate. The offset of the sapphire was fixed at 0.2 ± 0.1°.

The attenuation depth of CuKα line is estimated to be about 0.03 μm. Ω-mode scan profiles of the (1010) diffraction directly show the twisting of the film. Fig. 4 shows ω-mode scan X-ray rocking curve profiles of the (1010) diffraction from GaInN with different InN molar fractions including binary InN having the same thickness as GaInN. Those of the underlying GaN layer is also shown for comparison. As mentioned above, GaInN with InN molar fraction less than or equal to 0.21 showed coherent growth, while binary InN showed perfect relaxation. Accordingly, coherently grown GaInN showed almost the same twisting as the underlying GaN layer while relaxed InN showed wide twisting. It is evident from this figure that, (1) coherently grown GaInN does not show lattice relaxation, and (2) large lattice mismatch of 11% of InN against GaN was accommodated by twisting.

![XRC of (1010) diffraction](image)

Fig. 4 X-ray rocking curve profile of (1010) diffraction from GaInN 40 nm thick on thick GaN. Molar fraction of the InN of each layer is, from the bottom, 0, 0.09, 0.21 and 1. Note that vertical scales are plotted in log scale.
Structural Properties of GaInN/GaN MQWs on GaN

Up to now, all the LDs based on nitrides have either single quantum well or multi quantum wells structure as an active layer. Structural properties of GaInN/GaN MQWs have been characterized by the X-ray diffraction. Samples consisting of a low-temperature-deposited AlN buffer layer (30 nm), GaN layer (2 μm) and Ga<sub>1-x</sub>In<sub>x</sub>N/GaN MQWs having five quantum wells, which were nominally undoped, were fabricated on the sapphire substrate by OMVPE. Thickness of the Ga<sub>1-x</sub>In<sub>x</sub>N well layers and the GaN barrier layers were 11 monolayers (MLs) and 22 MLs, respectively. Fig. 5 (a) shows X-ray diffraction profile of (0002) diffraction from Ga<sub>1-y</sub>In<sub>y</sub>N/GaN MQW structure taken by 2θ/ω-scan. Second order satellite peaks were clearly observed, which indicates that the interface is smooth and a well-controlled MQW was fabricated. In fig. 5 (a), calculated profiles for the different number of the GaInN MLs in the well layer based on the dynamical theory are shown. The calculated profile agrees quite well with the experimental one only when GaInN well thickness is estimated to be 11 MLs. Fig. 5 (b) also shows calculated profiles for GaInN having different InN molar fraction. The calculated profile agrees well only when the InN molar fraction is estimated to be 18%. From these results, it is confirmed that the GaInN well layer thickness can be controlled to within one ML accuracy, the fluctuation of the alloy composition is less than 2%, and that strain relaxation in the GaInN layer is negligibly small.

![Fig. 5 X-ray diffraction profile of five pairs of GaInN/GaN MQWs grown on GaN. Designed thickness and InN molar fraction in 11 MLs and 18%, respectively. Thickness of GaN is planned to be 22 MLs. Fig. 5 (a) shows calculated profiles for the different number of the GaInN MLs (10, 11 and 12 MLs) based on the dynamical theory. Fig. 5 (b) shows calculated profiles for GaInN having different InN molar fractions (16, 18 and 20%).](image-url)
Effect of Strain on The Performance of The LDs

As mentioned above, it is found that (0001)-oriented thin GaInN layers can be grown coherently on a thick GaN layer, in other words, the GaInN layers were under biaxial compressive stress. In such a case, a piezoelectric field is induced since group III nitrides have large piezoelectric constants along the [0001] orientation [30-33]. Therefore, optical properties of (0001)-oriented GaInN strained QWs should be strongly affected due to the quantum-confined Stark effect (QCSE), as are the GaInAs strained QWs grown along [111] [34-37] and the CdS/CdSe superlattice grown along [0001] [38].

The influence of piezoelectric fields on optical properties of GaInN strained QWs and performance of the LDs have been studied extensively [39]. Injected electrons and holes into the wells should be separated by the strong internal piezoelectric field. If GaInN wells were grown coherently, the magnitude of the piezoelectric field in the well layer should depends on the InN molar fraction. For example, piezoelectric fields in GaInN well with InN molar fraction of 0.12, 0.13 and 0.18 are estimated to be 1.0, 1.2 and 1.5 MV/cm, respectively.

With increase of the carrier density at the well layer by injection or excitation, Coulomb screening of the piezoelectric field occurs. In order to clarify the effect of piezoelectric field on the stimulated emission properties of nitrides, optical pumping studies have been done with MQWs with different InN molar fractions. Fig. 6 shows the compositional dependence of the threshold energy density for stimulated emission by optical pumping at room temperature. The threshold energy density increases drastically with the increase of InN molar fraction. With increasing internal electric field caused by the piezoelectricity, carrier density for screening the electric field should increase. Estimated carrier density in order to completely screen the electric field is also shown by the broken line in the same figure. In this calculation, carrier density for screening is normalized to 1 for Ga$_{0.88}$In$_{0.12}$/GaN MQW [40].

![Fig. 6 Compositional dependence of the threshold energy density for stimulated emission by optical pumping at room temperature from GaInN/GaN MQWs. Experimental results are drawn in closed square. Broken line is the estimated carrier density in order to completely screen the electric field caused by the piezoelectricity. In this calculation, carrier density for screening is normalized to 1 for Ga$_{0.88}$In$_{0.12}$/GaN MQW [40].](image-url)
From these results, we have to conclude that the piezoelectric field caused by the strain seriously affects the performance of LDs based on nitrides, especially if they were grown along [0001] direction. For example, in case of LDs with Ga<sub>0.82</sub>In<sub>0.18</sub>N wells, about two orders of magnitude higher carrier density is necessary to screen the piezoelectric field compared to LDs with Ga<sub>0.89</sub>In<sub>0.12</sub>N wells.

SUMMARY

Crystallization process of the low temperature deposited AlN and GaN buffer layer has been observed in situ by TEM for the first time. Insertion of a second low temperature deposited buffer layer is found to be effective in eradicating etch pits. Structural properties of GaInN based heterostructure including quantum wells have been investigated. Coherently grown GaInN showed no crystal relaxation, while free standing InN showed wide twisting. Finally, effect of strain, i.e. the piezoelectric effect, on the properties of LDs has been clarified.

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