Structural properties of InN on GaN grown by metalorganic vapor-phase epitaxy

Shigeo Yamaguchi, a) Michihiko Kariya, Shugo Nitta, Tetsuya Takeuchi, Christian Wetzel, Hiroshi Amano, and Isamu Akasaki

Department of Electrical and Electronic Engineering, Meijo University, 1-501, Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, Japan

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InN has been expected to be a suitable material for electronic devices such as high mobility transistors because of its small effective mass compared to other nitrides. Heteroepitaxial InN films were grown by metalorganic vapor-phase epitaxy. The films have been structurally characterized by triple-axis x-ray diffraction (XRD) analysis in terms of lattice-mismatch dependence and InN film thickness dependence, and Hall measurements have been performed. In the XRD measurement, \( \omega \) and \( \omega - 2\theta \) scans were used, and the degree of tilting (the linewidth of x-ray signal, \( \Delta \omega \)) \((0002)\) reflection and that of twisting (\( \Delta \omega \)) \((10\bar{1}0)\) reflection have been separated. In addition, the degree of distribution of lattice constant \( c \) \((\Delta 2\theta_c)\) \((0002)\) reflection of InN films has been assessed. For study of the lattice-mismatch dependence, growth of InN films on GaN, AlN and directly on sapphire substrates was performed, and accordingly, \( \Delta \omega \) was found to range from about 500 to 4000 arcsec, and \( \Delta 2\theta \) from about 400 to 700 arcsec. Among those three kinds of samples, InN films grown on GaN showed the smallest \( \Delta \omega \) and \( \Delta 2\theta \) values. Observation of \( c \) - and \( a \)-lattice parameters has shown that the InN on GaN is affected by the residual strain. On the other hand, InN thickness dependence of XRD showed that \( \Delta \omega \) was changed from about 700 to 500 arcsec, and \( \Delta 2\theta \) from about 600 to 300 arcsec with increasing InN thickness from 400 to 2400 Å. In accordance with the thickness of InN, \( \Delta \omega \) was found to change from about 2500 to 1700 arcsec. Moreover, it was found that the InN film less than 1200 Å thick is composed of grain islands with different crystalline orientation and that the growth mode changes at a thickness of about 1200 Å—screw dislocations occur. It is found that the residual strain in InN films over 1200 Å thick is gradually released, resulting in almost the same orientation. This is reflected in the reduction of the mosaicity, the proceeding of relaxation and the surface morphology. Selection of GaN for the underlying layer of the InN film has been shown to lead to structural improvement of the epitaxial InN film. In fact, InN film with a thickness of 2400 Å grown on GaN has a Hall mobility of about 700 cm²/V s even at an electron carrier concentration of \( 5 \times 10^{19} \) cm⁻³. This value corresponds to that for GaAs at the same impurity concentration. © 1999 American Institute of Physics.

I. INTRODUCTION

Nitride semiconductors such as GaN, AlN, and InN have been intensively studied especially in terms of exploring the field of blue-emitting optical devices, and they have recently manifested themselves as prominent candidates for such devices.\(^1\)\(^2\) Although combinations of such binary materials can yield a wide spectral range of red (1.9 eV, InN) to ultraviolet light (6.2 eV, AlN), longer wavelengths from the orange to red spectral regions, have not yet been achieved. This is partly because the thermal instability of InN makes the growth of good quality films of Ga \(_1\)\(_x\)In \(_N\) with high In content difficult and partly because the lattice mismatch and mismatch of thermal expansion between the epitaxial film and substrate are very large.\(^3\)

For example, mixed crystals of GaN and InN, namely, Ga \(_{1-x}\)In \(_x\)N have been obtained only for the low range com-
InN has been grown so far by various methods, such as reactive sputtering,\textsuperscript{4,5} metalorganic vapor phase epitaxy (MOVPE),\textsuperscript{6,7} hydride vapor phase epitaxy (HVPE), radio-frequency (rf) sputtering,\textsuperscript{8} microwave-excited MOVPE\textsuperscript{9–11} and magnetron sputtering.\textsuperscript{12} However, high-quality InN films have not been obtained because of the incorporation of many defects. Considering this, improvement of the quality of $\alpha_x\beta_x\gamma_x$ Al$_2$O$_3$ epitaxial layers with a high In content may be realized on the basis of improvement of the quality of binary InN epilayers. This may be approached from two angles: one is from the selection of a suitable growth method, another by selecting an appropriate underlying layer of the InN film.

Moreover, InN has been expected to be used in electronic devices such as high electron mobility transistors (HEMTs) as well as optical devices. For the realization of such applications, the use of high-temperature deposited GaN (high-quality GaN) is essential in the fabrication of devices because only GaN has the required high quality among nitride semiconductors for device fabrication. In this article, we have shown first that InN can be grown on GaN and that the structural properties of InN can be improved compared to InN without a GaN layer. In fact, an electron Hall mobility of InN has been observed of 700 cm$^2$/V s at an electron concentration of 5 x 10$^{19}$ cm$^{-3}$, as high as that of GaAs at the same electron concentration.

In this study, atmospheric MOVPE was used, and the effect of a GaN layer on InN films was studied. These films were deposited on a sapphire c-plane [$\alpha_x\beta_x\gamma_x$ Al$_2$O$_3$ (0001) wafer] with the c axis parallel to the growth direction. In this article, we present the results of the investigation of the structural properties and the growth mechanism of heteroepitaxial InN films grown on GaN. The assessment of the structural properties of InN has been performed by x-ray diffraction.

II. EXPERIMENTAL PROCEDURE

Epilayers were grown by MOVPE. Trimethylindium (TMI), trimethylgallium (TMG), and ammonia (NH$_3$) sources were used with a hydrogen and a nitrogen carrier gas. In$_x$Al$_{1-x}$N, AlN, and GaN films were grown at 450, 600, and 1050 °C, respectively. For the growth of InN films, the V/III ratio was about 10$.^5$ Thicknesses of AlN and GaN were 300 nm and 2 $\mu$m, respectively. The c plane [0001] oriented Al$_2$O$_3$ substrates were used.

All samples were structurally characterized by x-ray diffraction (XRD) measurement, and the surface morphology was studied. Using a triple-axis x-ray diffractometer, we measured the diffraction peak widths of $\omega - 2\theta$ and $\omega$ scans as a function of lattice mismatch of InN to the underlying layer or substrate and as a function of InN film thickness. Hall measurement was also performed.

III. RESULTS AND DISCUSSION

A. Crystallographic orientation of InN

Most of the InN films have been grown directly on $\alpha_x\beta_x\gamma_x$ Al$_2$O$_3$. The (0001) InN on (0001) Al$_2$O$_3$ can take one of two crystallographic orientations:\textsuperscript{6} (a) $[10\overline{1}0]_{\text{InN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$ or (b) $[2\overline{1}\overline{1}0]_{\text{InN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$. The value of lattice mismatch in case (a) ($-25.4\%$) is smaller than that in case (b) ($+29.2\%$). GaN and AlN have been reported to have the following epitaxial relationship: $[2\overline{1}\overline{1}0]_{\text{GaN/AlN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$. For GaN, the lattice constant $a$ is 3.186 Å and the lattice mismatch in the $[2\overline{1}\overline{1}0]_{\text{GaN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$ orientation is $+16.0\%$. This mismatch is considerably smaller than that of $-33.0\%$ in the $[10\overline{1}0]_{\text{GaN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$ orientation. Obviously, the epitaxial layer is grown more easily in the $[2\overline{1}\overline{1}0]_{\text{GaN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$ orientation. For AlN, the lattice constant $a$ is 3.112 Å and the reported epitaxial relationship is the same as for GaN. For the (0001) plane of InN, however, two arrangements $[10\overline{1}0]_{\text{InN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$ and $[2\overline{1}\overline{1}0]_{\text{InN}}/[10\overline{1}0]_{\text{Al}_2\text{O}_3}$ in the (0001) plane of InN crystal have been observed$^9$ since the lattice mismatches of InN are relatively close in the two arrangements while those of GaN and AlN differ largely.

In order to study the structural properties of InN films as a function of lattice mismatch, three types of InN films were prepared: An InN film grown on a sapphire substrate (a) with and (b) without an AlN layer. The lattice mismatch was +29.2% and +14.0%, respectively, in the $[2\overline{1}\overline{1}0]$ direction; (c) InN film on GaN grown on a sapphire substrate with the low-temperature (LT)-deposited AlN buffer layer. The lattice mismatch was +11.5%. Thickness of all three InN layers was set to be 800 Å, which was estimated by scanning electron microscopy (SEM).

B. Triple axis x-ray diffraction analysis: Lattice mismatch dependence of InN on its structural properties

In XRD measurements, mosaicity, compositional variations, and strain (relaxation) can be separated.$^{13,14}$ A mosaic crystal is generally defined as an ensemble of perfect crystal blocks with lattice planes tilted with respect to each other with block sizes varying around a mean value. The tilting of the lattice planes causes spectral broadening in the XRD $\omega$ scan. These structural properties are reflected in the XRD measurement, and there is a typical relationship between the XRD methods and crystalline structures. In the XRD measurement, $\omega$ scan (rocking scan) and $\omega - 2\theta$ scan have been conventionally used. These two popular scans represent crystalline mosaicity and the degree of distribution of the lattice constant, respectively. The mosaicity in the hexagonal system can be divided into two portions, that is, tilting (misorientation in c axis) and twisting (misorientation in a axis). On the other hand, the degree of distribution of a or c axis implies the relaxation (coherency of a or c axis or strain broadening). Clarification of the relationship between these two types of scans and the effects can aid us to understand the resultant data.

While the $\omega$ scan provides information on the mosaic structure of films, the peak widths of the $\omega - 2\theta$ peak are limited by crystalline coherence lengths and heterogeneous strain distributions.
Figure 1 shows the $\omega-2\theta$ scan (conventional $\theta-2\theta$ scan, radial scan) XRD spectrum of typical InN heteroepitaxial layer. This is indicative of [0001]-oriented hexagonal InN, which was epitaxially grown on GaN. The GaN was grown on the (0001) sapphire substrate with AlN buffer layer. The lattice constant $c$ of InN is estimated by the value of $2\theta$ to be 5.7020 Å, which is in good agreement with the reported values, though they are scattered in the range from 5.69 to 5.96 Å. Peaks of $2\theta$ for InN films grown on AlN and directly on sapphire also had almost the same value as that of InN grown on GaN.

The $\phi$ scans of the InN (1012) peaks are presented in Figs. 2(a)–2(c). InN films were grown on (a) an Al$_2$O$_3$ substrate, on (b) AlN on the substrate, and on (c) GaN on the substrate with an AlN buffer layer. The three peaks of the sapphire substrate reflect its trigonal structure. The hexagonal structure of InN produces six distinct equally spaced peaks. The absence of any other random peaks suggests that the film grains predominantly grow in the direction of [0001]. The 30 degree shift between the InN peaks and those of sapphire is explained by in-plane rotation of the InN lattice with respect to the sapphire substrate. It should be noted that the surface condition of the substrate may be considered to influence the orientation of the epitaxial film. Such types of conditions can increase the number of initial nuclei, which causes them to coalesce in the early stage of the film growth, thereby influencing the orientation of a continuous film. Indeed, such an effect is clearly represented in Fig. 1(a), where InN is found to be grown in the [210]$_{\text{InN}}$/[1010]$_{\text{Al}_2\text{O}_3}$ direction. This is opposite to the direction expected from the lattice mismatches described above.

Figure 3 shows the tilting in the c axis (depicted by $\omega_c$) and the degree of distribution of lattice constant $c$ ($\Delta2\theta$). Data along the y axis are plotted on a logarithmic scale. First, as expected from the difference of lattice mismatches, both $\Delta\omega_c$ and $\Delta2\theta$ of the InN film grown on GaN show the smallest full width at half maximum (FWHMs) among the three samples. Furthermore, an additional tendency can be seen in the figure. Both $\Delta\omega_c$ and $\Delta2\theta$ of InN films grown on an AlN or Al$_2$O$_3$ substrate show almost the same value, about 4000 and 600 arcsec, respectively. Another factor which may affect the growth of InN films is considered to be the residual strain which results from the thermal stress caused by the difference of the thermal expansions between these two materials. Other complex mechanisms may lie in the effect which causes the strain. Of course, considering the difference of lattice mismatch, InN over several hundred Å thick is not coherently grown on the GaN layer. However, if crystal relaxation is not completed, some strain may remain in the
crystalline structure. In fact, residual strain has been reported to be present in GaN with LT-deposited AlN.\textsuperscript{22–27} The presence of residual strain in InN grown on GaN is confirmed by the results shown in Fig. 4. Two parameters, lattice constants $c$ and $a$, for InN films on AlN and Al\textsubscript{2}O\textsubscript{3} are not very different, indicating that the relaxation has a similar degree. On the other hand, as far as the InN film grown on GaN is concerned, lattice constant $a$ is shorter and $c$ is longer compared to those for the other two films. This strongly suggests that strain remains in the film.

As seen above, it has been found that the heteroepitaxial InN film can be structurally improved through reduction of lattice mismatch to the underlying layer.

C. Triple axis XRD analysis: Thickness dependence of InN on its structural properties

While in Sec. III B we dealt with the relationship between structural properties of InN films and lattice mismatch, this section is concerned with the crystal relaxation in the structural properties of InN films. In order to study this property, the dependence on the thickness of InN films grown on GaN on structural properties was studied. Structural properties were assessed by XRD measurement in the same way as in Sec. III B.

Figure 5 shows the thickness dependence of the InN epitaxial layer on its structural properties, particularly focusing on the crystal mosaicity and the crystal relaxation, which are depicted by $\Delta \omega_a$ and $\Delta 2 \theta_c$, respectively. These values were obtained by XRD measurements. The reflection surface was a (0002) symmetrical one. Those two characteristic parameters show a similar tendency in Fig. 5, i.e., the mosaicity (tilting) decreases with increasing InN film thickness, and saturates at about 530 arcsec. The degree of distribution of lattice constant $c$ (the crystal relaxation) remains about 300 arcsec. The values of $\Delta 2 \theta_c$ for InN films with thicknesses of 400 and 800 Å are found to be in relative agreement with the values obtained, assuming a perfect crystal. Whereas, the values for InN films with thicknesses of 1200 and 2400 Å are found to deviate substantially from the ideal values for a perfect crystal. This suggests that while InN film within a thickness of 1200 Å is relaxed, to some extent, due to residual strain, above that thickness, InN tends to grow, taking a different orientation from that of the $c$ axis. This misorientation of the $c$ axis may result from weakens of the bond strength of InN. In fact, in contrast to InN, for GaN the $\Delta 2 \theta_c$ value was as small as 30 arcsec (not shown here).

Considering that reduction of mosaicity indicates coalescence, it is considered that the coalescence process does not proceed above an InN thickness of 1200 Å.

Figure 6 shows InN thickness dependence of lattice constants $c$ and $a$. The former was estimated by XRD $\omega-2 \theta$ scan, and the latter by (10\textbar 1\textbar 0) $\omega$ scan.

As was seen in the preceding section, an InN film on GaN less than 1200 Å thick has been found to be influenced by the residual strain energy. Taking this into account, the decrease of $a$ and the increase of $c$ with increasing InN thickness below 1200 Å indicates a partial release of the strain.

When the thickness of the InN film further increases, lattice constants $c$ and $a$ show the opposite tendency, that is, $c$ decreases and $a$ increases, which suggests the release of the InN film from residual strain.

Figures 7 and 8 show $\Delta \omega_a$ (twisting) and the offcut angle, respectively. The offcut angle is obtained such that the orientation relationship between the sapphire substrate and the InN layers is determined by rocking scans on the (0002) diffraction of InN and that of the substrate with various $\phi$ angles. The sample was rotated about its surface normal and the [0001] direction of the InN film rotated about the $\phi$ axis. Both Figs. 7 and 8 illustrate almost the same phenomena as described in Figs. 5 and 6.

In Fig. 7, $\Delta \omega_a$ peaks of an InN film thickness of about 1200 Å and then decreases. Considering the results in Figs. 5–8, at this thickness, the InN film is considered to change with respect to the growth mode, because the points were
found to change at this thickness. This mixing of two kinds of growth modes can cause $\Delta \omega_a$ to broaden. For example, $\phi$ also shows a peculiar tendency at 1200 Å thickness. This probably means that the orientation of the growth of InN is going. These structural properties assessed by XRD are found to be reflected in the surface morphology as shown in Fig. 9(a)–9(d). Upon increasing the thickness up to 800 Å, the morphology changes to show many additional white-colored wedges. This implies, of course, taking into account the results in Figs. 5–8, that growth in the unit cell begins because of the occurrence of twisting, and at 1200 Å, screw dislocations are seen. Obviously, a change in the growth mode occurs in the region of this thickness. On further increasing the thickness, the morphology changes to a relatively flat one.

Judging from the two cases described above, the following explanation for the InN epitaxy is suggested. At an earlier stage of InN growth, discrete or partially coherent islands of InN are formed and have slightly different crystal orientations and result in a large mosaicity before the film has coalesced. As InN film growth proceeds, these islands will adopt a similar orientation (which may be indicated by the occurrence of screw dislocations) and will eventually form a coherent epitaxial film which has a reduced mosaicity. The reduction of mosaicity with increasing InN epilayer thickness reflects the crystal growth process.

Data here show that crystalline quality ceases to improve after InN thickness of 1200 Å and, indeed, over that thickness, saturation is observed. Consequently, the improvement in crystal quality appears to be related both to dislocation density and to the reduction in the degree of misorientation which is present in the InN film. This phenomenon might be supported by the generation of screw dislocations, because screw dislocations contribute to the increase in the degree of mosaicity.

Above a thickness of 1200 Å, rearrangement of the InN film, which may modify the surface morphology, appears to occur. Additional steps in a different direction are observed in the background of the screw dislocations. It should be noted that scaling in the surface morphology is relatively large, which probably results from the occurrence of growth in units of grains or crystallites. This experimental observation can be supported by the fact that interaction between screw dislocations leads to twist boundaries.

Reduction of $\Delta \omega_a$ appears to yield the subsequent hexagonal structure. It appears that coalescence of the discrete islands in the original InN layer is not achieved. The hexagonal structure of InN is considered to be seeded from a discrete island. A featureless morphology in the background of the screw dislocations for 1200 Å thick InN implies the improved coalescence of the InN layer and may accelerate the coalescence process for the InN film with an increase in thickness. The nucleation layer, which may be called for the thin InN layer, appears to be the source of dislocations in InN films. The weakness of the InN bond strength may help InN islands determine different crystalline orientations. In that situation, during island coalescence, threading dislocation segments may be generated when misfit edge dislocations between adjacent islands are spatially out of phase. This may be the reason for the generation of screw dislocations. Furthermore, since the islands are slightly rotated, the low-angle tilt boundaries, which are composed of edge dislocations, might develop during coalescence.29 The generation of dislocations with screw components appears to proceed more completely for the InN film of thickness above 1200 Å.

As seen above, heteroepitaxial InN films have been found to improve structurally when grown on GaN. In fact, as shown in Fig. 10, such InN films have a high electron Hall mobility compared to InN films grown on layers other than GaN (the GaN was highly resistive). Additionally, it should be noted that the Hall mobility for InN with the thickness of 2400 Å is as high as about 700 cm²/V s even at $5 \times 10^{19}$ cm⁻³. The value corresponds to that for GaAs at the same carrier concentration. Reduction of unintentional impurity concentration will lead to a very high mobility.

**IV. CONCLUSION**

Heteroepitaxial InN films grown by atmospheric pressure MOVPE have been structurally characterized by XRD analysis in terms of lattice mismatch and InN film thickness dependence. In addition, the surface morphology was also studied. In XRD measurement, $\omega$ and $\omega-2\theta$ scans were used in order to estimate the degree of mosaicity and distribution of lattice constants of InN films. In the study on lattice-mismatch dependence, the layers just below InN were altered. Namely, the growth of InN films on GaN, AlN, and directly on sapphire was performed. As expected from the
values of lattice mismatch and the relationship of crystalline orientation, the InN film grown on GaN exhibited the smallest spectral broadening in $\omega$ and $\omega-2\theta$ scans of XRD among the three kinds of samples with respect to crystalline mosaicity and coherency. It is notable that the direct observation of lattice constants $c$ and $a$ has enabled us to check the presence of residual strain.

On the other hand, the study of InN film structural properties as a function of InN film thickness has revealed that an InN film less than 1200 Å thick is composed of grain islands with different crystalline orientations and that the growth mode changes at a thickness of about 1200 Å and screw dislocations are present in the surface morphology. Above that thickness, the residual strain in InN films has been found to be gradually released, resulting in almost the same orientation. This is reflected in the reduction of the mosaicity, the proceeding of relaxation, and the morphology. We have shown that the selection of GaN for the underlying layer of the InN film leads to the structural improvement of the InN film.

In fact, InN films grown on GaN have a high electron Hall mobility compared to InN films on layers other than GaN. It should also be noted that the Hall mobility for InN with a thickness of 2400 Å is as high as about 700 cm$^2$/V s even at $5 \times 10^{19}$ cm$^{-3}$. The value corresponds to that for GaAs at the same carrier concentration.

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