Defect formation mechanism and quality improvement of InAlN epilayers grown by metal–organic chemical vapor deposition

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The effect of growth pressure on defect formation in InAlN epilayers grown on GaN/sapphire templates by metal–organic chemical vapor deposition was systematically investigated in this study. From X-ray diffraction measurements, it was found that a serious phase separation occurred in the InAlN epilayers grown at 1 × 10^4 Pa (100 mbar). The inhomogeneity of the In composition was observed at the beginning of the InAlN growth as examined by transmission electron microscopy. The initial In composition inhomogeneity close to the InAlN/GaN interface was confirmed to play an important role in the formation of V-shaped defects and the phase separation. When the growth pressure increased from 1 × 10^4 Pa (100 mbar) to 5 × 10^4 Pa (500 mbar), the phase separation diminished over 3 × 10^4 Pa (300 mbar), and the In content continuously increased from 6.0 to 25%. However, in spite of the fact that there was no phase separation in the InAlN layer grown at 3 × 10^4 Pa (300 mbar), the inhomogeneity of the In composition still existed near the surface instead of the InAlN/GaN interface. This was caused by the fact that the In adatoms preferred to accumulate at the V-shaped defects which were induced by the low surface mobility and parasitic reaction of Al adatoms. Two distinct formation mechanisms of the V-shaped defects at the low and high growth pressures were confirmed. To explore the effect of thickness on the epilayer quality, a series of InAlN samples (In = ~20%) with various thicknesses ranging from 5 to 125 nm were investigated. The InAlN epilayer with a thickness of 10 nm showed the optimum crystallinity and minimum surface roughness. A higher growth pressure (≥3 × 10^4 Pa (300 mbar)) and a thinner thickness (≤10 nm) favored the In composition homogeneity and suppressed the formation of V-shaped defects. Both key growth parameters were demonstrated in detail to achieve a high-quality InAlN epilayer for device applications.

Introduction

Ternary InAlN alloys have attracted much attention due to their potential application in optoelectronic and electronic devices, such as light emitting diodes, ultraviolet photodiodes, solar cells, and high electron mobility transistors (HEMTs).1–5 InAlN has an adjustable bandgap with a wide range from 0.6 to 6.2 eV, and shows a good lattice match to GaN at In contents of 17–18%.6,7 Besides, a large spontaneous polarization difference in a lattice-matched InAlN/GaN heterostructure can induce a high two-dimensional electron gas sheet carrier density.8 Therefore, the leakage current that flows through the InAlN barrier can be suppressed by employing an InAlN/GaN heterostructure in HEMTs.9

Unfortunately, phase separation and composition inhomogeneity easily occur in InAlN layers due to the large immiscibility gap and the thermal stability discrepancy between InN and AlN.10 Moreover, even if InAlN layers are prepared on a GaN/sapphire template which has a good lattice match to InAlN, there are often some defects, such as intrinsic dislocations in the GaN layer, hillocks, and V-shaped defects on the GaN surface.11–13 These phenomena cause the difficulty in the preparation of InAlN layers with high quality. Realizing the mechanisms of InAlN growth and defect formation is a key solution for improving the epilayer quality of InAlN.

According to the literature, metal–organic chemical vapor deposition (MOCVD) is an adequate process for the preparation of InAlN epilayers.14–16 In this study, the effect of growth pressure on the characteristics and the defect formation mechanism of the InAlN epilayer grown by MOCVD was investigated in detail. Meanwhile, the influence of defect formation on the epilayer quality was further explored by increasing the InAlN layer thickness in order to obtain the...
optimal growth parameters for InAlN epilayers. We expected that a way to improve the quality of InAlN epilayers could be demonstrated by these systematic investigations.

**Experimental**

All samples were grown on 2 inch sapphire substrates by employing an Aixtron 200/4 RF-S MOCVD system. Ammonia (NH₃), trimethylindium (TMIn), trimethylaluminum (TMAI) and trimethylgallium (TMGa) were utilized as N, In, Al and Ga sources, respectively. An undoped GaN layer with a thickness of about 2 μm was pre-grown on sapphire as a growth template. The growth time and temperature were 1800 s and 750 °C. The V/III ratio was kept at 6800 for the InAlN epilayer growth. In the discussion of the effect of growth pressure on the growth of InAlN epilayers, the growth pressures were set at 1 × 10⁴ Pa (100 mbar), 2 × 10⁴ Pa (200 mbar), 3 × 10⁴ Pa (300 mbar), 4 × 10⁴ Pa (400 mbar) and 5 × 10⁴ Pa (500 mbar), which were denoted as samples A₁₀₀, A₂₀₀, A₃₀₀, A₄₀₀ and A₅₀₀ in sequence. The layer thicknesses of the samples were 214.5, 161, 115.4, 72 and 47 nm, respectively. Finally, to explore the effect of thickness on the defect formation in InAlN layers, the growth parameters were maintained at a growth pressure of 5 × 10⁴ Pa (500 mbar), a temperature of 770 °C and a V/III ratio of 6800. Only the growth time was adjusted from 500 to 7000 s to obtain distinct thicknesses. These samples were all denoted as sample B. The epilayer qualities of InAlN were determined by X-ray diffraction (XRD). The full width at half maximum (FWHM) of the InAlN layers were obtained by measuring the rocking curve of the (0002) InAlN diffraction peaks. The surface morphologies and the roughness of the samples were obtained by field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). The Auger chemical state and surface element distribution of the samples were analyzed by nano-Auger electron spectroscopy (nano-AES). Detailed crystal structures of the samples were observed by transmission electron microscopy (TEM).

**Results and discussion**

Fig. 1 shows the XRD spectra of samples A₁₀₀–A₅₀₀, the diffraction peaks of InAlN shift toward low angles with increasing growth pressure from 1 × 10⁴ Pa (100 mbar) to 5 × 10⁴ Pa (500 mbar). According to Bragg’s law, the (0002) lattice spacing (d-spacing) of InAlN epilayers, which shows the largest area ratio of the InAlN diffraction peaks, can be estimated to be 2.5118, 2.5243, 2.555, 2.5702 and 2.5804 Å for samples A₁₀₀, A₂₀₀, A₃₀₀, A₄₀₀ and A₅₀₀, respectively. In addition, the In contents of the samples are calculated to be 6.0%, 9.5%, 18%, 22.2% and 25% by employing Vegard’s law as follows: 

\[ d_{\text{InAlN}} = d_{\text{InN}} + (1 - x) d_{\text{AlN}}, \]

where the \( d_{\text{InAlN}} \) is the d-spacing of InAlN detected by XRD, and \( d_{\text{InN}} \) and \( d_{\text{AlN}} \) are the constant d-spacings of InN and AlN. These In contents represent the In concentration of the whole epilayer in each sample. It is clear that the In contents increase with the growth pressure. This also indicates that the Al contents should decrease with the growth pressure. Zhao et al. and Nakamura et al. proposed that TMAI easily reacts with NH₃ in the gas phase via a parasitic reaction at a high growth pressure instead of participating in the growth reaction on the epilayer surface. Therefore, the Al incorporation in the AlGaN epilayers should decrease with increasing growth pressure. Our study, which shows the reduction tendency of Al contents with raising growth pressure, is in good agreement with the literature. A serious phase separation can be only observed in samples A₁₀₀ and A₃₀₀ in the inset of Fig. 1. For sample A₁₀₀, the In composition in the InAlN layer includes 9.8% and 13% as well as 6.0%, exhibiting composition inhomogeneity. Meanwhile, sample A₂₀₀ also shows In composition inhomogeneity with 13.7% and 9.5%. Compared with samples A₁₀₀ and A₂₀₀, samples A₃₀₀–A₅₀₀ all show good homogeneity of In composition. The FWHM of the (0002) 2θ-scans for InAlN epilayers in samples A₁₀₀–A₅₀₀ are estimated to be 368, 385 and 393 arcsec, respectively. Obviously, the crystallinity can be degraded after increasing the growth pressure. One of the possible factors degrading the crystallinity is the existence of strain. The strain increases with increasing growth pressure from 3 × 10⁴ Pa (300 mbar) to 5 × 10⁴ Pa (500 mbar) in this study (not shown here), and the strain is possibly caused by the lattice mismatch between InAlN and GaN. As a result, we suggest that the slight increase in FWHM could be ascribed to the lattice mismatch. Furthermore, it is worth noting that the strain of sample A₁₀₀ (in = 18%) is the smallest, implying that the lattice of the InAlN layer could be well matched to the GaN underlayer. A transition of the in-plane strain field in InAlN layers from the tensile (In = 6.0%) to the compressive (In = 25%) state with increasing growth pressure to 5 × 10⁴ Pa (500 mbar) can be clearly seen. This implies that the morphologies and the growth mechanisms of the InAlN layers should be distinct from 1 × 10⁴ Pa (100 mbar) to 5 × 10⁴ Pa (500 mbar).
The surface morphologies of samples $A_{100}$–$A_{500}$ are presented in Fig. 2(a)–(e). For sample $A_{100}$, many random stick-like and small disk-like grains are distributed on the InAlN epilayer surface (Fig. 2(a)). As the growth pressure increases to $2 \times 10^4$ Pa (200 mbar), sample $A_{200}$ exhibits larger stick-like grains than sample $A_{100}$, as shown in Fig. 2(b). Above $3 \times 10^4$ Pa (300 mbar), the grains on the InAlN layer surface of all samples show a disk-like shape as displayed in Fig. 2(c)–(e), regardless of the growth pressure. The grain size decreases to around 20–44 nm for sample $A_{300}$ and around 22–33 nm for sample $A_{400}$. From Fig. 2(e), sample $A_{500}$ possesses a smoother surface than the other samples. As we know, Al contents are definitely much higher than In contents due to the low probability of the Al-related parasitic reaction occurring at a low growth pressure. Moreover, Oh et al. pointed out that the surface diffusion length of the Al adatom increases by decreasing the growth pressure.\textsuperscript{19} This can assist in the coalescence of Al adatoms. Therefore, we consider that the formation of the stick-like grains with a large grain size on the InAlN surface could be caused by the enhancement of the surface mobility and the diffusion length of the Al adatoms at a low growth pressure.

From Fig. 3, the surface roughness is measured at gridded areas of $2 \mu m \times 2 \mu m$. The surface roughness decreases to 1.3 nm as the growth pressure increases from $1 \times 10^4$ Pa (100 mbar) to $5 \times 10^4$ Pa (500 mbar). The surface roughness among all samples can be observed in sample $A_{500}$ because of the slow growth rate, as shown in Fig. 3.

From the XRD spectra, we have known that the In composition inhomogeneity can exist during InAlN growth. This could be one of the factors causing the formation of InAlN epilayers with a rough surface and different morphologies. Thus, the relation between the In distribution and the InAlN growth will be discussed in detail as follows. The distribution of Al and In on the surface can be identified by nano-AES, as shown in Fig. 4. The Al distribution in samples $A_{100}$, $A_{300}$ and $A_{500}$ is uniform, as presented in Fig. 4(b). The intensity of the In distribution is weak and unclear only in sample $A_{100}$, implying that a small amount of In is found in the InAlN layer, as shown in Fig. 4(c). This is consistent with the
estimated result from XRD analysis which shows the lowest In content at $1 \times 10^4$ Pa (100 mbar). Additionally, although no phase separation is observed in sample A100, measured by XRD, one can notice that a non-uniform In distribution can be observed on the surface, as shown in Fig. 4(c). Nano-AES is a surface analysis method, whereas XRD is an analysis method which detects a deep range. Consequently, this region, where In is distributed, determined by nano-AES, could be small and very near the surface for sample A100. Meanwhile, compared with sample A100, sample A500 has a more uniform In distribution. As mentioned above, the mechanisms of the In composition distribution seem different at distinct growth pressures. According to the literature, In easily accumulates at the V-shaped defects in the top InAlN layer, causing composition inhomogeneity as the InAlN layer thickness increases.20 We suggest that the rough surface could be ascribed to the formation of V-shaped defects where In accumulates in our study. In the following discussion, we will use TEM to further observe our samples to confirm the relation between the In distribution and the V-shaped defects.

The cross-sectional high resolution TEM (HR-TEM) images of samples A100 and A300 are displayed in Fig. 5. From Fig. 5(a), the thickness of the InAlN layer in sample A100 is estimated to be 214.5 nm. Fig. 5(b) displays region 1 of sample A100 at the InAlN/GaN interface in Fig. 5(a), and shows that three zones with different $d$-spacings are found in the InAlN layers. The zone with a $d$-spacing of 2.521 Å is the majority, and shows an In content of 8.6%. The In-rich zones with In contents of 23.3% and 28.8% reveal a $d$-spacing of 2.574 and 2.594 Å as marked by pink and blue circles, respectively. Obviously, the In composition inhomogeneity can initially occur near the InAlN/GaN interface. At a low growth pressure (sample A100), the formation probability of the Al-related parasitic reaction is low, and the Al surface mobility is high enough. In contrast, In is difficult to incorporate and thus the number of In adatoms is deficient. Therefore, both the In-poor and In-rich InAlN grains could simultaneously form at the beginning of the InAlN growth. When the InAlN layer successively grows in the intermediate interface in region 2 in Fig. 5(a), another $d$-spacing of 2.588 Å (In = 27.2%) is observed (Fig. 5(c)) aside from the $d$-spacing values found in region 1. Above region 2, region 3 is found which is near the surface and marked in Fig. 5(a), showing only a $d$-spacing of 2.521 Å (In = 8.6%), as shown in Fig. 5(d). We suggest that the grains with different In contents could cause the formation of strain. For the relaxation of this strain, the layer should have some defects, such as V-shaped defects. In addition, a certain growth structure could be formed through these defects. This growth structure is possibly a columnar structure as seen in the cross-sectional TEM image in Fig. 5(a). Furthermore, since it is already known that Al dominates the growth at $1 \times 10^4$ Pa (100 mbar), the In-poor InAlN grains with a $d$-spacing of 2.521 Å (In = 8.6%), namely the Al-rich grains, should uniformly and mainly grow at the final growth stage. Fig. 5(e) displays sample A300 with a thickness of 115.4 nm. The lattice fringes of region 1, region 2 and region 3 are shown in Fig. 5(f)–(h), respectively. At the beginning of the growth (region 1), the grains of sample A300 show more uniform In composition than sample A100. However, region 2 (Fig. 5(g)) also shows different In compositions which are similar to region 2 in sample A100. Interestingly, In composition inhomogeneity still arises during the growth of InAlN layers, even if the InAlN layers have a good lattice match to the GaN/sapphire templates. These In compositions are 18% ($d = 2.555$ Å), 23.6% ($d = 2.575$ Å) and 28.8% ($d = 2.594$ Å). Among these three In compositions, In = 23.6% and In = 28.8% both exist in the V-shaped region marked by the cyan line in Fig. 5(g). When the InAlN layer continuously grows until the whole growth finishes (region 3), another
InAlN lattice with a d-spacing of 2.626 Å (In = 37.7%) is observed close to the surface (Fig. 5[h]). As mentioned above, it can be suggested that the lattices with 2.555 Å (In = 18%) should be major, whereas lattices with other d-spacings should be caused by the composition inhomogeneity. This is also well consistent with the measurement result obtained by XRD. Since lattices with other d-spacings except 2.555 Å are in the V-shaped region, we consider that the formation of V-shaped regions, namely V-shaped defects, could be the factor causing the composition inhomogeneity. In general, at a high growth pressure, both the incorporation and the surface mobility of the Al adatoms deteriorate due to the Al-related parasitic reaction, reducing the probability of lateral growth of InAlN layers. Therefore, the V-shaped defects could be induced even if the InAlN layer has a good lattice match to GaN and the In composition is homogeneous near the interface of the InAlN and the GaN/sapphire template. Interestingly, one can also find that the formation of V-shaped defects seems to occur over a critical thickness. In addition, an energy barrier exists between the V-shaped defects and the sequence layers. This can result in the reduction of the migration of adatoms, causing the surface to become rough.\(^{13,21,22}\) As mentioned above, the thickness could play an important role in affecting the growth of InAlN. This indicates that if one can control the thickness to be below a critical value, an InAlN layer with good crystallinity can be achieved by suppressing the formation of V-shaped defects and the composition inhomogeneity. This will be confirmed in the following sections.

To describe the growth mechanism in detail at different growth pressures, we demonstrate the growth mechanisms of samples A\(_{100}\) and A\(_{300}\) based on the results obtained from TEM analyses, as illustrated in Fig. 6. At the first growth step of sample A\(_{100}\) (Fig. 6(a)), In composition inhomogeneity of the InAlN layer comprising In-rich and In-poor grains occurs due to the low incorporation efficiency of In at a low growth pressure. Meanwhile, this low growth pressure can effectively assist Al in reducing the formation probability of the Al-related parasitic reaction, and enhancing the surface mobility to cause the formation of an InAlN layer which includes most In-poor grains at the beginning of the growth. Furthermore, the In-poor InAlN grains possess significant tensile strain and present a concave surface structure. For the relaxation of the tensile strain, the V-shaped defects can be induced during the growth. In addition, the V-shaped defects could serve as a place where In adatoms prefer to incorporate to form the In-rich grains, as shown at the second growth step in Fig. 6(b). At the third growth step (Fig. 6(c)), the InAlN can grow in a columnar configuration rather than a dense film configuration because of the strain relaxation induced by the grains with distinct In compositions. Therefore, a rough surface with hillocks and pits can be observed. For the sample grown at \(3 \times 10^4\) Pa (300 mbar), the high growth pressure assists in the improvement of In incorporation, so the InAlN layers show good In composition homogeneity in the initial growth stage, as shown at the first growth step in Fig. 6(d).

However, as the layer continuously grows, the V-shaped defects could be formed due to the Al-related parasitic reaction and low surface mobility. At the final growth step (Fig. 6(f)), the In adatoms favor accumulation at the V-shaped defects to achieve In-rich grains. Moreover, when the thickness increases, both the V-shaped defects and the In-rich grains are formed in the InAlN layer, followed by the display of a rough structure on the surface. As illustrated in the InAlN growth mechanisms at \(1 \times 10^4\) Pa (100 mbar) and \(3 \times 10^4\) Pa (300 mbar), it can be clearly realized that two distinct factors cause the formation of V-shaped defects. One is the inhomogeneity of the In composition during the initial growth at a low growth pressure. The other is the Al-related parasitic reaction and the low surface mobility of Al adatoms at a high growth pressure.

To further understand the effect of thickness on the characteristics of the InAlN layer, the XRD spectra of sample B with thicknesses from 5 to 125 nm are shown in Fig. 7. The In composition of sample B is maintained at around 20%. Phase separation occurs in the InAlN layer when the thicknesses are 64 and 125 nm. The FWHM of the (0002) ω-scan rocking curve and the surface roughness for sample B are presented in Table 1. InAlN layers with good crystallinity show FWHM values of 253 and 255 arcsec in sample B with
Fig. 7 X-ray diffraction spectra of sample B with various thicknesses (t).

Table 1 Parameters of sample B including the thickness (t), FWHM of (0002) ω-scan rocking curve and surface roughness (2 μm × 2 μm)

<table>
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<tr>
<th>Thickness (t) (nm)</th>
<th>(0002) FWHM (arcsec)</th>
<th>Surface roughness (nm)</th>
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<tr>
<td>5</td>
<td>253</td>
<td>0.7</td>
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<tr>
<td>10</td>
<td>255</td>
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<td>39</td>
<td>268</td>
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<td>64</td>
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<td>125</td>
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thicknesses of 5 and 10 nm, respectively. Meanwhile, the surface roughness of these two samples is 0.7 nm. As the thickness increases from 39 to 125 nm, the FWHM of the InAlN layers increases to 313 arcsec, and the surface roughness increases to 2 nm. These indicate that the large FWHM, the rough surface and the phase separation occur beyond the layer thickness of 10 nm. In other words, 10 nm is the critical thickness for achieving a high quality InAlN layer.

Fig. 8 shows the surface morphologies of sample B with various thicknesses. A smooth surface is observed in sample B under a thickness ≤10 nm, as shown in Fig. 8(a) and (b). When the thickness increases from 39 to 125 nm (Fig. 8(c)–(e)), pits form, and the size of the pit gradually increases with the thickness. The literature refers to this phenomenon as compressive strain of the InAlN layer which can be relaxed via the formation of hillocks and V-shaped defects on the layer surface.13 Furthermore, the sample with In = ~20% shows compressive strain (not shown here). We believe that these pits in our study could be caused by the hillocks and V-shaped defects in the InAlN layer for the relaxation of the strain. In other words, the InAlN layer should have less defects under a thickness ≤10 nm than under a thickness >10 nm.

The high quality InAlN layer with a thickness of 10 nm exhibits a uniform d-spacing of 2.561 Å (In = 19.7%), as displayed in Fig. 9(a). When the thickness increases to 125 nm (Fig. 9(b)), a saw-tooth morphology is visible on the InAlN surface. Fig. 9(c) displays the lattice image near the surface of the 125 nm-thick InAlN layer where region 1 is marked in Fig. 9(b). There is In composition inhomogeneity including two distinct In contents. It is notable that a high In content of 30.5% with a d-spacing of 2.6 Å appears at the bottom of the V-shaped regions. These two distinct In contents confirm the occurrence of phase separation determined by XRD. This also indicates that the phase separation is related to the V-shaped defects. According to the critical layer thickness of InAlN, our results are in good agreement with the model developed by Holec et al.20,23 We conclude that a thick thickness is harmful to the preparation of the InAlN layer with high quality, because In concentration inhomogeneity and the formation of V-shape defects occur. Obviously, an adequate thickness is a very important factor in achieving an InAlN epilayer with high quality. The quality of the InAlN epilayer could be effectively improved by lowering the thickness below a critical value. In other words, if one would like to achieve a high quality InAlN epilayer, the optimum growth pressure and thin thickness are both necessary.

Fig. 8 Surface morphologies of sample B with thicknesses (t) of (a) 5, (b) 10, (c) 39, (d) 64 and (e) 125 nm.

Fig. 9 (a) HR-TEM image of sample B with a thickness of 10 nm at the InAlN/GaN interface. (b) Cross-sectional TEM image and (c) HR-TEM image of sample B with a thickness of 125 nm near the surface.
Conclusions

The In contents of the InAlN layers increased from 6.0% to 25% as the growth pressure increased from $1 \times 10^4$ Pa (100 mbar) to $5 \times 10^4$ Pa (500 mbar). A serious phase separation was found in the InAlN layer grown at $1 \times 10^4$ Pa (100 mbar) by XRD and TEM analyses. The phase separation resulted from the initial In composition inhomogeneity. The In composition inhomogeneity was the main factor causing the formation of V-shaped defects at a low growth pressure. At $3 \times 10^4$ Pa (300 mbar), the InAlN layer exhibited a uniform In composition observed by XRD analysis. However, actually, In composition inhomogeneity still occurred in the InAlN layer displayed in the HR-TEM images. This could be attributed to the fact that In adatoms preferred to accumulate at the V-shaped defects which were induced by the low surface mobility of Al adatoms and the Al-related parasitic reaction at a high growth pressure. In the discussion of the effect of thickness on the InAlN layers, it was found that a phase separation occurred in the InAlN layers as the thickness increased to 64 and 125 nm. This indicated that there was In composition inhomogeneity. A good crystallinity of the InAlN layer with a (0002) FWHM of 255 arcsec and a surface roughness of 0.7 nm was achieved at a thickness of 10 nm which was the critical thickness. Moreover, this sample displayed In composition inhomogeneity and V-shaped defects.

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Notes and references