Characterization of the Crystalline Quality on GaN on Sapphire and Ternary Alloys

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SUMMARY

The growth of GaN on sapphire by OMVPE using a low-temperature deposited buffer layer was characterized by in situ TEM observation. The crystalline quality, especially tilting and twisting of the mosaic GaN crystal, was characterized by conventional X-ray diffraction together with grazing-incidence X-ray diffraction. Strain and relaxation of the AlGaN and GaInN on GaN were also characterized by asymmetrical X-ray diffraction. © 1998 Scripta Technica, Electron Comm Jpn Pt 2, 81(10): 48–54, 1998

Key words: Low temperature deposited buffer layer; mosaic structure; twist and tilt; strain and relaxation.

1. Introduction

Group III nitride-based blue and green light emitting diodes (LED) have already been commercialized, and laser diodes (LD) in the near ultra-violet (UV) and deep purple region have been fabricated. Moreover, a high-power field-effect transistor that operates in the GHz region, and also a solar-blind high-sensitivity UV detector have been constructed. All of these novel devices are fabricated on highly lattice-mismatched substrates, such as sapphire or 6H-SiC. This is quite extraordinary if we compare it with other systems, such as GaAs-based devices or InP-based devices, in which lattice matching is believed to be the most important requirement.

In this paper, we will report the growth modes, especially the initial growth stage, of GaN on sapphire at the atomic scale, and the crystalline properties of GaN on sapphire. Ternary alloys such as AlGaN and GaInN are also important for the fabrication of novel devices. We also report on the crystalline quality of ternary alloys on GaN.

2. Growth Mode of GaN on Sapphire at Atomic Scale

When c-axis–oriented GaN is grown on (0001) sapphire, the in-plane lattice mismatch can be as large as 16.1% at room temperature. Therefore, it is quite difficult to grow high-quality GaN directly on a sapphire substrate. In the following discussion, we assume fairly controlled conditions for the growth of nitrides by organometallic vapor phase epitaxy (OMVPE). Figure 1(a) shows schematically the growth process of GaN directly grown on sapphire substrate. In the initial stage, three-dimensional GaN islands are partially formed. The origin of GaN island formation is either an atomic step side of sapphire or a dislocation site. In order to relieve the large stress caused by the difference of the in-plane lattice constants between GaN and sapphire, the islands might be grown with slight tilting and/or twisting compared with the crystal orientation of the sapphire. In the next stage, due to a difference in the growth rate of GaN on sapphire and that on GaN, or, in other words, due to the difference in the consumption rate of the source gases (in this case Ga-alkyls such as TMGa or TEGa), selective growth occurs. The consumption rate of Ga-alkyls is expected to be much higher on a GaN surface. Therefore,
the three-dimensional GaN islands with tilting and twisting become larger and larger until they coalesce. Large crystal defects are formed at the interfaces between islands. Such GaN shows strong n-type conductivity and low electron mobility, and p-type GaN had never previously been achieved.

In order to improve the crystalline quality of GaN on sapphire, first, a single crystalline AlN layer was intermediately grown between the GaN and sapphire substrate by molecular beam epitaxy [1]. However, the residual donor concentration was still in excess of $10^{19} \text{ cm}^{-3}$, and the Hall mobility was less than 50 cm$^2$/Vs. By using a low-tempera-

Fig. 1. (a) Schematic viewgraph of the OMVPE growth of GaN directly on sapphire. (b) Schematic viewgraph of the crystallization of a low-temperature AlN buffer layer deposited by OMVPE on sapphire, observed by TEM with high-temperature sample holder. [8] (c) Schematic viewgraph of the initial growth of GaN on crystallized AlN buffer layer. [9]
ture deposited AlN [2] or GaN [3] buffer layer before the growth of GaN at high temperature, the situation was changed dramatically, and high-quality GaN with a low residual donor concentration, a high electron mobility, a narrow X-ray rocking curve, free exciton emission, and stimulated emission at room temperature, among other features, have been obtained. This finding led to the first successful p-type GaN [4, 5], pn-junction LED [4], and blue/UV-LED [6], and to observation of the quantum size effect [7].

Figure 1(b) schematically shows the crystallization process while ramping up the temperature of the low-temperature deposited AlN buffer layer (LT-AlN) on sapphire, and Fig. 1(c) shows schematically the crystal growth process of the high-temperature grown GaN layer (HT-GaN) on crystallized LT-AlN as observed by in situ transmission electron microscopy (TEM) [8] and high resolution scanning electron microscopy (SEM) [9], respectively. In most cases, the thickness of the LT-AlN is about 20 to 100 nm and the deposition temperature is about 350 to 600 °C. As-deposited LT-AlN consists of very fine crystallites. During ramping up from the deposition temperature to the epitaxial temperature, about 950 to 1100 °C, the fine crystallites merge to form large grains. This atomic rearrangement occurs from the sapphire side and proceeds to the surface side. When the substrate temperature reaches the epitaxial temperature, truncated hexagonal mesa islands surrounded by (0001) and {101_1} facets are formed, and the whole LT-AlN layer is then composed of such islands, forming a brick-like structure. Compared to GaN islands grown directly on sapphire, the process of lattice mismatch relaxation should be different. In the case of HT-GaN growth on LT-AlN, selective growth like that of GaN directly grown on sapphire may not occur, but orientational selectivity occurs. Largely misoriented crystallites are surrounded by dislocations and embedded. Finally, the crystal orientation of the whole HT-GaN layer becomes aligned.

It is well known that an HT-GaN layer grown on sapphire using LT-buffer layer has a mosaic structure composed of columns with diameters of 0.1 µm to a few µm. Next, methods of characterizing the crystalline quality of these layers using X-ray diffraction, and the relationship between these properties with other properties such as optical properties and electrical properties, are discussed. Each column itself contains few threading dislocations. Threading dislocations are formed around each column because the columns are slightly misoriented with respect to each other. The misorientation is mainly divided into two parts, tilting and twisting. Tilting is the misorientation of the c-axis of the columns, while twisting is the in-plane rotation of the columns. X-ray diffraction itself is a method of measuring the diffraction profile in the reciprocal lattice space. By using X-ray diffraction, not only the lattice spacing, but also the tilting and twisting of the mosaic structure can be characterized. Figure 2(a) shows schematically the X-ray diffraction profile from GaN having a mosaic structure around the (0002) diffraction spot in the

![Fig. 2. Schematic viewgraph of the X-ray diffraction mapping in the three-dimensional reciprocal lattice space from the GaN having mosaic spread; (a) shows X-ray diffraction mapping around the (0002) diffraction; (b) shows that around (1010) diffraction. a Shows diffraction profile taken by ω-mode scan. b Shows diffraction profile taken by 2θ/ω-mode scan with analyzer crystal.](image-url)
three-dimensional reciprocal lattice map (RLM). In the ordinal X-ray diffraction measurement, the \( \omega \)-mode and \( 2\theta/\omega \)-mode are traces of “a” and “b”, respectively. If the dispersion of the incident X-rays is negligibly small and thickness of GaN is thick enough, “a” and “b” reflect the tilt profile and fluctuations in the lattice constant, respectively [10, 11]. In many cases, the tilt profile is wider than the fluctuation in the lattice constant, which results in a disk-like profile of X-ray diffraction in RLM. Table 1 shows one example of the \( \Delta \omega_a \) and \( \Delta c \) of GaN grown on sapphire by OMPVE using an LT-AlN buffer layer. The lattice constant \( c \) can be precisely measured by using such symmetrical diffraction, while in a plane lattice, constant \( a \) can be measured in combination with symmetrical diffraction and asymmetrical diffraction such as (11\( \bar{2} \)4), (202\( \bar{4} \)), (101\( \bar{5} \)). In order to characterize twisting of the layer, we cannot use such asymmetrical diffraction. We need to rock the sample perpendicular to the rocking direction of symmetrical diffraction measurement. As shown in Fig. 2(b), (10\( \bar{1} \)0) diffraction is promising for measurement of both in plane lattice constant \( a \) and twisting. In Fig. 2(b), “a” shows the \( \omega \)-mode rocking curve profile, which reflects twisting of the film, while “b” shows the \( 2\theta/\omega \)-mode profile which reflects fluctuations in the lattice constant \( a \). Experimental results on \( \Delta \omega_a \) and \( \Delta a \) are given in Table 1.

### 3. Heteroepitaxy of AlGaN and GaInN Ternary Alloys on GaN

In order to fabricate high-performance LEDs or LDs, heteroepitaxy of ternary alloys is essential. The binary compounds AlN, GaN, and InN are lattice-mismatched with each other. Therefore, understanding the crystalline quality of AlGaN and GaInN, especially the strain and relaxation caused by lattice mismatch, is one of the most critical issues.

The in-plane lattice mismatch between AlN and GaN is at most 2.4%, while that of InN and GaN can be as large as 11%. In this paper, we characterize the crystalline quality of AlGaN and GaInN on GaN, with AlN and InN molar fraction of less than 0.3 for both ternary alloys.

In order to characterize the macroscopic strain features of ternary alloys or the relaxation of the dislocations, X-ray diffraction is very useful. By measuring the X-ray diffraction profile in the RLM around the asymmetrical diffraction spot, for example, (11\( \bar{2} \)4) or (202\( \bar{4} \)) in the reciprocal lattice map, we can directly characterize the strain and relaxation situation of the ternary alloys on binary GaN. Figure 4 schematically shows the RLM around (0004), (202\( \bar{4} \)) and (10\( \bar{1} \)0) diffraction spots of the GaInN and AlGaN grown on GaN. The abscissa is proportional to the inverse of the lattice constant \( a \), while the ordinate is proportional to the inverse of the lattice constant \( c \). In the figure, both the fully relaxed case and the fully strained case are shown. If the abscissas of the peak positions of the asymmetrical diffraction of the ternary alloys are just aligned to that of GaN, the in-plane lattice constants of the ternary alloys are the same as that of GaN. This is the fully strained case, sometimes called coherent growth. But if the peak positions of the asymmetrical diffraction of the ternary alloys are just aligned to that of GaN, the in-plane lattice constants of the ternary alloys are the same as that of GaN. This is the fully relaxed case, called free standing case. It is very clear from this figure that to determine the alloy composition of the strained ternary alloys, special attention is necessary. When the ternary alloys are fully relaxed, we can determine the alloy composition by precisely measuring the \( 2\theta/\omega \)-mode symmetrical diffraction profile and assuming Vegard’s law. Otherwise, if ternary alloys are grown coherently, we measure the \( 2\theta/\omega \)-mode symmetrical diffraction and have to calculate...
Fig. 4. Two-dimensional reciprocal space mapping around (2024) diffraction of AlGaN and GaInN grown on GaN. Both those of coherently grown AlGaN and GaInN and perfectly relaxed AlGaN and GaInN are represented.

Fig. 5. (a) AlGaN and (b) GaInN grown coherently on GaN. Actual critical layer thickness above which ternary alloys show lattice relaxation is thought to be much thicker than these results.
by assuming Hooke’s law [12]. If the layers are strained but partially relaxed, we need to measure both $a$ and $c$.

Figure 5 shows the experimentally determined thickness of AlGaN and GaInN, which showed coherent growth on GaN. Theoretical results of Matthews and Blakeslee [13] and of Fisher and others [14], both of whose approaches assumed a balance between the strain energy and energy of generation of misfit dislocation, are shown for comparison. As shown in the figure, the range of thickness of ternary alloys in which the ternary alloys show coherent growth is much wider than that of the misfit dislocations estimated from the above-mentioned theory, and the critical thickness for lattice relaxation is expected to be much thicker, as shown by the arrow.

4. Conclusions

The growth modes of GaN on sapphire, the crystalline quality of GaN on sapphire, and the crystalline quality of the ternary alloys AlGaN and GaInN on GaN are surveyed. The density of threading dislocations in the GaN layer grown on sapphire by OMVPE using LT-buffer layer ranges from $10^8$ to $10^{11}$ cm$^{-2}$. Recently, by using the lateral epitaxial overgrowth technique, commonly used in silicon-on-insulator growth [15], high-quality GaN with a dislocation density of $10^6$ to $10^7$ cm$^{-2}$ GaN has been achieved [16]. Lateral epitaxial growth reduces threading of dislocations. GaN with a much lower dislocation density or even dislocation-free GaN will surely improve the performance of LEDs, LDs, or FETS. They are also important for identification of the intrinsic properties of nitrides.

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