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# Novel aspects of the growth of nitrides by MOVPE

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**Abstract**

Recent topics in the growth of group III nitrides by MOVPE are reviewed. The process of low-temperature deposition of the buffer layer and the effect of the low-temperature-deposited interlayer on the growth of AlGaN are discussed. The growth of AlGaN on grooved GaN and on substrates is reviewed. Finally, recent topics on the growth of In-containing alloys in terms of the future aspects of new devices are presented.

(Some figures in this article are in colour only in the electronic version; see `www.iop.org`)

## 1. Introduction

The first demonstration of growth by metallorganic vapour phase epitaxy (MOVPE) of GaN and AlN films was carried out by Manasevit *et al* in 1971 [1]. They used triethylgallium and ammonia as source gases, and obtained highly *c*-axis oriented films on sapphire(0001) and on 6H-SiC(0001) substrates. From that point, it took 13 years to demonstrate a mis-type light-emitting diode (LED) based on GaN, which was achieved by Kawabata *et al* [2], although its performance was limited. Poor crystalline quality prohibits the functioning of high-performance devices.

A great advance in crystal growth was achieved in 1986 [3]. Use of a low-temperature-(LT-) deposited buffer layer enabled the realization of high-quality GaN films. Currently, the LT-buffer technique is one of the most popular *de-facto*-standard methods for the growth of GaN on sapphire by MOVPE.

Conductivity control of GaN was achieved in the late 1980s by doping with Si in case of n-type GaN [4], and by doping with Mg with a special treatment in the case of p-type GaN [5].

In addition to this high-yield growth technology and the conductivity control, establishment of the growth of highly luminescent GaInN [6] led to the commercialization of blue LEDs [7].

Optimization of the structure for the quantum wells with GaInN wells and GaN barriers enabled the realization of high-efficiency LEDs in which band-to-band transition was used [8, 9], and then led to the achievement of the nitride-based violet laser diodes [10], which was unforeseen in the 1980s.

Currently, the market for nitride-based optoelectronic devices is growing larger and larger. It should be pointed out that this success is based on finding and understanding the properties of nitrides and establishing the technology for utilizing them. In this section, issues of the MOVPE growth of nitrides, that is, GaN, AlGaN, GaInN and AlInN are reviewed.

## 2. Growth of GaN using an LT buffer layer

As shown in figures 1(a) and 1(b), the LT buffer layer growth proceeds as follows: (1) deposition of AlN (or GaN) at low temperature, (2) rearrangement of the atoms with linear increase of the substrate temperature and (3) growth of GaN at epitaxial temperature. Before this process, the effect of the nitridation of the sapphire substrate is sometimes carried out. When (0001) sapphire is exposed in a flow containing ammonia at around 1100 °C or higher, highly *c*-axis oriented AlN is formed on the surface, which is called a nitridation process. The optimum deposition condition for the LT buffer layer is affected by whether the sapphire is nitrided or not. In this review, the process without nitridation is explained.

### *2.1. Deposition of AlN (or GaN)*

The optimum thickness of an AlN layer deposited at around 500 °C is 20–50 nm. As-deposited LT-AlN is composed of fine crystallites with a diameter of 3–5 nm. In the case of LT-GaN, the layer is composed of highly *c*-axis oriented grains with a diameter larger than that of AlN. One group reported the inclusion of the cubic phase GaN [11].

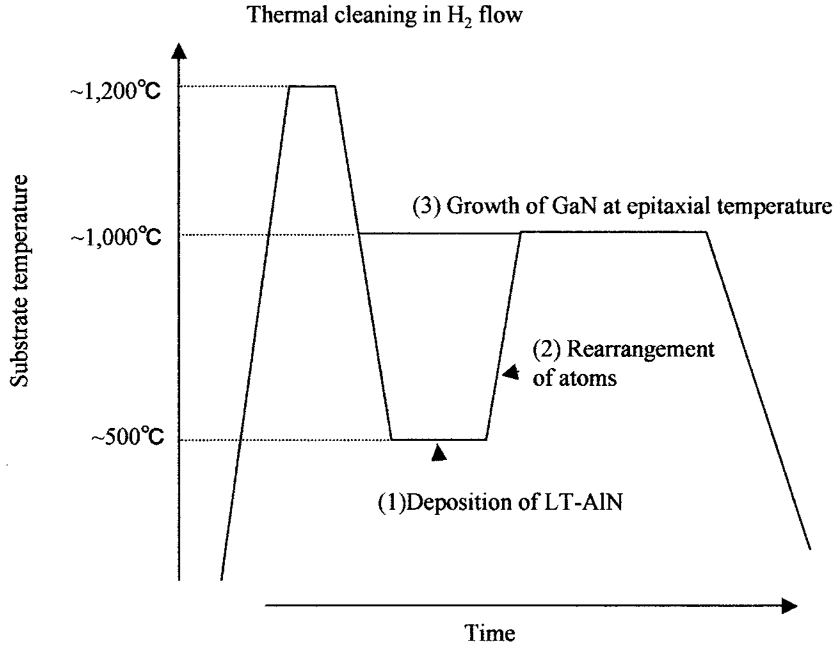
### *2.2. Rearrangement of the atom*

High-temperature transmission electron microscopy (TEM) observation showed that rearrangement of the atoms occurred during increase of the substrate temperature from the deposition temperature to the epitaxial temperature at around 1050 °C. In the case of LT-AlN, fine crystallites changed to columns with a diameter of 10–50 nm. A TEM image of the LT-AlN after growth of GaN is shown in figure 2. Crystal orientation and quality of the sapphire substrate may be transferred through these columns. In comparison, LT-GaN forms large single crystal islands. Size and density are dependent on the temperature-ramp condition.

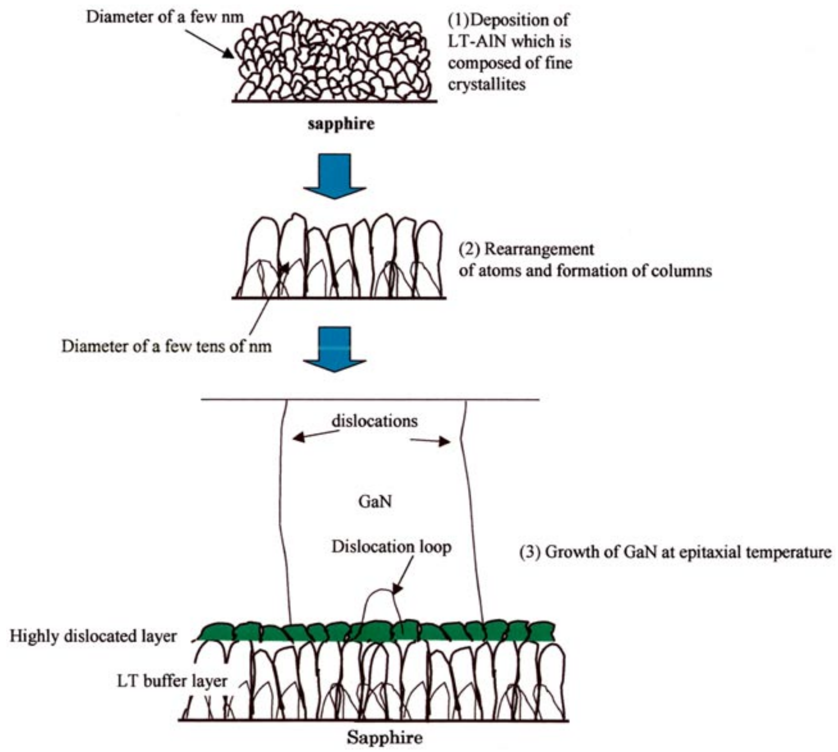
### *2.3. Growth of GaN at epitaxial temperature*

The TEM image in figure 2 shows that a high-density defect region with a thickness of 10–30 nm is formed after growing GaN on LT-AlN, at which many of the dislocations are terminated. Dislocations with a density of $10^8$–$10^{10}$ $cm^{-2}$ remain in the upper part of the GaN layer [12]. The dominant types are pure-edge and mixed dislocations. The density of the pure-screw dislocation is less than $10^8$ $cm^{-2}$.

Figure 3 schematically shows the macroscopic structure of GaN grown on different LT buffer layers. GaN is grown under tensile stress when LT-GaN is used as the buffer layer. The origin of the grown-in tensile stress is suggested to be a coalescence of the islands during high-temperature growth [13], or the successive growth on tensile-strained LT-GaN [11]. In comparison, if LT-AlN is used as the buffer layer, GaN is initially grown under compressive stress, which then changes to tensile stress. The lattice constant of AlN is smaller than that of GaN. Therefore, GaN is expected to be grown on each AlN column under compressive stress at the very initial stage. It is soon relaxed and tensile stress builds.




(a)




(b)

**Figure 1.** (a) Temperature sequence of the MOVPE growth of GaN and the process of the LT buffer layer. (b) Schematic structure of the LT buffer layer in different processes.

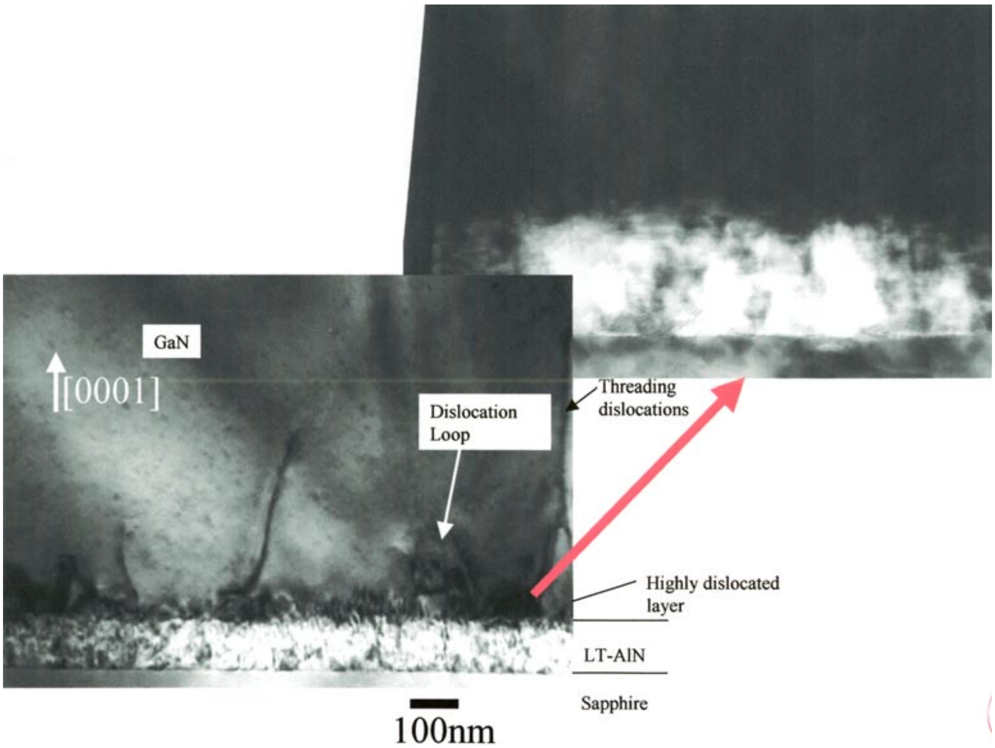



**Figure 2.** Cross-sectional TEM image of the GaN grown on sapphire covered with LT-AlN. The expanded image in the upper right shows the columnar structure of LT-AlN.


**Figure 3.** Macroscopic schematic structure of GaN grown on different LT buffer layers. In the case of LT-GaN, GaN is grown under constant tensile stress, while in the case of LT-AlN GaN is grown under compressive stress at the very initial stage, which then changes to tensile stress.

## 3. Growth of AlGaN using an LT interlayer

Compared to GaN, it is not so easy to grow high-quality and thick AlGaN. Although the crystalline quality of AlGaN on sapphire is improved by using an LT buffer layer, it progressively worsens with increasing AlN molar fraction [14]. The crystalline quality was significantly improved when an AlGaN layer was grown on a high-quality GaN layer. But a crack network originating from the tensile stress induced by the lattice mismatch between AlGaN and GaN is generated with a high density if the thickness of AlGaN exceeds a critical value [15].

The fracture problem in an AlGaN-on-GaN heterostructure was solved by utilizing another LT-AlN layer. Figure 4 schematically shows how to use another LT-AlN layer. The LT-AlN is inserted between the underlying GaN layer and the upper AlGaN layer, and is called an 'LT interlayer' [16]. The major effect of the LT interlayer is the reduction of tensile stress during growth and reduction of the threading dislocations which have screw components. Figure 5 shows the difference of the grown-in stress of the $Al_{0.18}Ga_{0.82}N$ on GaN (a) with and (b) without the LT-AlN interlayer. Nearly free-standing AlGaN can be grown on the LT interlayer, while relaxation occurs during growth of $Al_{0.18}Ga_{0.82}N$, which is confirmed by the steep decrease of the stress × thickness product in figure 5(b). It is important to emphasize that the crystalline quality of this AlGaN is far superior to that growth on sapphire covered with an LT buffer layer, which was confirmed by the TEM observation. The results are summarized in table 1. The reduction of the density of screw and mixed threading dislocations leads to the reduction of the leakage current in solar blind UV photoconductors and pin photodiodes. This result indicates that screw and/or mixed dislocations act as the leakage current path. A flame sensor which shows a response to the extremely low-intensity UV light of 10 nW $cm^{-2}$ has been achieved [17, 18].

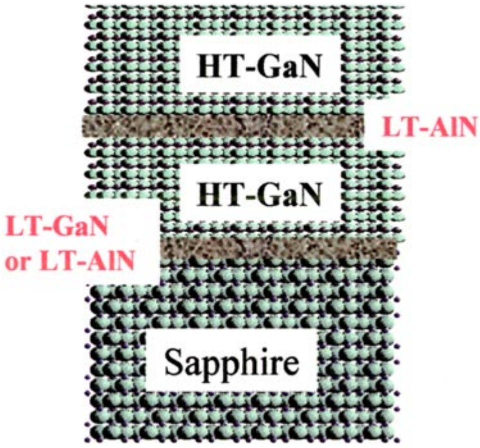



**Figure 4.** Schematic structure explaining how to use an LT interlayer.

**Table 1.** Summary of the density of each threading dislocation in $Al_{0.47}Ga_{0.53}N$ ($cm^{-2}$).

| | Pure edge | Pure screw | Mixed | Total |
|---|---|---|---|---|
| With LT interlayer | $> 10^{11}$ | $>10^{11}$ | $>10^{11}$ | $2 \times 10^{11}$ |
| Without LT interlayer | $8–10 \times 10^{9}$ | $<10^{6}$ | $<10^{7}$ | $8–10 \times 10^{9}$ |

One of the disadvantages of the LT-AlN interlayer technique is the increase of the density of edge dislocations, which are found to act as a nonradiative recombination centre [19]. Therefore, the fabrication of highly luminescent AlGaN was difficult.

## 4. Growth of low dislocation density AlGaN using grooved GaN or sapphire substrate

The epitaxial lateral overgrowth technique [20, 21] using a dielectric mask such as $SiO_x$ or $SiN_x$, which is very effective in growing low-dislocation-density GaN on sapphire, SiC or

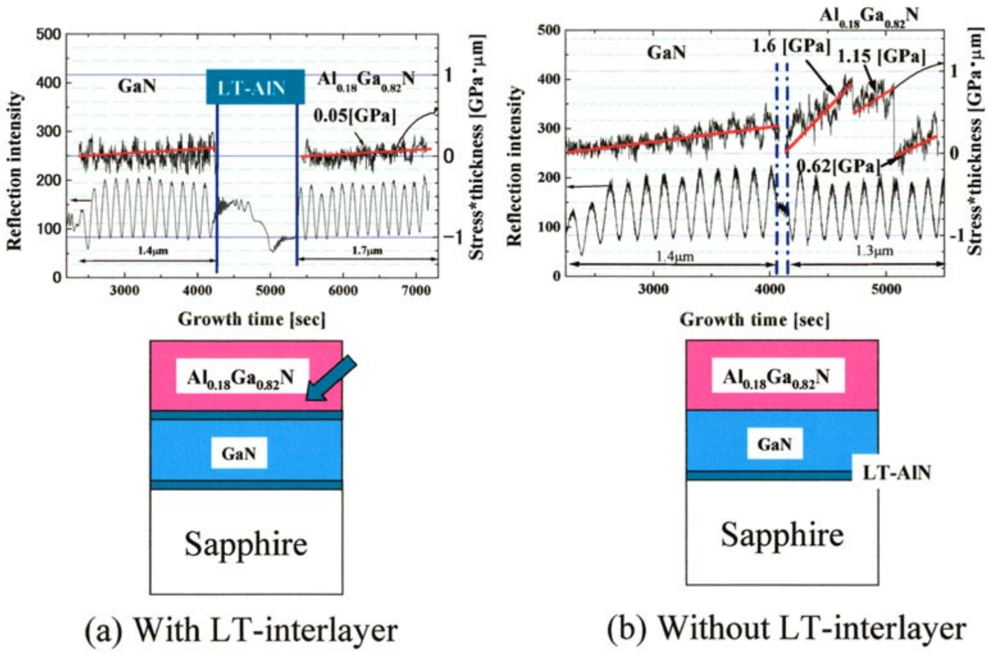



**Figure 5.** Schematic structure of AlGaN/GaN heterostructure grown (a) with and (b) without LT interlayer. Upper figures show the stress × thickness product and reflectivity measured *in situ*. The value of the grown-in tensile stress for each growth process is also shown.

Si, cannot be applied in the growth of AlGaN especially with a high AlN molar fraction due to the deposition of polycrystalline islands on the mask. Another method of growing low-dislocation-density AlGaN is to use grooved GaN [22, 23]. Figure 6 schematically shows the structure for utilizing grooved GaN. Again, it should be emphasized that the LT interlayer is essential to reduce fracture problems. Figure 7 shows the CL image at cryogenic temperatures of the $Al_{0.25}Ga_{0.75}N$ grown on grooved GaN covered with the LT interlayer. As shown in the figure, several dark spots can be seen in the grooved region while it is entirely dark in a terrace region. This result clearly shows that edge dislocation in AlGaN acts as a nonradiative recombination centre. The density of the dark spot on the grooved region is around $10^7$ cm$^{-2}$ at the most. Therefore, reduction of the threading dislocation density by as many as two orders of magnitude was achieved. A high-efficiency UV-LED with GaN-based wells was fabricated using this technique. The EL spectrum is shown in figure 8. Strong and narrow UV emission peaking at 352 nm with a FWHM of 6 nm was observed, which is much narrower than that of GaInN-based LEDs by a factor of two. The output power exceeds 1 mW at a forward current of 100 mA.

This process is rather complex because etching and regrowth is inevitable. Another process is proposed for the growth of AlGaN, which is the use of a grooved substrate [24, 25]. In this process, grooves are initially formed on the surface of a sapphire, SiC or Si substrate. Then, growth of AlGaN utilizing an LT buffer layer proceeds. The groove should be sufficiently deep that the laterally grown AlGaN from the terrace covers the groove region before the top of the AlGaN grown from the bottom of the groove reaches the laterally grown AlGaN. Figure 9(a) schematically shows this process. Figure 9(b) shows the cross-sectional TEM image of $Al_{0.05}Ga_{0.95}N$ grown on a grooved sapphire substrate. This process has several

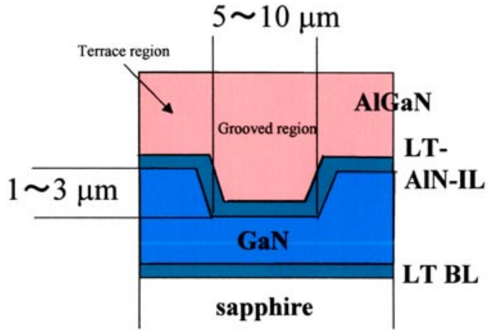



**Figure 6.** Schematic structure of AlGaN on grooved GaN covered with LT interlayer.

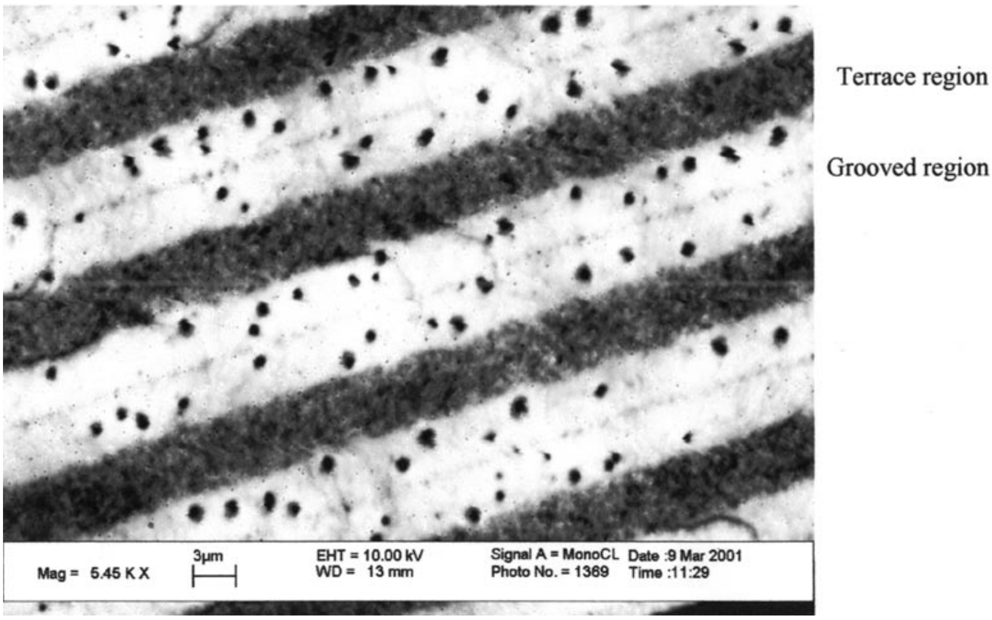



**Figure 7.** CL image taken at cryogenic temperature of $Al_{0.25}Ga_{0.75}N$ grown on grooved GaN covered with GaN. (Courtesy of Professor Bo Monemar.)

advantages over other processes. For example, it does not require etching and regrowth, and it is possible to reduce the thermal stress caused by the difference of the thermal expansion coefficient between AlGaN and the substrate.

## 5. Growth of In-containing alloys

The first growth of single crystalline GaInN by MOVPE was realized by Nagatomo *et al* [26] and Yoshimoto *et al* [6] in 1989 and 1991, respectively. Since then, considerable work has been done by many nitride research groups all over the world. Currently, high-efficiency blue and green LEDs are commercially available, and many reviews have been published already.

In this review, another candidate for In-containing alloys is discussed. AlInN and AlGaInN alloys are promising because of the significant feasibility of controlling band gap and lattice

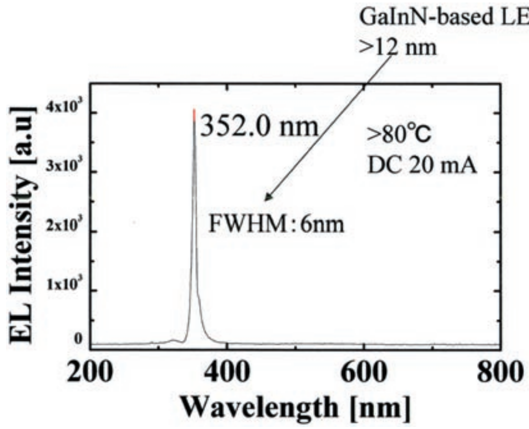



**Figure 8.** EL spectrum of UV-LED with AlGaN/GaN MQW fabricated using grooved GaN and LT interlayer growth.

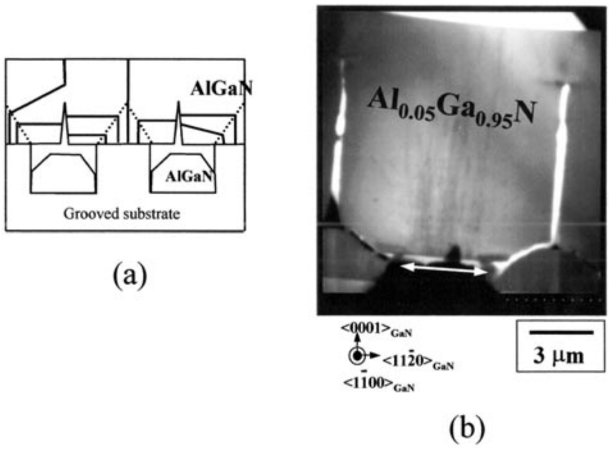



**Figure 9.** Schematic structure and the cross sectional TEM image of $Al_{0.05}Ga_{0.95}N$ grown on grooved sapphire substrate.

constants in a wide range. However, due to the large difference of the epitaxial temperature of AlN and InN, it is very difficult to grow single crystalline AlInN. Single crystalline and luminescence AlInN was first grown by Yamaguchi *et al* in 1998 [27]. As shown in figure 10, PL from UV down to infrared was observed, which suggests large bowing of the band gap in this system. Several groups have used AlInN or AlGaInN as the barrier layers in the MQWs [28, 29], and have observed the superior properties when they are applied to UV emitters and UV detectors.

In addition to optoelectronics devices, application to electronics devices is also promising because it is possible to control the lattice mismatch between GaN, either compressive or tensile strain. It is well known that large spontaneous polarization in addition to the piezoelectric field [30, 31] induces a high-density two-dimensional electron gas at the interface between GaN and AlGaN in the heterostructure. Thus, the operational condition of the conventional nitride-based HFET is limited to the normally on type. Use of the AlInN/GaN heterostructure may lead to the realization of both normally on and normally off types of FET.

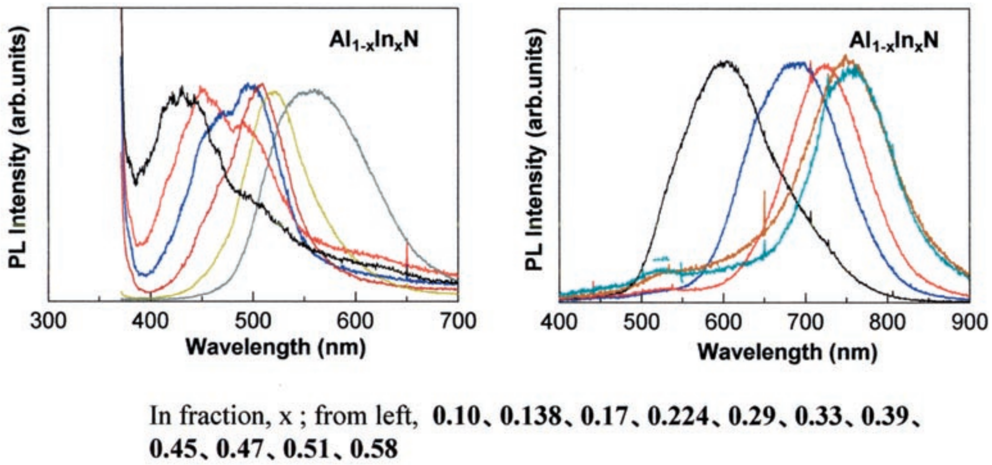



**Figure 10.** PL spectrum at room temperature of $Al_{1-x}In_xN$ with different molar fractions.

## 6. Summary

In this report, recent topics in the growth of GaN and other nitrides by MOVPE have been reviewed. As shown, an accumulation of a large quantity of outstanding work, in particular in the area of MOVPE growth has led to the fabrication of high-performance devices, many of which could not be foreseen in the 1980s. Further progress in these areas will surely open new areas in electronics and optoelectronics and continue to impact the compound semiconductor world.

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