Impact of high-temperature metalorganic vapor phase epitaxial growth of AlGaN-based UV-A, UV-B and UV-C quantum wells on the improvement of their internal quantum efficiency

H Amano
Department of Electronics and Computer Science, Akasaki Research Center, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
E-mail: amano@nuee.nagoya-u.ac.jp

Abstract. High-temperature metalorganic vapor phase epitaxial (MOVPE) growth leads to the realization of high-quality AlN on a c-plane sapphire substrate and the successful growth of low-threading-dislocation-density (TDD) AlN and AlGaN by the grooved template technique. The ABC model in Shockley-Read-Hall (SRH) statistics was used to investigate the non-radiative and radiative processes of AlGaN-based quantum wells (QWs) having different TDDs. The internal quantum efficiency (IQE) was found to be equally dependent on TDD regardless of the emission wavelength. A similar dependence is confirmed in the relationship between TDD and nonradiative recombination coefficient $A$ in UV-A, UV-B and UV-C QWs and in violet, blue and blue-green QWs.

1. Introduction

Considerable efforts have been carried out to improve the performance of AlGaN-based UV-A, UV-B and UV-C LEDs by many researchers. Nevertheless, their external quantum efficiency (EQE) is much lower than those of InGaN-based blue LEDs. Clarifying the factors that limit their EQE is necessary in improving their performance. In general, there are three factors that limit the efficiency of LEDs: (1) IQE, (2) carrier injection efficiency and (3) light extraction efficiency. Among these, IQE is dependent on the radiative recombination rate of each material and the rate of nonradiative recombination. Theoretically, the radiative recombination coefficient of free excitons in AlN is larger than that of GaN or InN [1]. Therefore, AlGaN-based QWs should be more radiative or should have a higher IQE than InGaN-based QWs. However, there is no report showing that the IQEs of AlGaN-based QWs are comparable to or even higher than those of InGaN-based QWs. Thus, a systematic study was conducted to confirm that the IQEs of UV-A, UV-B and UV-C QWs are comparable to those of violet, blue or blue-green QWs.

If UV-A, UV-B and UV-C LED structures are grown on a GaN substrate or a GaN template, crack generation caused by the grown-in tensile stress is a fatal problem that prevents the fabrication of the LEDs. Therefore, the growth of AlGaN-based UV-A, UV-B and UV-C LED structures on an AlN substrate or an AlN template is inevitable. If AlGaN is grown on AlN, the generation of mismatch-induced defects such as misfit dislocations is another serious problem. Therefore, reduction of the
TDD and clarification of the TDD dependence of IQE are the first steps toward improving the performance of UV-A, UV-B and UV-C LEDs.

Recently, we have developed a custom-built MOVPE system that can operate with a growth temperature of as high as 2,073 K, enabling the growth of AlN and AlGaN having an atomically flat surface with a growth rate higher than 6 µm/h on a c-plane sapphire substrate. This MOVPE system is also effective for growing a low-residual-impurity AlN underlying layer and a high-Al-content AlGaN layer; thus, the effect of carbon-related nonradiative recombination can be neglected [2]. AlN on a c-plane sapphire substrate with a TDD of as low as 3×10^8 cm^-2 can be successfully grown.

By using this high-temperature MOVPE system, the TDD in AlN and AlGaN on an AlN template can be controlled by a grooved template technique [3]. In this paper, the effects of the high-temperature MOVPE growth of AlN on a c-plane sapphire substrate and the growth on a grooved template on the reduction of the TDD in an AlGaN are shown.

Next, sets of QWs with emission wavelengths of 230, 250, 300 and 350 nm having different TDDs were grown, and the IQE of each sample was characterized by ABC model in SRH statistics [4]. As references, the TDD dependence of the IQEs of violet, blue and blue-green QWs grown on a free-standing GaN substrate or on a Si substrate was also compared.

2. Experiments

AlN of 2 µm thickness was grown at 1,400°C on a c-plane sapphire substrate using a custom-built MOVPE system having a face down configuration with a water-cooled gas injector [2]. Figure 1 shows a schematic of the MOVPE reactor. Surface temperature was measured by using a pyrometer and monitored from the bottom of the flow channel. The carrier gas was hydrogen. Growth was conducted at 100 Torr. The molar fraction of trimethyl-aluminum (TMAI) to ammonia (NH₃) was 116.

![Figure 1. Schematic of the high-temperature MOVPE system.](image)

After the growth of AlN, a periodic trench pattern was formed along <10-10> of AlN by dry etching. The groove depth and width were 2 and 3 µm, respectively. Then, again, samples were mounted on the susceptor in the reactor and AlGaN and QWs were successively grown. AlGaN and QWs were also grown on planar AlN.
The TDD of each sample was measured using the \( \omega \)-mode X-ray rocking curve (XRC) obtained from c-plane and m-plane reflections. The full width at half maximum (FWHM) of the c-plane XRC is related to the density of dislocations having a screw component, and that of the m-plane XRC is related to the density of dislocations having an edge component. In every sample, the FWHM of the m-plane XRC is wider than that of the c-plane XRC, which means that the density of the edge-type dislocation is higher than that of the screw-type dislocation [5]. In some samples, the density of the edge-type dislocation was also confirmed by plan-view transmission electron microscopy (TEM) observation. The discrepancy of the calculated TDD obtained from XRC measurement and that obtained by counting using TEM images was less than 15%. The dark spot density determined by cathodoluminescence was also confirmed to coincide with the density of dislocations having edge components.

The IQEs of the UV/DUV MQWs with different TDDs were characterized by measuring excitation-density-dependent photoluminescence (PL) using an ArF excimer laser with a wavelength of 193 nm as the excitation source, which is known as SRH analysis [6-9]. Neutral density filters were used to control the excitation density. All the measurements were performed at room temperature.

When the generation rate \((G)\) is equal to the total recombination rate \((R)\), and if the excitation carrier density is sufficiently low for Auger recombination to be negligible, \(G=R\) and PL integrated intensity are given using the following formulas.

\[
G = R = An + Bn^2 \quad \text{(1)}
\]

\[
I_{PL} = \eta Bn^2 \quad \text{(2)}
\]

Here, \(n\) is the excitation carrier density, \(A\) is the nonradiative recombination constant, \(B\) is the radiative recombination constant and \(\eta\) is a constant determined on the basis of the PL collection efficiency. In this study, we fix \(B\) as \(0.2 \times 10^{-10} \text{ cm}^3/\text{s}\) [10]. This value was obtained by measuring of the radiative lifetime of a thin GaN layer on a c-plane sapphire substrate, although several values have also been reported. In the case of free exciton recombination, \(B\) is larger than those for free-electron and free-hole recombination [1]. Differences in the \(B\) value cause an error in the absolute IQE value. It is currently unclear which value of \(B\) should be used. However, the relative trend of the TDD dependence of IQE can be discussed regardless of the chosen value of \(B\).

By combining the above two formulas, \(G\) can be rewritten as

\[
G = \frac{A}{\sqrt{B\eta}} \sqrt{I_{PL}} + \frac{1}{\eta} \frac{I_{PL}}{I_{PL}} \quad \text{(3)}
\]

Then, nonradiative coefficient \(A\) is deduced by curve fitting and the IQE can be expressed as

\[
IQE = \frac{Bn^2}{An + Bn^2} \quad \text{(4)}
\]

3. Results and discussion

Figure 2 shows the atomic force microscopy (AFM) images of AlN grown at (a) 800°C, (b) 1,000°C and (c) 1,400°C. The effect of the high temperature growth on the improvement of the surface flatness
is evident. Root mean square surface roughnesses of the samples are 1.79, 0.47 and 0.098 nm, respectively.

Figures 3-5 show the AFM image, cross-sectional TEM image and plan-view TEM image of the AlN grown on a trench-patterned AlN template. The total thickness is approximately 20 µm. The coalescence position cannot be identified from the AFM image. The plan view TEM image shows that the TDD is less than $10^7$ cm$^{-2}$.

![Figure 2. 1 µm$^2$ AFM images of AlN grown at (a) 800°C, (b) 1,000°C, and (c) 1,400°C.](image)

![Figure 3. 5 µm × 5 µm AFM image of AlN grown on trench-patterned AlN template.](image)

![Figure 4. Cross-sectional TEM image of AlN grown on trench-patterned AlN template.](image)

![Figure 5. Plan-view TEM image of AlN grown on trench-patterned AlN template.](image)
Figure 6 summarizes the compositional dependence of the TDD in AlGaN grown on a planar AlN template (broken line) and on a grooved AlN template (solid line). Thus, we can control TDD in AlGaN over the entire compositional range.

![Figure 6](image)

**Figure 6.** Compositional dependence of the TDD in AlGaN grown on planar AlN template (broken line) and on grooved AlN template (solid line).

Figures 7 and 8 show an example of the relationship between generation rate $G$ and photoluminescence (PL) intensity ($I_{PL}$) (Figure 7) and IQE as a function of excitation carrier density $n$ (Figure 8) for QWs emitting 230 nm UV-C having different TDDs.

![Figure 7](image)

**Figure 7.** Experimental results and fitting curves of the $G$ and $I_{PL}$ for 230 nm QWs having different TDDs. Nonradiative coefficient $A$ is deduced from this fitting curve using formula (3).

![Figure 8](image)

**Figure 8.** Calculated IQE using formula (4) as a function of $n$ for samples shown in Fig.7.

The same procedure was performed for every sample to deduce the nonradiative recombination coefficient $A$. Figure 9 summarizes the TDD dependences of $A$ for the 230, 250, 300 and 350 nm QWs. Those of 420 to 495 nm c-plane QWs grown on free-standing GaN having very low dislocation density and semipolar QWs on patterned Si substrate are plotted for comparison. From the results, it is
clear that $A$ is linearly dependent on TDD, $A \approx 0.05xTDD + 8.1E6 \ [s^{-1}]$, and independent of the emission wavelength. Again, it should be emphasized that this $A$ coefficient is deduced assuming the $B$ coefficient to be $2.0x10^{-10} \ cm^3/s$. In this assumption, a nonradiative coefficient $A$ of approximately $10^7 \ s^{-1}$ seems to be the limit of accuracy.

4. Summary

The impact of the high-temperature MOVPE of AlN and AlGaN and the effect of TDD on the IQEs of UV-A, UV-B and UV-C quantum wells were confirmed for the first time. There is still an ambiguity of the absolute value of the internal quantum efficiency when ABC model in Shockley-Read-Hall statistics is used because of the uncertainty of the radiative recombination coefficient $B$. However, it is evident that there is a very similar trend for AlGaN-based UV-A, UV-B, UV-C and InGaN-based violet, blue or blue-green QWs as a function of TDD. A simple conclusion can be obtained, that is, high-internal-quantum-efficiency UV QWs should be realized by reducing the threading dislocation density.

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