InGaN quantum wells with improved photoluminescence properties through strain-controlled modification of the InGaN underlayer

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Received December 18, 2018; revised February 4, 2019; accepted March 1, 2019; published online May 20, 2019

The effect of internal strain on the luminescence properties of an InGaN single quantum well (SQW) was investigated as a function of modification via an underlayer (UL). Single In0.25Ga0.75N SQWs (λ = 520 nm) 3 nm thick were grown on various ULs on a sapphire substrate, where the two UL types included (1) a buffer layer onto which an InGaN layer with a very small amount of In was inserted and (2) a buffer layer grown using different carrier gases. The SQWs were then analyzed by temperature-dependent time-resolved photoluminescence, scanning electron microscopy and cathodoluminescence. The experimental results show that the density of non-radiative recombination centers and the level of potential fluctuation in the SQWs decrease with insertion of an In0.25Ga0.75N UL possessing a quite low but sufficient indium content (x = 0.007). The density of non-radiative recombination centers in the SQW on the H2 carrier-grown UL, however, is large. © 2019 The Japan Society of Applied Physics

1. Introduction

Gallium nitride (GaN)-based semiconductors are widely used for optical devices such as blue light-emitting diodes and laser diodes. A specific feature of GaN is that its light emission efficiency is better than that of other III–V optical devices, even though it has many dislocations.1–3 Another feature of an InGaN optical device is that it can cover a wide range of emission wavelengths, from violet to infra-red, by varying the indium content in the quantum well (QW).4–6 However, an InGaN/GaN QW with a higher indium content has many issues that must be overcome technically. For example, crystal defects are generated and the emission efficiency is degraded as a result of lattice strain between the QW and barrier, and the light emission property degrades because of the inhomogeneous distribution of indium in the QW.2–4

One solution to overcome these issues is to control and reduce the strain in the QW while maintaining a high indium content. In the case of GaN heteroepitaxial layers on c-plane sapphire substrates, threading dislocations are generated in the GaN buffer layers owing to the lattice mismatch between GaN and sapphire. Many reports have shown improved optical properties of InGaN QWs by insertion of underlayers (ULs) beneath the QWs, where the reported ULs have consisted of InGaN monolayers with dilute indium compositions, an InGaN/GaN superlattice, and combinations of these.5–15 The various mechanisms of the improvements exhibited by the ULs have been discussed and proposed in these previous works. One of the proposed mechanisms is an increase of the carrier recombination rate at the InGaN/GaN QWs owing to a reduction the quantum-confined Stark effect. This reduction is obtained by reducing the internal piezoelectric field via relieving strain in the QWs,7–9 or because the UL acts as an electron reservoir layer.9,10 Another proposed mechanism is an increase of radiative recombination efficiency in the InGaN/GaN QW owing to a reduction of non-radiative recombination centers in the QW itself via improvement of the film quality.13–15

It is also important to investigate the properties of the V-shaped pits that are observed to generate on the threading dislocations. Some works have reported that these V-shaped pits improve the optical property of the InGaN QW.16,17 Other works, however, have reported that the V-shaped defects induce current leakage at the pn-junctions of GaN-based devices,18 and thus seem to lower the reliability of mass-produced devices. The density of the V-shaped pits has also been reported to be affected by the insertion of ULs.19,20 In the majority of the previous research regarding ULs, an InGaN/GaN superlattice or a thick InGaN layer with x > 0.01 have been applied. Few reports, have been made regarding a UL with a relatively low indium content (i.e., x < 0.01). There remains a possibility, however, that the effect of a dilute InGaN UL such as x < 0.01 can improve the QW optical properties.

In this study, we prepared single QWs (SQWs) on thick InGaN ULs with relatively low indium contents (x < 0.01) to control the QW strain. Then, the temperature-dependent time-resolved photoluminescence (TRPL) of the samples was measured and analyzed using a simple two-level system21 to evaluate the density of non-radiative recombination centers and the level of potential fluctuation in the SQWs. In addition, we investigated a SQW on an undoped-GaN buffer layer grown with H2 carrier gas, but the ULs were grown with N2 carrier gas.

2. Experimental methods

The In0.25Ga0.75N/GaN SQWs were grown on buffer layers with four different types of ULs. For all of the samples, low-temperature GaN was grown on (0001) sapphire substrates, upon which a thick undoped-GaN buffer layer (3.6 μm) was grown. These initial layers were grown with H2 carrier gas, but the ULs were grown with N2 carrier gas. The effects of internal strain on the luminescence properties of an InGaN single quantum well (SQW) was investigated as a function of modification via an underlayer (UL).
capping layer. The ULs were an undoped-GaN layer (sample B), or layers of $\text{In}_x\text{Ga}_{1-x}\text{N}$ with $x = 0.0003$ (sample C) or $x = 0.007$ (sample D). The structure of all of the SQWs comprised a 3 nm thick $\text{In}_{0.25}\text{Ga}_{0.75}\text{N}$ well on a 1 nm thick GaN barrier. The photoluminescence wavelengths of $\text{InGaN}$ SQWs for all four samples were varied around 520 nm between 4–300 K. All of these layers (i.e., ULs, 9 nm thick undoped-GaN buffer layers, QWs, barriers and capping layers) were grown with $\text{N}_2$ carrier gas. The growth temperatures of the thick undoped-GaN buffer layer grown with $\text{H}_2$ carrier gas in all four samples and the ULs in sample B, C, D are 1030 °C, 870 °C, respectively. The indium content of each UL was controlled by changing the flow of indium precursor. A schematic of the epitaxial structures of these four samples is given in Fig. 1.

The luminescence properties of the samples were obtained using temperature-dependent TRPL and cathodoluminescence (CL). The TRPL measurements were carried out between 4 K–300 K and by means of the second harmonic of a mode-locked picosecond Ti:sapphire laser with a 385 nm wavelength and 80 MHz repetition rate as an excitation source. The laser power was 15 mW and the beam was focused to a spot diameter of approximately 100 μm. Monochromatic CL images were obtained using a JEOL JSM-7000F and Gatan Mono CL 3+ at the wavelengths of the GaN and $\text{In}_{0.25}\text{Ga}_{0.75}\text{N}$ SQW luminescence peaks, respectively. The acceleration voltage of the scanning electron microscope (SEM) during CL observation was 5.0 kV and the sample temperature was around 83 K. The surface morphologies of the samples were analyzed using an SEM (HITACHI S-4800) at an acceleration voltage of 2.0 kV.

3. Results and discussion

3.1. Temperature-dependent TRPL

Figure 2 shows the decay curves of the photoluminescence intensity obtained from TRPL measurements, obtained at 4 K and 160 K, as typical data. Figure 3 shows the TRPL decay time as a function of the measurement temperature (4 K–300 K) for the four samples. The experimental results show that the decay times of samples A, B and C are almost constant in the low-temperature range (4 K–20 K), and around 20 K–40 K the decay times begin to decrease monotonically with increasing temperature. The turning point where the trend changes from a constant to a decrease is ~20 K for sample A and ~40 K for samples B and C, where the point for sample B is slightly higher than that for

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sample C. For sample D, however, the decay time monotonically decreases with increasing temperature over the entire measured temperature range.

To analyze the dependencies of the TRPL decay time on the measurement temperatures, we employed the simple two-level system, where it is given that

\[ \frac{1}{\tau_d} = \frac{1}{\tau_0} + \frac{1}{\tau_{nr}} + A \sqrt{T} \exp \left( -\frac{T_0}{T} \right), \tag{1} \]

where \( \tau_d \) is the TRPL decay time, \( \tau_0 \) is the decay time of the carriers at the localized lower state at low temperatures, \( \tau_{nr} \) is the non-radiative recombination lifetime of carriers at the extended state, and \( A \) and \( T_0 \) are fitting parameters. The energy potential of an InGaN QW with a high indium content fluctuates owing to the inhomogeneous distribution of indium, the well thickness variation, etc. It is assumed that only two levels, namely a higher level and a lower level, exist in the fluctuation of the energy potential, where the lower energy level is a localized state corresponding to a valley in the fluctuating potential and the higher energy level is an extended state into which carriers are activated. The energy spacing between these localized states corresponds to \( k_B T_0 \). The coefficient \( A \) (ns \(^{-1} \) K \(^{-0.5} \)) includes the factor of the non-radiative defect density, and is proportional to the defect density in the InGaN SQW. For the temperature-dependent decay time profiles, the turning point corresponds to the threshold to overcome this energy spacing. Therefore, increasing the temperature of this point means that the level of energy potential fluctuation increases. The decrease rate of decay time at high temperature correlates with non-radiative recombination rate, namely the density of non-radiative recombination centers. Hence, the large slope of decay time at high temperature means that the density of non-radiative recombination centers is high. Herein, Eq. (1) was used to fit the experimental data, and the results are shown as the solid lines in Fig. 3. The obtained fitting parameters \( A \) and \( T_0 \) are listed in Table I and plotted in Fig. 4.

The \( A \) value of sample A is the highest among the four samples, while the \( T_0 \) value of sample A is in a median level. In the case where the UL was grown with N\(_2\) carrier gas, both the \( A \) and \( T_0 \) decreased in the order of samples B, C, D. These results show that the density of the non-radiative defect centers and the level of energy potential fluctuations decreased as the indium contents of In\(_{x}\)Ga\(_{1-x}\)N ULs increased for the sample with quite low indium content \( (x < 0.01) \). This is the first report about relationship between the indium content of ULs and the non-radiative defect center density, the potential fluctuation in the InGaN SQW.

### 3.2. Surface observations by SEM

Figure 5 shows SEM images of the four sample surfaces in this study. All of the dark spots evident in the SEM images were observed in high-magnification (image not shown) as pits with a hexagonal shape, and are therefore the V-shaped pits frequently reported in the literature.\(^{22-25}\) No V-shaped pits were observed on the surface of sample A [Fig. 5(a)]. However, numerous V-shaped pits were observed on the surfaces of samples B and C, where the density of the V-shaped pits was greater on sample B [Fig. 5(b)] than on sample C [Fig. 5(c)]. Further, only a few V-shaped pits were observed on the surface of sample D, signifying a low pit density [Fig. 5(d)]. These SEM observations indicate that the V-shaped pit density decreases with increasing indium content in the InGaN ULs grown with N\(_2\) carrier gas, and no V-shaped pits developed in the GaN-templates grown with H\(_2\) carrier gas. The V-shaped pits exhibited a hexagonal cone shape that consists of six \{10\(1\)\} facets, and thus their depths were deduced from their diameter. It was found that all of the V-shaped pits in samples B, C and D were generated in the UL of the sample.

In the case of InGaN epitaxial growth, it is generally required to lower the crystal growth temperature in order to increase the indium content, so that lateral growth is suppressed and V-shaped pits tend to be formed. For this reason, the V-shaped pit density tends to increase. In the In\(_{x}\)Ga\(_{1-x}\)N UL of this study, the indium content is very low \( (x < 0.01) \), so this effect is not noticeable. On the other hand, V-shaped pit formation is sensitive not only to the degree of lateral growth mode but also to strain as reported by Ref. 26.

### Table I. Values of the Eq. (1) fitting parameters \( A \) (ns \(^{-1} \) K \(^{-0.5} \)) and \( T_0 \) (K), as calculated for the samples.

| Sample | A (ns \(^{-1} \) K \(^{-0.5} \)) | \( T_0 \) (K) |
|--------|----------------|--------------|
| A      | 0.029          | 135          |
| B      | 0.019          | 262          |
| C      | 0.017          | 201          |
| D      | 0.005          | 2             |

![Fig. 4.](image) (Color online) Values of the fitting parameters \( A \) (ns \(^{-1} \) K \(^{-0.5} \)) and \( T_0 \) (K) of the samples, calculated using Eq. (1).

![Fig. 5.](image) SEM images of the surfaces of samples (a) A, (b) B, (c) C and (d) D. The values in the lower left corner of the images indicate the V-shaped pit density.
In this study, since the strain changes due to a change in indium content of the UL, we think that the pit density changes. Furthermore, in the case of H₂ carrier gas, higher growth temperature which promotes lateral growth makes the V-shaped pits difficult to form.

3.3. CL observation

We observed the monochromatic CL of samples A and B to examine the distributions of the non-radiative recombination centers detected by temperature-dependent TRPL. Figure 6 shows the surface SEM images and the CL images of GaN (\(\lambda = 360\) nm) and In\(_{0.25}\)Ga\(_{0.75}\)N (\(\lambda = 480\) nm) luminescent wavelengths of the same area on sample A [Fig. 6(a)] and sample B [Fig. 6(b)]. Each CL image was taken by setting the monochromator at the wavelength with local maximum intensities of GaN and In\(_{0.25}\)Ga\(_{0.75}\)N SQW. Since CL measurements were carried out under high excitation condition, the peak wavelength was shorter than that of the photoluminescence measurements. In sample B, which contains V-shaped pits, the dark areas in the GaN CL image correspond to the positions of the V-shaped pits. However, dark spots are also observed in the GaN CL image of sample A, wherein no V-shaped pits were observed. For GaN-template layer on a (0001) sapphire substrate, threading dislocations are generated whose densities are on the order of 10\(^8\)–10\(^9\) cm\(^{-2}\).\(^{29–32}\) The density of these dark spots observed in the GaN CL in our samples are on the order of 10\(^7\) cm\(^{-2}\), and therefore we posit that these dark spots are threading dislocations.

Comparing the CL images for GaN and InGaN, some non-radiative recombination centers are identified in addition to the threading dislocations, as evidenced by the fact that the dark areas in each image do not overlap. The threading dislocation densities are considered nearly equivalent for each sample herein because the same GaN-template was used. However, the densities of the non-radiative recombination centers, as revealed by the value of \(A\) and obtained from analysis of the temperature-dependent TRPL, are different. These results also suggest that, in addition to threading dislocations, non-radiative recombination centers such as point defects around the QW\(^{33–35}\) also exist in the samples. One candidate of point defects can be nitrogen vacancies (V\(_N\)), which are suppressed by the insertion of an In-containing UL.\(^{35}\) As the temperature-dependent TRPL revealed that the \(A\) value of sample A is large, the non-radiative recombination center density is high in the InGaN SQW on a GaN-template grown with H₂ carrier gas. This can be owing to the diffusion of excessive hydrogen from the underneath to the QW during growth. Thus, excessive hydrogen atoms are also thought to be candidates for point defects.

We note that some V-shaped pits were observed as bright areas, where this phenomenon was a shape effect wherein the luminescence from InGaN diffused into the QW and emitted at the sidewalls of the V-shaped pits via scattering.

To summarize the results, in the case of the sample in which the SQW was grown on a GaN-template deposited with H₂ carrier gas (sample A), no V-shaped pits were observed but the density of non-radiative recombination centers (\(A\)) was highest among the four samples herein. In the case of the samples in which ULs grown with N₂ carrier gas were inserted (samples B, C and D), the V-shaped pit densities, the densities of non-radiative recombination centers (\(A\)) and the level of potential fluctuations (\(T_0\)) decreased with increasing indium content in the InGaN ULs. It has been previously reported that there is a strong tendency for thick GaN films on sapphire to grow in tensile strain.\(^{36}\) Thus, tensile strain will accumulate in the upper region of the GaN-template layer and will transfer to the ULs.
thickness and/or internal stress exceeds a certain critical point, the V-shaped pits are generated from the threading dislocations.26) Once the V-shaped pits are formed, accumulated tensile strain is relieved in the vicinity thereof. This allows the lattice constant of the GaN layer underneath the QWs to recover towards that of an unstrained lattice, causing the lattice mismatch between the InGaN QWs and the surrounding GaN layers to also recover towards that of the InGaN QW and the unstrained GaN layers.

Based on our experimental results, the low but sufficient content of indium (i.e., \( x < 0.01 \) in In\(_{x}\)Ga\(_{1-x}\)N) in the UL suppresses the generation of V-shaped pits. In this case, the V-shaped pit formation does not play a major role in mitigating the accumulated tensile strain. Thus, the tensile strain induced by growth on sapphire substrates can be maintained. This signifies that the InGaN QW is surrounded by “tensile strained” GaN layers whose lattice constant is close to that of the InGaN QW. Therefore, the stress in an InGaN QW without V-shaped pit formation is less than that with the V-shaped pit formation. A reduced stress in the InGaN QW can improve its film quality, thereby reducing the number of non-radiative recombination centers and point defects, and the potential fluctuation also decreases. It is also posited that maintaining the tensile strain suppresses the diffusion of point defects from the UL to the InGaN QW, which may also decrease the number of non-radiative recombination centers. In addition, as discussed by Ref. 35, an In-containing UL suppresses the diffusion of point defects to the InGaN QW. However, further studies are needed to clarify the function of the UL from the viewpoint of the relation between strain and point defect diffusion.

4. Conclusions

Four different samples comprising an In\(_{0.25}\)Ga\(_{0.75}\)N SQW on various thick In\(_{x}\)Ga\(_{1-x}\)N ULs were prepared, whose indium contents were quite low (\( x < 0.01 \)). The densities of the V-shaped pits and non-radiative recombination centers (\( A \)) were analyzed, as well as the levels of potential fluctuations in the InGaN QW (\( T_0 \)) by means of temperature-dependent TRPL, SEM and CL. In the case of ULs grown with N\(_2\) carrier gas, the V-shaped pit densities, \( A \), and \( T_0 \) of the InGaN SQW decreases with increasing indium content in the UL. This signifies that the photoluminescence property of the InGaN QW is improved by insertion of modified InGaN ULs with low but sufficient indium content. In the case of the SQW grown on the GaN-template deposited with H\(_2\) carrier gas, the value of \( A \) is relatively high. The non-radiative recombination centers detected by temperature-dependent TRPL (\( A \)) in our samples are thought to be point defects around the InGaN QW.

Acknowledgments

One of the authors (A. A. Y.) would like to thank financial support from the Japan Society for the Promotion of Science: JP17H05341.