Theoretical study of composition fluctuation in InGaN films on various substrates

K Mukose¹ and M Sano¹

¹Faculty of Engineering, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
E-mail: mukose@ee.kagu.tus.ac.jp

Abstract. The residual strain due to composition fluctuation in InGaN films grown epitaxially on various InGaN/GaN multiple quantum well (MQW) structures was simulated numerically by a novel method based on first principles. It was found that the strain energy due to the interlayer shear stress caused by the composition fluctuation in InGaN/GaN MQW could be controlled by the InGaN/GaN layer thickness ratio. The critical temperature, which is the maximum substrate temperature at which composition fluctuation can occur, was also investigated as well, and was also found to be dependent on the structure of the MQW.

1. Introduction

InₓGa₁₋ₓN with a wurtzite structure is a semiconductor, and its direct band gap is considered to be potentially variable from 3.510 to 0.78 eV [1] depending on the composition x. This compound has been used to successfully fabricate some optical devices such as light emitting diodes (LEDs) [2] and laser diodes [3]; in the future, it is expected that this compound will be used to develop tunable optical devices with a wide wavelength range from near-infrared to ultraviolet. The objective of this study is to understand the mechanisms of epitaxial growth and control properties of InGaN films on various substrates.

In the ternary alloy InGaN, the indium composition has been known to exhibit spatial inhomogeneity under different growth conditions [4—6]. Some theoretical studies conducted in the past have revealed that a ternary system is not thermodynamically stable [7, 8]. The influence of strain on phase separation has also been studied theoretically [9]. It is generally believed that the fluctuation in the composition of indium in InGaN is responsible for the formation of quantum disk structures in InGaN quantum wells; these quantum disks localize excitons and influence the spontaneous emission rate [5, 6, 10].

Some long-range atomic orderings have been observed to coexist with the compositional phase separation in wurtzite InGaN [11—13]. These chemical ordering have been explained theoretically with a model of adsorption of indium atoms at certain positions on the surface of the alloy during the crystal growth process [14].

In this study, the structure dependency of the interlayer shear strain caused by fluctuation in the composition of an InGaN film grown epitaxially on an InGaN/GaN multiple quantum well (MQW) structure was investigated quantitatively by using the first-principles-based approach.
2. Simulation method

Our simulation model for InGaN films contains triangular pillar-shaped cells, where the composition ratio, strain, and stress in each cell follow an equation of state, which has been determined by *ab initio* electronic structure calculations, as shown in figure 1. The volume and shape of the cells were optimized to minimize the free energy in the system. In this study, the residual strain due to spatial fluctuation in the composition of indium in InGaN films grown epitaxially on the InGaN/GaN MQW was simulated theoretically by using this novel model.

![Figure 1. Flow chart of the simulation model for an InGaN film on a substrate.](image)

The equation of state, which is the relation between the lattice constants and the internal energy in InGaN of various composition ratios, was evaluated using a first-principles electronic state calculation. The calculations were performed using the “PWscf” code [15], which is a package of programs within the density functional theory (DFT), and by using *ab initio* pseudopotentials and a plane-wave basis set.

In this study, it is assumed that phase separation coexists with the $c$-plane atomic ordering in InGaN thin films on substrates. The thin films are assumed to have one of five structures: two of these are the GaN and InN type while the other three are the $c$-plane atomic ordered structures of In$_{0.25}$Ga$_{0.75}$N, In$_{0.5}$Ga$_{0.5}$N, and In$_{0.75}$Ga$_{0.25}$N, as shown in figure 2. The In atoms and Ga atoms are stacked alternately at equilibrium positions near the (1/3, 2/3, 0; 2/3, 1/3, 1/2) sites, and the N atoms are at the equilibrium positions near the (1/3, 2/3, u; 2/3, 1/3, 1/2+u) sites of the pseudo-hexagonal structure. The stacking sequences of the layers of the group-III atoms are In-Ga-Ga-Ga-In-Ga-Ga-Ga-… for In$_{0.25}$Ga$_{0.75}$N, In-Ga-In-Ga-… for In$_{0.5}$Ga$_{0.5}$N, and In-In-In-Ga-In-In-In-Ga-… for In$_{0.75}$Ga$_{0.25}$N. These structures of In$_{0.25}$Ga$_{0.75}$N and In$_{0.5}$Ga$_{0.5}$N are consistent with the former observation by Behbehani *et al.* [12].
Figure 2. c-plane atomic orderings in In$_x$Ga$_{1-x}$N. Nitrogen atoms are not shown in the figure.

The model of the InGaN/GaN MQW is shown in figure 3. The InGaN layers and GaN layers are alternately stacked in the direction of the c-axis. Here the $N_w$ is the number of atomic layers in the each well layer of InGaN, and the $N_b$ is that in the each barrier layer of GaN. There has been assumed to be no lattice defect in the model. The average linear atomic densities of in-layer directions were fixed to the values of bulk GaN, under an assumption that the MQW was grown on a thick enough GaN substrate, while that of the out-of-layer direction was optimized. A phase separation in one InGaN layer is assumed to influence the strain in the next InGaN layer and cause a similar separation in that InGaN layer.

Figure 3. Model of the InGaN/GaN MQW.
One can investigate various spatial patterns of phase separations by using triangular pillar-shaped cells models. In this study, simple stripe patterns were investigated systematically for different average compositions, as shown in figure 4.

![Figure 4. Simple stripe models of compositional phase separation of In$_{x}$Ga$_{1-x}$N.](image)

3. Results and discussions

The critical temperature, which is the maximum substrate temperature at which compositional phase separation in InGaN can occur, was estimated by dividing the free energy difference from the homogeneous state to the separated state by the corresponding entropy. The average composition dependence of the critical temperature of an InGaN film on an InGaN/GaN MQW is shown in figure 5. It was observed that the larger the InGaN/GaN layer thickness ratio, the higher is the critical temperature, as shown in figure 6. In the other words, the small InGaN/GaN layer thickness ratio suppresses the composition fluctuation.

![Figure 5. Average composition dependence of the critical temperature of In$_{x}$Ga$_{1-x}$N film on In$_{x}$Ga$_{1-x}$N/GaN MQW for different layer thickness ratios $N_W/N_B$.](image)
Figure 6. Structure dependence of the critical temperature of an $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ film on $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}/\text{GaN}$ MQW structures.

For the separated state in each $\text{In}_{x}\text{Ga}_{1-x}\text{N}/\text{GaN}$ MQW structure, the strain energy due to the interlayer shear stress along the $<0\bar{1}\bar{1}0>$ direction of the pseudohexagonal heterostructure was evaluated, as shown in figures 7 and 8. It was found that the strain energy can be widely controlled by the structure, as shown in figure 10. The residual strain energy is maximized when the average indium composition $x$ is about 0.5 and the $\text{InGaN}/\text{GaN}$ layer thickness ratio is approximately 1.

Figure 7. Average composition dependence of the strain energy due to interlayer shear stress along the $<10\bar{1}0>$ direction in the phase-separated $\text{In}_{x}\text{Ga}_{1-x}\text{N}/\text{GaN}$ MQW with layer thickness ratio $\frac{N_{W}}{N_{B}} \leq 1$. 
Figure 8. Average composition dependence of the strain energy due to interlayer shear stress along the \( <10\overline{1}0> \) direction in the phase-separated In\(_x\)Ga\(_{1-x}\)N/GaN MQW with layer thickness ratio \( N_W/N_B > 1 \).

Figure 9. Structure dependence of the strain energy due to interlayer shear stress along the \( <10\overline{1}0> \) direction in the phase-separated In\(_x\)Ga\(_{1-x}\)N/GaN MQW with layer thickness ratio \( N_W/N_B \).

A rough estimate of the minimum average length between defects that can be caused by this interlayer shear strain in In\(_{0.5}\)Ga\(_{0.5}\)N/GaN MQW with \( N_W/N_B = 1 \) is approximately 70 nm, as dividing the length of the corresponding Burgers vector by the strain. That is, it seems that a quantum disk structure of a diameter of that is shorter than about 140 nm can be formed with no defect in the In\(_{0.5}\)Ga\(_{0.5}\)N layers of the MQW structure, if no other mechanism is present.
4. Conclusions
We used a novel simulation method based on first principles to numerically investigate the structure dependency of the interlayer shear strain caused by composition fluctuations in InGaN films grown epitaxially on an InGaN/GaN MQW structure. The residual strain energy was found to be strongly dependent on the structure. The critical temperature, which is the maximum temperature at which the composition fluctuation can occur, was found to reduce significantly when the InGaN/GaN layer thickness ratio in the MQW was reduced.

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