Probing the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ spatial alloy fluctuation via UV-photoluminescence and Raman at submicron scale

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We present a straightforward method for the study of alloy spatial compositional distribution at the submicron scale via photoluminescence and Raman spectroscopy. The spatial dependence of the band gap light-emission energy of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys at composition $0 \leq x \leq 1$ was studied via deep UV-photoluminescence and Raman microscopy in order to address the issue of the spatial alloy fluctuation. The data were acquired in a random fashion from an area of $\sim 1 \text{ mm}^2$ on the sample at steps of $\sim 1\text{--}200 \mu\text{m}$ utilizing the 244 nm laser line of probing spot size $\sim 300 \text{ nm}$ radius. Our study indicates that the photoluminescence emission energy exhibits random type variations depending on locality: the alloys of composition $x = 0.12$, $x = 0.22$, $x = 0.50$, and $x = 0.70$ exhibit average variations of ~ 10 , 30 , 45 , and 25 meV , respectively. The photoluminescence of the pure GaN exhibits no significant spatial fluctuation. The stress contribution to the observed photoluminescence fluctuations was investigated via Raman analysis and was taken into account in order to estimate the local compositional fluctuation Δx . Our results indicate that for the higher Al composition alloys $x = 0.50$ and 0.70 the stress and the compositional fluctuation can be resolved, resulting in average spatial fluctuations of $\Delta x = 0.004$ and 0.002 , respectively. © 2002 American Institute of Physics. [DOI: 10.1063/1.1526918]

The great potential of UV nitride-based optical devices has prompted numerous studies focusing on the properties of this family of materials that includes InN, GaN, AlN, and their alloys.^{1–5} One of the most attractive properties of the nitrides is the nature of their wide band gaps, which in the wurtzite structure have the values of 1.95 eV for InN, 3.45 eV for GaN and 6.2 for AlN. Moreover the solid solutions in the Al–Ga–N system have been realized, enabling the growth of an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductor of a desired band gap in the range 3.45 up to 6.2 eV via the choice of the composition x .⁶ Among the crucial aspects in the fundamental properties of these materials are the nature of the atomic distribution and alloy fluctuations, since atomic segregation, clustering, or uneven distribution would result in a broad-band emission line of low efficiency which is not desirable for a viable optical device. A powerful technique that can study these aspects is photoluminescence (PL) with submicron probing spot: the local band gap light emission energy is a measure of the alloy composition at that locality, and measurements can be acquired across a sample in order to study the issue of compositional fluctuations. However, due to mismatch of the lattice constant as well as the thermal expansion coefficient between the film and the substrate, a residual stress is present which affects the PL emission energy. Thus, the combined effects of stress as well as composition need to be considered. In this letter we present a study concerning the issue of compositional distribution in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys at composition $0 \leq x \leq 1$ via deep UV PL

and Raman microscopy. We combined Raman analysis, which yields information on the stress state of the alloys, with PL study in order to address the compositional fluctuations at submicron scale in $\text{Al}_x\text{Ga}_{1-x}\text{N}$. Our results indicate that the alloys do not exhibit clustering or significant atomic segregation and the observed minor nonuniformities are due to random alloying.

In our experiments the 244 nm (5.01 eV) line of the second-harmonic generation laser was utilized. The JY-Horiba Raman/PL system consists of the high-resolution T64000 monochromator and an UV microscope capable of focusing spot size $\sim 300 \text{ nm}$ radius. For each sample about ten PL data points were acquired at steps of $\sim 1\text{--}200 \mu\text{m}$ across a 1 mm^2 area. In order to gain an insight into the distribution profile we acquired about 100 data points on the sample of composition $x = 0.5$. The experiments were carried out at room temperature. The $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys films were grown via metalorganic chemical vapor deposition on 6H-SiC (0001) substrates: the thickness of the films is $\sim 1 \mu\text{m}$ and the composition, x , was determined via Rutherford backscattering as well as energy dispersive x-ray and Auger spectroscopy.⁷ The experimental error in the composition determination is $\sim 5\%$.

In the first part of our study we investigated the PL energy light emission behavior as a function on the composition x in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys. The PL emission in GaN is of excitonic nature,⁸ also known as a near band gap emission, and as such we will refer to our PL emission as a band gap emission for brevity. Figure 1 depicts the compositional dependence of PL emission energy. In Fig. 1 the dots are our

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FIG. 1. The PL peak position as a function of composition. The inset to the figure presents characteristic spectra acquired from $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ at two adjacent spots. The spectral variation is 39 meV.

experimental data while the line is a fit to the expected quadratic form⁹

$$E_g(x) = E_g(\text{GaN})(1-x) + E_g(\text{AlN})x - bx(1-x). \quad (1)$$

In this relation $E_g(\text{GaN})$, and $E_g(\text{AlN})$ are the band gaps of GaN and AlN, respectively; from our experimental result $E_g(\text{GaN}) = 3.4$ eV and the value of 6.2 for $E_g(\text{AlN})$ at room temperature was taken from the literature.¹⁰ The parameter b in Eq. (1) is the so-called bowing parameter and is a measure of the deviation from linearity. The deviation from a linear behavior in many alloy systems that possess part covalent and part ionic bondings has been previously attributed to the effect of a local disorder in the ionic bonding due to the presence of different cations (anions).⁹ Our fit to the experimental data resulted in a bowing parameter value of $b = 1.2$ eV; values ranging from 0.3 up to 1.78 eV have been previously reported.¹ The actual value of b in the nitride system is still an open issue.

For the second part of our study we acquired multiple PL spectra from an area $\sim 1 \text{ mm}^2$ on the sample in steps of $\sim 1\text{--}200 \mu\text{m}$. We repeated that procedure for the samples of composition 0, 0.12, 0.22, 0.50, and 0.70. We found that the alloys of composition $x = 0.12$, $x = 0.22$, and $x = 0.70$ exhibit average variations of 10, 30, and 25 meV, respectively. On the other hand, the PL of GaN exhibits no significant spatial dependence while the alloy of $x = 0.50$ exhibits the largest variation ~ 42 meV. The inset to Fig. 1 depicts characteristic spectra taken from the alloy of composition $x = 0.50$ at two adjacent spots on the sample of spectral variation of 39 meV. In order to gain a further insight into the type of distribution, we collected about 100 data points at random from an area $\sim 2 \text{ mm}^2$ on the sample of composition $x = 0.5$. We found that our data concur with a Gaussian distribution of spectral variance $\Delta E_g = 42$ meV as depicted in Fig. 2.

In order to estimate the compositional spatial fluctuation from the measured PL variance ΔE_g , first one has to take into account the effect of stress on the PL. To study the stress in the alloys we employed Raman scattering, and analyzed

FIG. 2. The spatial distribution of the PL energy. The dots represent our data; the line is the Gaussian fit to the data.

the data within the framework of the mode behavior of the E_2 mode, since composition as well as stress results in a combined shift of the Raman peak position. Previous studies concerning the Raman mode behavior in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ have analyzed the compositional dependence of the Raman line;^{11,12} however, unconvoluted shift due to stress is always present in the data. Figure 3 depicts the compositional dependence of the E_2 and the $A_1(\text{LO})$ Raman modes in our alloys. As can be seen in Fig. 3 the $A_1(\text{LO})$ has one-mode behavior and the E_2 has a two-mode dependence (i.e., for composition > 0.7 two Raman lines can be resolved in the spectra). Our results concur with the previously published studies and similarly to these studies our data includes the stress effect as well.

In the following discussion concerning the stress effect we analyzed E_2 mode since it has a weaker composition dependence than that of the $A_1(\text{LO})$ mode, and as such is a more suitable mode for stress analysis. From our data presented in Fig. 3 we found that the E_2 mode exhibits a relative change of about 0.8 cm^{-1} per 1% composition (0.01 in our composition units). The study of the spatial dependence of the E_2 mode indicates an average deviation of $\sim 1 \text{ cm}^{-1}$ for the 0.12 sample and $\sim 3 \text{ cm}^{-1}$ for the 0.22 and the 0.5 samples, while the alloys of composition 0.7 exhibit deviation $\sim 2 \text{ cm}^{-1}$. The E_2 mode of the GaN sample exhibits no significant spatial variations. Figure 4 presents the spatial

FIG. 3. The Raman peak position as a function of composition. The upper branch is the $A_1(\text{LO})$ mode; the lower is the E_2 mode. The inset to the figure presents the Raman spectra of the E_2 mode acquired at two different spots of the 0.22 alloy. The peak position exhibits variation $\sim 3 \text{ cm}^{-1}$; however, no variation in the linewidths, $W = 16 \text{ cm}^{-1}$ is observed.

FIG. 4. The spatial distribution of the E_2 Raman mode of the 0.5 alloy. The average variation is $\sim 3 \text{ cm}^{-1}$.

distribution of the E_2 Raman mode of the 0.5 sample. Since the samples have cracking which implies the presence of stress, it cannot be the case that the entire observed Raman shifts are due to composition effect. Our previous investigation concerning Raman characteristics of these samples indicated that stress fluctuations up to 4 cm^{-1} are typical in this family of alloys.¹³ That conclusion was based on the analysis of the peak position and the linewidth. The Raman peak position can vary due to both stress and composition; however, the linewidth is mainly a function of the compositional disorder, i.e., broadening due to the configurational disorder effect.^{13–15} Our Raman peak positions exhibit spatial fluctuations, but no significant changes in the linewidths were evident as can be seen in the inset to Fig. 3. This suggests that the observed Raman shifts are mainly due to stress in the studied alloys.

Previous studies on the effect of pressure on the nitride Raman modes found that the E_2 in GaN and AlN have stress coefficients of 4.24 and $4.99 \text{ cm}^{-1}/\text{GPa}$, respectively.¹⁶ Therefore the 1, 3, and 2 cm^{-1} average shifts correspond to stress of ~ 0.22 , 0.65, and 0.44 GPa , respectively. Moreover, the PL pressure coefficient of GaN is 47 meV/GPa ,¹⁷ which implies that the calculated stress values should result in a PL peak variation of ~ 10 , 30, and 20 meV , respectively. Our PL data for the high composition alloys of 0.50 (42 meV) and 0.7 (25 meV) exceed their PL variation due to stress (30 and 20 meV , respectively) and we attribute the difference to the compositional effect.

In order to estimate the local compositional fluctuation, Δx , from the measured PL variance ΔE_g , one has to differentiate Eq. (1) to get

$$\Delta x = \Delta E_g / (1.6 + 2.4x). \quad (2)$$

After accounting for the stress contribution, we found the compositional spatial variance to be ~ 0.004 and 0.002 for compositions of 0.50 and 0.70, respectively. Our findings are reasonable: for higher Al composition alloys a more prominent spatial fluctuation is highly probable.

The randomness of the alloy distribution may be complementarily investigated within the framework of the excitonic linewidth for small alloy fluctuations.¹⁸ A model calculation for the excitonic linewidth, σ , of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ random alloy predicts the following behavior:¹⁸

$$\sigma = \frac{dE_g(x)}{dx} 0.41 \sqrt{8 \ln(2)x(1-x)} \frac{V_c}{4\pi a_{\text{ex}}^3/3}. \quad (3)$$

In this relation that holds for the cold temperature regime, V_c is the volume of the primitive cell, and a_{ex} is the exciton Bohr radius: both are a function of composition. In order to check whether our finding of $\Delta E_g/\Delta x (= 12 \text{ meV}/0.004)$ agrees with the model, we used this result in Eq. (3) and calculated σ to be 42 meV for the composition 0.5. The PL linewidth of our $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ at 77 K is $\sim 50 \text{ meV}$; thus our results concerning the compositional fluctuation are in good agreement with the model. We are currently undertaking the further investigation of the PL characteristics as a function of temperature. Moreover, we plan to combine x-ray diffraction of high lateral resolution with our submicron PL and Raman scattering. These methods are complementary in nature from the point of view of studying alloy-distribution issues such as stress, composition, and lattice constants.

In summary, we utilized submicron UV-PL and Raman spectroscopy to study the spatial alloy fluctuation of $\text{Al}_x\text{Ga}_{1-x}\text{N}$. We found that for our optical-system resolution limit, i.e., probing spot size of 300 nm radius, the alloys of high Al compositions exhibit minor spatial fluctuations as is expected from a randomly distributed alloy system.

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