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Raman spectra investigation of InAlGaN quaternary alloys grown by metalorganic chemical vapor deposition

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Raman analysis of the A_1 (LO) mode of AlGaN-like phonons of the InAlGaN/GaN heterostructures in the composition range 1.38% ≦ In ≦ 2.73% and 8.01% ≦ Al ≦ 13.97% is presented. The line shape of A_1 (LO) mode of AlGaN-like phonons was observed to exhibit a significant asymmetry and Raman linewidth toward the lower energy side. The spatial correlation model is discussed and is shown to account the line shape. The spatial correlation model calculations also indicate the lack of a long-range order in the higher Al to In ratio of InAlGaN/GaN alloys. These results were confirmed by x-ray diffraction and the correlation length L decreases as the increasing of Al to In ratio corresponding to the absence of the long-range order in the alloy. The Raman linewidth of the AlGaN-like A_1 (LO) mode was found to exhibit a maximum at the higher Al to In ratio indicative of a random disordered alloy system. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4752420]

I. INTRODUCTION

The importance of InAlGaN system of quaternary alloys offers the opportunities to modify their fundamental physical properties over a wide range by purposely varying In or Al compositions in InAlGaN to change the band gap while keeping lattice matched with GaN, which can be used to reduce dislocation density and piezoelectric field.[1–3] Therefore, InAlGaN quaternary alloys have been successfully introduced to be good for luminescence enhancement, especially in the ultraviolet (UV) regions.[1–3] In spite of the significant progress in the preparation of these quaternary alloys of InAlGaN achieved in recent years by adjusting the alloy compositions, many of their basic characteristics still remain uncertain.[4–6] Furthermore, there are few papers focused on the typical feature of alloys for a disorder in atomic distributions over lattice sites to bring out the properties of electron states or lattice dynamics.[4–6] Particularly, it is true for the phonon spectrum because such an analysis can provide not only insight into the atomic structures but also bonding properties to direct a better understanding of the electronic properties and applications in the InAlGaN quaternary alloys.[4–6] Raman scattering has been used to study the physical properties of InAlGaN quaternary alloys and the Raman spectra show difference of various phonon modes with compositional disorder, including the phonon frequency shift, changes of linewidth and asymmetry, and coming out of disorder-activated modes.[4–6] Recently, considerable attention has been devoted to the discussions of the phonons related to the InGaN-like A_1 (LO) modes or AlGaN-like A_1 (LO) modes in the InAlGaN quaternary alloys.[4–6] However, the relation between alloy disorder and the line shape (linewidth and asymmetry) of A_1 (LO) mode of AlGaN-like phonons in the InAlGaN quaternary alloys has not been fully studied.

In this paper, a detailed investigation on the influence of the Raman spectra caused by alloy compositional fluctuations (ACFs) in the different quaternary alloys of InAlGaN/GaN heterostructures will be provided. Moreover, we pay attention to the GaN A_1 (LO) mode and AlGaN-like A_1 (LO) mode in the Raman shift range of 675–800 cm^{-1} at room temperature. The linewidth and asymmetry of Raman line shape in the AlGaN-like A_1 (LO) mode can be investigated in terms of the spatial correlation (SC) model regarding to the finite correlation length of a propagating phonon due to the ACFs.[7]

II. EXPERIMENTAL

Quaternary heterostructure samples of the alloy system In-Al-Ga-N with indium (In) content from 1.38% to 2.73% and aluminum (Al) content from 8.01% to 13.97% were grown on the c-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD) method. Each of the produced quaternary alloys were grown on top of the AlN buffer layer (25 nm) and consisted of one InAlGaN layer (0.23 μm) with a GaN layer (0.25 μm) in between. The growth temperature of 1050 °C and pressure of 300 Torr were applied for the growth of underlying GaN epilayer. InAlGaN layers were grown at 780 °C, while In and Al compositions were controlled by varying the flow rates of trimethylindium (TMIn) and trimethylaluminum (TMAl), respectively. The alloy compositions were determined by x-ray photoelectron spectroscopy (XPS) and are listed in Table I for all of the three samples. The structural properties of the InAlGaN/GaN heterostructure quaternary alloys were analyzed by high resolution x-ray diffraction (HRXRD). The Raman spectra were measured at room temperature by using the Renishaw System (inVia Raman microscope) while the spectra were excited using the 514.5 nm line of an Ar^+ laser at an incident power

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TABLE I. Sample number, composition, ratio of Al to In, the values of linewidth Γ, and correlation length L for the AlGaN-like A_1 (LO) phonon modes in our InAlGaN/GaN heterostructure quaternary alloys.

Sample	In (%)	Al (%)	Al to In	Γ (cm^{-1})	L (Å)
M12	1.38	10.52	7.6	15.0	62
M14	2.73	13.97	5.1	14.0	66
M28	1.64	8.01	4.9	13.0	69

of 10 mW with the experimental error $\pm 1\,cm^{-1}$ for linewidth and $\pm 0.5\,cm^{-1}$ for peak position, respectively.

III. RESULTS AND DISCUSSION

Room temperature Raman spectra of the different InAlGaN samples over the range of 450–800 cm^{-1} are illustrated in Fig. 1. For the InAlGaN layer grown on GaN, those Raman peaks have shown that there are three resolved phonon structures observed in each Raman spectrum of InAlGaN quaternary alloys and the assignments of our Raman modes are based on the previous Raman studies of InAlGaN quaternary alloys.[2–6] In (a)–(c) of Fig. 1, one peak position located in the region of 550–575 cm^{-1} corresponds to the GaN E_2(high) mode and GaN A_1 (LO) mode is located at around 735 cm^{-1}, respectively. Furthermore, from 700 to 800 cm^{-1}, the AlGaN-like A_1 (LO) mode is located at around 750 cm^{-1} described by the Gaussian fit (dotted line) of the Raman line shape and the spectra are displayed in (d)–(f) of Fig. 1. The A_1 (LO) mode of InGaN-like, expected at around 700 cm^{-1} is not detectable, probably it is because the In composition is much less than Al composition in our quaternary samples.[2–6] Then, it is seen that most of the Raman peaks from our samples correspond well to those of the other InAlGaN quaternary alloys,[2–6] the Raman spectra of our quaternary samples have shown their particular characteristics to verify that both of the E_2(high) mode of GaN and A_1 (LO) mode of GaN are from the substrates, while the A_1 (LO) modes of AlGaN-like are similar to the Al-rich A_1 (LO) phonon lines from the earlier reports.[2–6]

Figure 2 shows the room temperature Raman spectra of the AlGaN-like A_1 (LO) modes from our quaternary samples M12, M14, and M28 in the range of 675–800 cm^{-1}, respectively. As displayed in Fig. 2, the spectra line shape for all three samples reveal asymmetric broadening (Raman linewidth) and a shift to lower frequency of the AlGaN-like A_1 (LO) mode with increasing the ratio of Al to In. To the best of our knowledge, both topological and structural

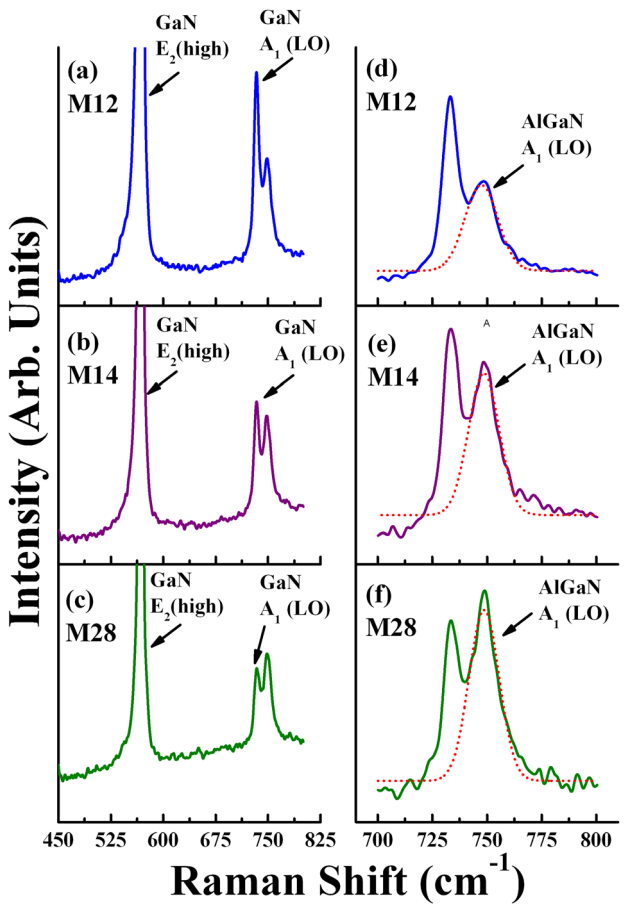

FIG. 1. Room temperature Raman spectra of the different InAlGaN samples over the range of 450–800 cm^{-1} are illustrated. In (a)–(c), one peak position located in the region of 550–575 cm^{-1} corresponds to the GaN E_2(high) mode and GaN A_1 (LO) mode located at around 735 cm^{-1}, respectively. In (d)–(f), from 700 to 800 cm^{-1}, the AlGaN-like A_1 (LO) mode is located at around 750 cm^{-1} described by the Gaussian fit (dotted line) of the Raman line shape.

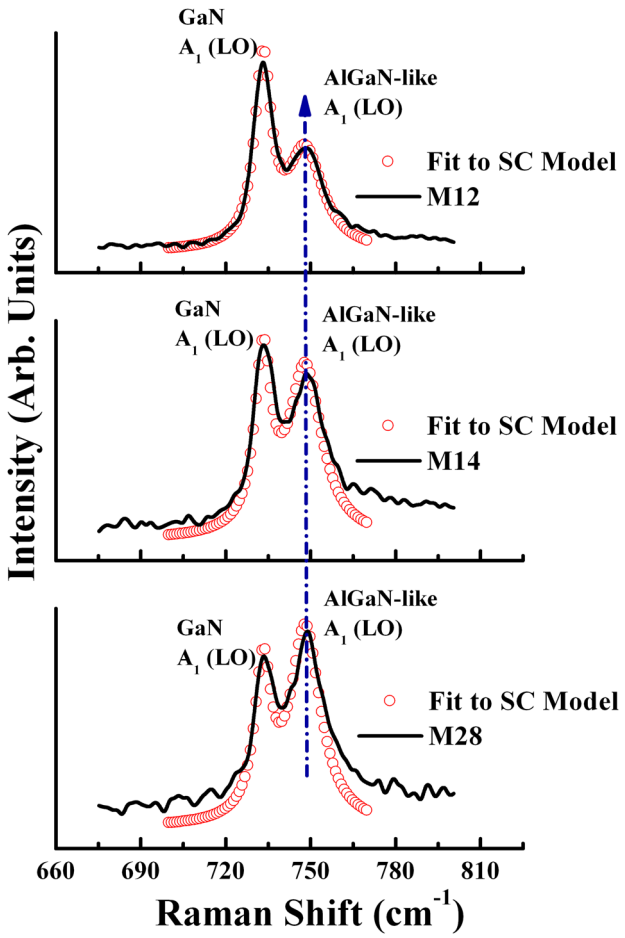

FIG. 2. Room temperature Raman spectra of the AlGaN-like A_1 (LO) modes from our quaternary samples M12, M14, and M28 are in the range of 675–800 cm^{-1}, respectively. The spectra line shape for all three samples reveal asymmetric Raman linewidth and a shift to lower frequency of the AlGaN-like A_1 (LO) mode with increasing the ratio of Al to In.

disorder may result from the process of atom substitution in alloy semiconductors. For allowed phonons, these disorders result basically in the breaking of the translational symmetry, leading to the contribution of $q \neq 0$ phonons to the Raman line shape, corresponding to the so-called finite-size effects.[7–12] This extensively drives the line shape asymmetry, which can be analyzed in terms of the SC model regarding to the finite correlation length of a propagating phonon due to the ACFs.[7–12]

For an ideal crystal, because of the momentum conservation, only phonons at the center of the Brillouin zone ($q = 0$) can be observed by Raman scattering. As the crystal is alloying, the phonons can be confined in space owing to the potential fluctuations of the alloy disorder, which give rise to a relaxation of the $q = 0$ selection rule in Raman scattering.[7–12] Then, the spatial correlation length of phonon in alloys becomes finite. The finite phonon mode will lead to the broadening and asymmetry of the Raman line shape. With the SC model, we can evaluate the asymmetric broadening of Raman scattering by the theoretical calculation. The Raman peak of AlGaN-like A_1 (LO) mode in Fig. 2 shows an asymmetric line shape, which can be described by the SC model.[7–12]

Based on the SC model, the Gaussian spatial correlation function $\exp(-2r^2/L^2)$, where L is the phonon correlation length, has been effectively used to account for q-vector relaxation related to finite-size effects and structural disorder.[7–12] Then, the Raman intensity $I(\omega)$ at a frequency ω can be written as follows:

$$I(\omega) \propto \int \frac{\exp(-q^2L^2/4)}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} d^3q, \tag{1}$$

where q is the reduced wave vector in the unit of $2\pi/a$, a is the lattice constant, and Γ_0 is the linewidth of the material which is GaN and AlGaN in this study.[7–12] In our case, the Raman linewidth is around 7 cm^{-1} for GaN A_1 (LO) mode and 13–15 cm^{-1} for AlGaN-like A_1 (LO) mode, respectively. Here, we consider that the Gaussian distribution is associated with the finite size of thin film region and rewrite Eq. (1) as follows:[10]

$$I(\omega) \propto \int \frac{\exp(-q^2L_1^2/16\pi^2)}{[\omega_1 - \omega_1(q)]^2 + (\Gamma_1/2)^2} d^3q + \int \frac{\exp(-q^2L_2^2/16\pi^2)}{[\omega_2 - \omega_2(q)]^2 + (\Gamma_2/2)^2} d^3q. \tag{2}$$

For the dispersion $\omega_1(q)$ and $\omega_2(q)$, we take the following analytic model relationship:[7–12]

$$\omega_1(q) = C_1 + D_1\cos(\pi q) \text{ and } \omega_2(q) = C_2 + D_2\cos(\pi q). \tag{3}$$

According to the *ab initio* phonon-dispersion relations, C_1 and D_1 were calculated for the GaN A_1 (LO) mode, while C_2 and D_2 were calculated for the AlGaN-like A_1 (LO) mode, respectively. Equations (2) and (3) show that if L is finite, the q selection rule may relax and additional transitions by phonon with lower energy at $q \neq 0$ may occur, which lead to the broadening and asymmetry of the Raman line shape. The opened circles in Fig. 2 exhibit the calculated results with the SC model, which are somewhat in good agreement with the experimental data. At present, we merely focus on the transformation of the correlation length L and the Raman linewidth Γ in AlGaN-like A_1 (LO) mode assigned from our samples, then the values of L and Γ can be evaluated from the Raman line shape fitting and are also listed in Table I.

From the results of Table I, as the ratio of Al to In is increased, it is found that the correlation length L decreases but the Raman linewidth Γ increases. The correlation length L is determined from our calculations to be in the range of 62–69 Å, a relatively small value suggesting a clear absence of long-range order in the alloy system.[5] In order to further investigate this assumption, each of our InAlGaN quaternary alloys were characterized by the HRXRD measurements to carry out the (004) $\omega - 2\theta$ scan. The HRXRD spectra are shown in Fig. 3 and are relatively comparable to our previous results.[13] In Fig. 3, the separated diffraction peaks are associated with GaN and InAlGaN, respectively, which confirm that the quaternary InAlGaN alloys were epitaxially grown on GaN. The alloy system of In-Al-Ga-N samples with the Al to In ratio of around 4.8, which are lattice matched to the underlying GaN layer, exhibited the best structural and optical properties, so only one GaN peak is observed for M28 in Fig. 3.[14] However, as the Al to In ratio increased more, the InAlGaN diffraction peaks appear on the right side of GaN peak. When the Al to In ratio is increased further to be around 7.6, a more isolated InAlGaN peak appears. The separated distance between GaN and InAlGaN peaks in M12 (dotted line) is carried out to be the largest one, demonstrating the biggest lattice mismatch and strain existing in M12 among the three samples.[14] Therefore, the HRXRD confirms the Raman analysis that M12 in this study does not reveal considerable long-range ordering.

More studies related to the InAlGaN/GaN heterostructures may be obtained from the Raman linewidth and

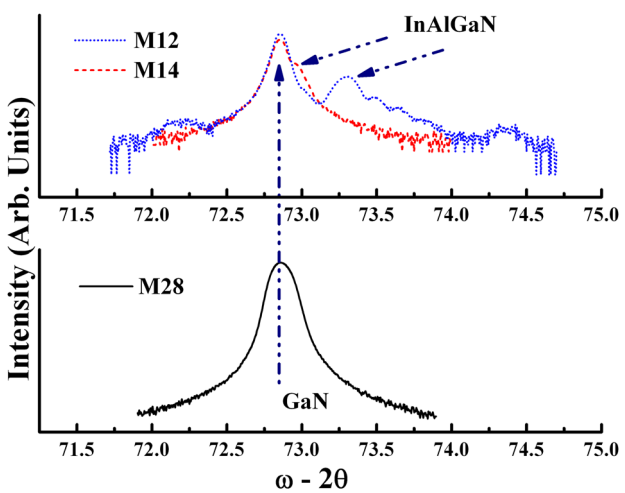

FIG. 3. Three samples of our InAlGaN/GaN heterostructures were characterized by HRXRD to carry out the (004) $\omega - 2\theta$ scan. The separated diffraction peaks are associated with GaN and InAlGaN, respectively, which confirm that the quaternary InAlGaN alloys were epitaxially grown on GaN.

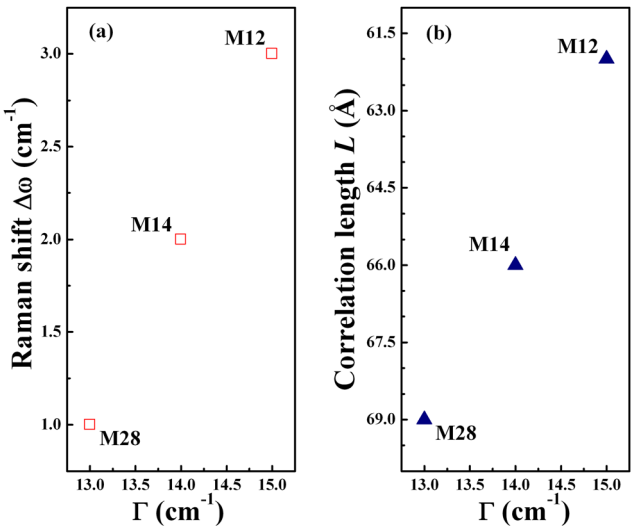

FIG. 4. The Raman shift $\Delta\omega$ (opened squares) from 750 cm^{-1} as a function of the Raman linewidth Γ and the correlation length L (closed triangles) as a function of Raman linewidth Γ are displayed in (a) and (b), respectively. The Raman linewidth performance follows a trend which displays a maximum for M12, a value at which a maximum disorder is supposed to be expected in a random system.

correlation length behavior for the AlGaN-like A_1 (LO) phonon. The Raman shift $\Delta\omega$ (opened squares) from 750 cm^{-1} as a function of the Raman linewidth Γ and the correlation length L (closed triangles) as a function of Raman linewidth Γ are displayed in Figs. 4(a) and 4(b), respectively. The Raman linewidth performance follows a trend which displays a maximum for M12, a value at which a maximum disorder is supposed to be expected in a random system. Thus, our data suggest that the distribution of the InAlGaN/GaN alloy constituents for the higher Al to In ratio is random. It is also shown that the agreement between the experimental and calculated linewidth and shift of AlGaN-like A_1 (LO) phonon signal is reasonable. In the case of a single crystal with very low non-stoichiometry, the correlation length will tend towards infinity. In this study, the correlation length was discussed as a fitting parameter to investigate the localized region of AlGaN-like A_1 (LO) phonon. The value of L increases with decreasing Al to In ratio, which indicates that the phonon extended region becomes larger. Hence, we have demonstrated experimentally that the L value is a very appropriate parameter accounting for the disorder of InAlGaN/GaN heterostructires.

IV. CONCLUSIONS

In summary, the asymmetric behavior of the AlGaN-like A_1 (LO) Raman linewidth of InAlGaN/GaN heterostructures was attributed to the activation of phonons of $q \cong 0$ arising from the disordered state of the alloys. Thus, the microscopic nature of the InAlGaN/GaN disorder is discussed by investigating the compositional dependence of AlGaN-like A_1 (LO) mode and is able to be quantitatively explained in terms of the SC model. X-ray diffraction supports the results; the correlation length L decreases as the increasing of Al to In ratio corresponding to the absence of the long-range order in the alloy.

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