Luminescence properties of $In_xGa_{1-x}N$ ($x \sim 0.04$) films grown by metal organic vapour phase epitaxy*

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$In_xGa_{1-x}N$ ($x \sim 0.04$) films are grown by metal organic vapour phase epitaxy. For the samples grown on GaN directly, the relaxation of InGaN happens when its thickness is beyond a critical value. A broad band is observed in the luminescence spectrum, and its intensity increases with the increasing degree of relaxation. Secondary ion mass spectrometry measurement rules out the possibility of the broad band originating from impurities in InGaN. The combination of the energy-dispersive X-ray spectra and the cathodeluminescence measurements shows that the origin of the broad band is attributed to the indium composition inhomogeneity caused by the phase separation effect. The measurement results of the tensile-strained sample further demonstrate the conclusions.

Keywords: InGaN, phase separation, composition inhomogeneity

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1. Introduction

In recent years, InGaN has aroused a wide interest and has been regarded as a potential material for a variety of devices, such as solar cells and photon detectors.[1−4] In these devices, the thicknesses of InGaN layers are more than several tens of nanometers. This is much thicker than those of quantum wells, which are widely utilized in blue light emitting diodes (LEDs) and laser diodes (LDs). The characteristics of a thick InGaN layer are very different from those of a thin InGaN layer, because the latter is usually fully compressively strained in the quantum wells. Hence, it is important to investigate the physical properties of a thick InGaN layer, including its strain state and luminescence properties.

Indium composition inhomogeneity is a very important phenomenon in InGaN, and can markedly influence the performances of InGaN-based devices.[5−7] In addition, the impurities can also affect the quality of InGaN.[8−10] In the photoluminescence (PL) and cathodeluminescence (CL) spectra of InGaN, it is frequently observed that a broad band exists on the low-energy side of the InGaN band edge peak.[7,11,12] Some researchers considered that this was from the high indium composition region caused by composition inhomogeneity,[7,11] while others believed that it was related to the impurities.[12] Therefore, the fundamentals of InGaN luminescence is still not clear. In this work, InGaN films with various thicknesses and different strain states are investigated. It is demonstrated that the broad band is due to indium composition inhomogeneity, which is mainly induced by the phase separation effect.

2. Experiment

Five samples, labeled as A–E, are grown on (0001) sapphire substrates in an AIXTRON 2000HT metal organic vapour phase epitaxy (MOVPE) system. After the formation of a 30-nm low temperature GaN buffer layer, a 2-μm GaN bulk layer is grown on it at 1040 °C with H_2 serving as the carrier gas. Then, the growth temperature is reduced and the carrier gas is switched to N_2 for InGaN growth. For samples A–D, an InGaN layer is directly grown on GaN at 800 °C. The thicknesses of the InGaN layers in samples A−D are 65, 120, 240, and 360 nm, respectively. For sample E, before the growth of InGaN film, a 15-nm InGaN

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buffer layer is grown at 550 °C first and then annealed at 800 °C for 12 min. Subsequently, a 65-nm InGaN layer is grown at 800 °C. The V/III ratios of InGaN in all the samples are kept constant.

After growth, high-resolution X-ray diffraction (XRD) measurement is performed in a triple-crystal diffractometer with a 4-bounce symmetric Ge (220) monochromator and a 3-bounce channel-cut Ge (220) analyser. A 30-mW 325-nm He-Cd laser is used as an excitation source for PL measurement. CL spectra are measured at 300 K using a commercial Gatan MonoCL3+ installed on a scanning electron microscope (Quanta 200F). Secondary ion mass spectrometry (SIMS) analysis was carried out by the Evans Analytical Group. Energy-dispersive X-ray spectrum (EDS) measurements were carried out on a Hitachi S-5500 scanning electron microscope.

3. Results and discussion

The reciprocal space mappings of samples A–D , measured around (114) reflection by XRD, are shown in Fig. 1, where fully compressive-strain and full relaxation are marked by $R = 0$ and $R = 1$ lines, respectively. It is found that the strain state of the 65-nm InGaN in sample A is homogeneous and nearly completely fully compressively strained. As the thickness of the InGaN film increases, the reciprocal lattice point (RLP) of the InGaN becomes broader and a diffraction signal can be detected around the fully relaxed ($R = 1$) position. For sample D, the 360-nm InGaN film, RLP of InGaN becomes even broader, while partially and fully relaxed components can be observed clearly. Comparison among the reciprocal space mappings of the four samples reveals that the RLP of InGaN progressively expands from a nearly fully strained ($R = 0$) position to a nearly fully relaxed ($R = 1$) position with the increasing thickness. This is frequently observed since strain relaxation in InGaN/GaN epilayers occurs when an InGaN epilayer exceeds its critical thickness.[13,14] The reciprocal lattice constants Q_x and Q_z of the compressively strained and relaxed InGaN both can be obtained from the reciprocal lattice mappings directly. Then the actual lattice constants a and c can be calculated. Hence, the indium composition x can be calculated by a univariate cubic equation, which was published by Schuster *et al.*[15] As a result, with thickness increasing from 65 nm to 360 nm, the indium composition increases slightly. The indium composition of fully compressively strained InGaN in sample A is about 3.9%, while the fully compressively strained part and the relaxed part in sample D increase to 4.0% and 4.2%, respectively, which is caused by a surface pulling effect.[16,17] Hence, the indium compositions of the four samples are around 4%.

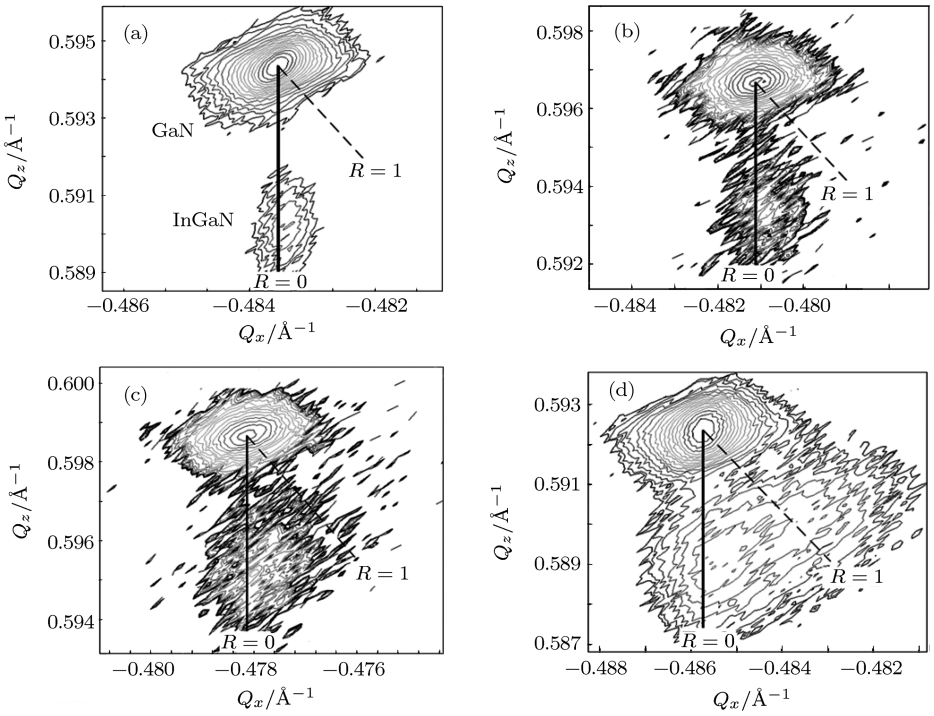


Fig. 1. Reciprocal space mappings of (a) sample A, (b) sample B, (c) sample C, and (d) sample D, measured around (114) surface reflection. $R = 0$ and $R = 1$ lines represent the fully compressively strained position and fully relaxed position of $In_{0.04}Ga_{0.96}N$, respectively.

The PL spectra of samples A–D at 300 K are shown in Fig. 2. In sample A, there is only one band edge peak of a compressively strained InGaN epilayer around 395 nm. However, as thickness increases, Gauss deconvolution shows that another narrow peak can be observed separately in Samples B, C and D around 404–408 nm and its intensity increases rapidly. Due to the compressive strain, the band gap of strained InGaN is higher than that of the relaxed one.[18] Therefore, the obvious redshift originates from the enhancement of the relaxation degree and the narrow peak around 404–408 nm is the band edge peak of the relaxed InGaN. On the other hand, no broad band exists in the thin InGaN film of sample A. However, as the thickness of InGaN increases, a broad band around 450 nm ($\sim$ 270 meV lower than the InGaN band edge peak) arises and its intensity relative to the InGaN band edge peak also increases.

From Fig. 2(a) to Fig. 2(c), it is shown that intensities of the band edge peak of the compressively strained and relaxed InGaN increase as the InGaN thickness increases. One of the reasons is that the thicknesses of both strained and relaxed InGaN increase from sample A to sample C, and more excitation laser photons can be absorbed by InGaN, hence the PL intensity will increase. Meanwhile, three-dimensional growth is induced and the surface becomes rough as the thickness increases. The surface root mean square roughnesses of samples A–D are 1.0, 4.0, 4.9 and 15.2 nm, respectively. The roughened surface can efficiently increase the light extraction efficiency in PL tests, which has been reported by Jmerik *et al.*[19] The increased rate of the PL intensity of the relaxed InGaN band edge peak is much higher than that of the strained InGaN. One of the reasons for which is that the relaxed InGaN is on the top of the compressively strained InGaN and therefore photons from the relaxed InGaN can be extracted more easily from the rough surface. In addition, the band gap of relaxed InGaN is smaller than that of the compressively strained InGaN. Hence, photons from the band edge of the strained InGaN can be absorbed by the relaxed InGaN. Hence, the intensity of relaxed InGaN is even higher than that of the compressively strained InGaN in samples C and D.

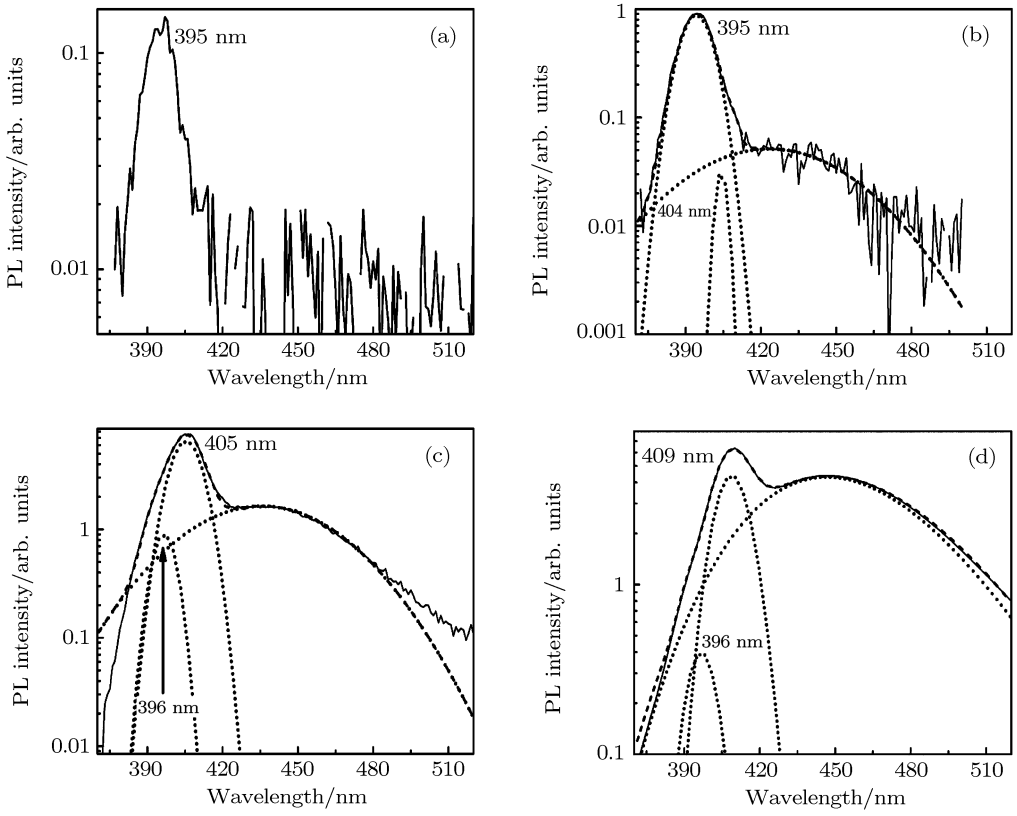


Fig. 2. PL spectra of (a) sample A, (b) sample B, (c) sample C, and (d) sample D at 300 K. The solid lines represent the measured spectra, the dashed lines represent the Gaussian fitting curves of the spectra and the dotted lines represent the deconvolutions of the Gaussian fitting curves.

As thickness increases, the intensity of the broad band around 450 nm increases and the intensity of the broad band is the highest in sample D. This demonstrates that the broad band is related to the InGaN relaxation process. The intensities of the band edge peaks of the strained and the relaxed InGaN in sample D are lower than those in sample C, while the strain relaxation in sample D is the most obvious and the intensity of the broad band in sample D is the highest. This behaviour implies that the broad band peak can attract carriers from the InGaN band edge.

To further investigate the relationship between the thickness and the broad PL band around 450 nm, the PL spectra of samples A and D are measured at 10 K. As shown in Fig. 3, the broad band is still hard to observe in sample A , while it is obvious in sample D even at 10 K. This demonstrates that the broad band is closely related to the stress-relaxation of InGaN film. Moreover, the two narrow peaks at 10 K around 400 nm in sample D are obvious, and correspond to the band edge peaks of compressively strained and relaxed InGaN, respectively, as shown in Fig. 1(d). The band edge peak of compressively strained InGaN is more obvious than that at 300 K, which implies that carriers in compressively strained InGaN can migrate to relaxed InGaN at room temperature and be captured since the band gap of relaxed InGaN is smaller than compressively strained InGaN. The intensity of the broad band related to relaxed InGaN band edge is lower than that at 300 K. This demonstrates that the broad band peak can attract carriers from the InGaN band edge at room temperature.

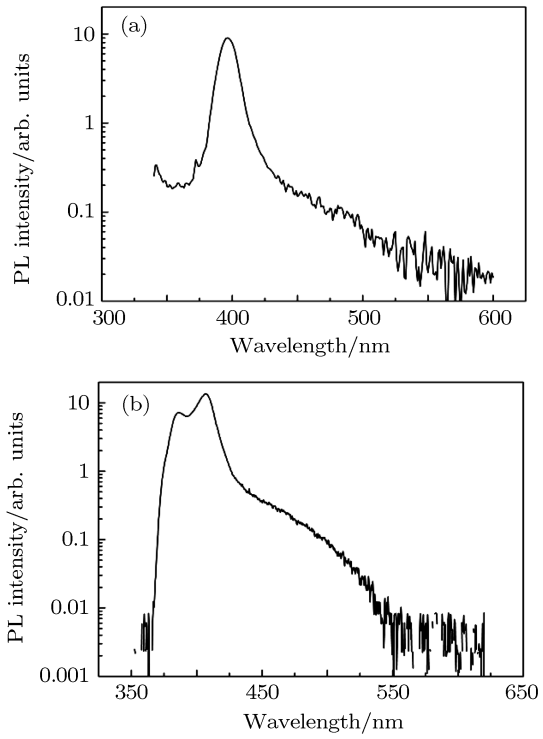


Fig. 3. PL spectra of (a) sample A and (b) sample D at 10 K.

The broad band seems similar to the spectra of some impurities. Magnesium (Mg) in InGaN as p-type doping can induce the emission in a long wavelength range.[12,20] However, the InGaN epilayer in the work is unintentionally doped and Mg is not detected by SIMS measurement either, so the possibility of Mg can be eliminated. Gallium vacancy (V_{Ga}) is related to the yellow band in nitride materials.[21,22] Nitrogen vacancy (V_N) and hydrogen (H) frequently form a complex with Mg or V_{Ga}, and hence can also be eliminated.[21,23,24] Carbon at a nitrogen site (C_N) is another strong candidate beside Mg as an acceptor in GaN with a binding energy of about 230–272 meV.[25,26] Oxygen at a nitrogen site (O_N) is also believed to be an origin of the blue band in nitride materials.[21,27] Therefore, C and O impurities are the most probable origins of the 450-nm broad band in our unintentionally doped InGaN epilayer. Thus, SIMS measurements of C and O are carried out on samples A–D. To eliminate the effect of surface contaminants, the samples are cleaned and the data of the first 20-nm near the sample surface are not adopted. The data are recorded while the density of atoms is stable. As shown in Fig. 4, the densities of both C and O in GaN keep constant in GaN and are similar to the measurements by Koleske *et al.*[28] The SIMS measurements are carried out in a calibrated system twice and similar results are obtained. Therefore, the experimental data are reliable. The densities of both C and O in all the samples just increase in the InGaN epilayer beyond the interface of GaN/InGaN. However, the density profiles in InGaN are not the same in the four samples with the same thickness and they are independent of the strain state of InGaN. In all of the samples, the densities of C and O near the surface are much higher than those near the InGaN/GaN interface, and the densities near the surface have the same orders of magnitude. In sample A, the 450 nm PL band is difficult to observe while the C and O densities are comparable to those in sample D. Therefore, it can be deduced that the broad band around 450 nm is independent of C and O impurities. The C and O densities near the surface are more than 1.0×10^{20} cm^{-3}. This is similar to the result measured in AlGaN, which is published by Bradley *et al.*[29] The high density of impurities near the surface may be caused by the diffu-

sions of C and O from the surface during the temperature decreasing after the growth in MOPVE chamber since the crystal quality of InGaN is poor and impurities are easily incorporated into it. Further study is desired to understand the detailed kinetics.

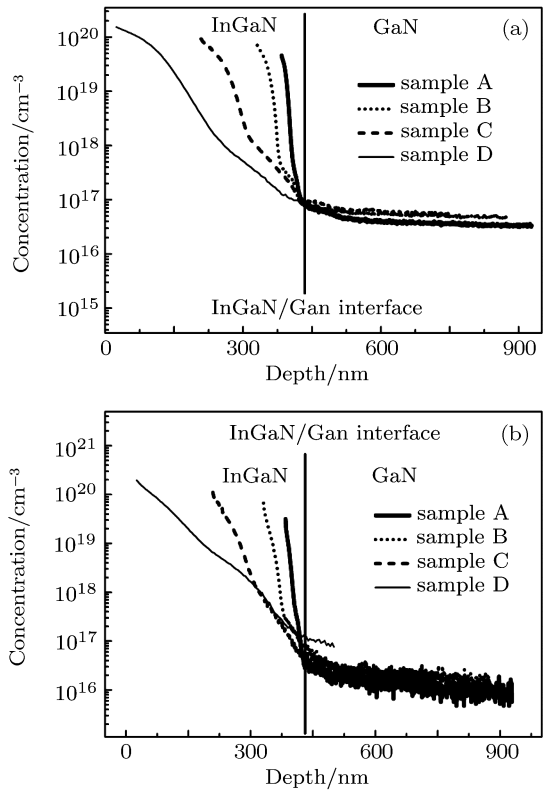


Fig. 4. SIMS depth profiles of (a) carbon and (b) oxygen in samples A–D.

EDS measurement of samples A and D are shown in Fig. 5. In sample A, most parts of the surface are planar and the indium composition of the planar area is kept constant. The surface roughness of sample D is much larger than that of sample A, and three-dimensional growth is evident. From Fig. 5, it is demonstrated that the total indium composition of the islands is relatively high. The absolute quantities are not very exact if the penetration depth and width of incident electrons are considered. However, it can be concluded that the relative indium composition inhomogeneity in sample D ($\sim 45\%$) is stronger than that in sample A ($\sim 15\%$). As the thickness of InGaN epilayer increases above its critical thickness, three-dimensional growth is induced to relax the compressive stress and the surface roughness increases, which can enhance the light extraction efficiency.[30] Meanwhile, more indium atoms can diffuse into the islands since the diffusion capability of indium adatoms is higher than that of gallium adatoms.[31] With a high indium composition, phase separation is easily induced in InGaN, which causes indium composition inhomogeneity.[32,33] In addition, the relaxation of InGaN will make its lateral lattice increase. This is conducive to indium incorporation and will induce the composition pulling effect.[16,17] Thus, it is another factor that enhances phase separation in InGaN. Finally, the radiative recombination of carriers occurs in the high indium composition regions in the islands and generates the broad band at about 450 nm in the spectra.

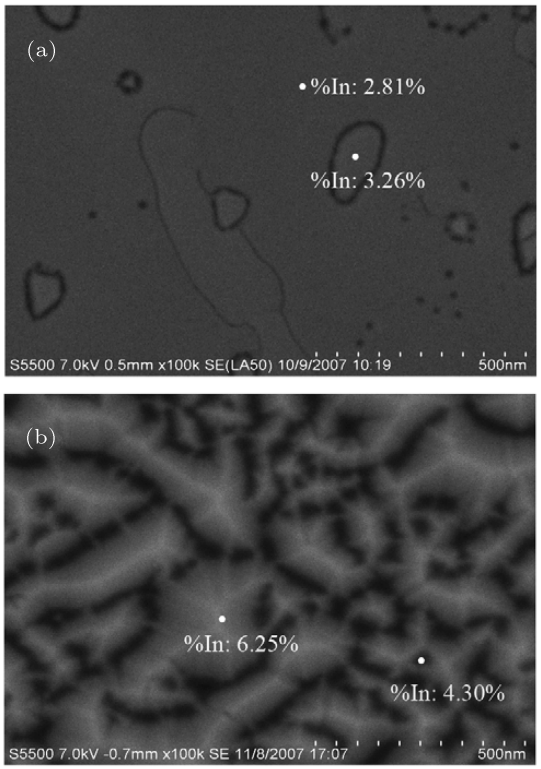


Fig. 5. SEM images and EDS measurement results of (a) sample A and (b) sample D. White dots indicate the centres of the incident electron beam area in EDS measurement.

To confirm that indium composition inhomogeneity is the origin of the broad band around 450 nm in sample D, surface and cross-sectional CL measurements are carried out at 300 K. Samples A–C are very thin, it is difficult to focus the electron beam on the cross section of InGaN and the resolution is not high enough either. The CL results are shown in Fig. 6. From Fig. 6(a) to Fig. 6(c), it is revealed that the signals of the band edge peak of InGaN and broad band are both mainly from the islands. Since more indium atoms combine into the islands, indium composition inhomogeneity caused by phase separation is facilitated in the islands.[32,33] Therefore, high indium

composition regions are generated in the islands and the broad band of photon emission is around 450 nm. Meanwhile, the signal of the band edge peak of InGaN layer is also strong in the islands, which implies that the indium composition in the other part of the islands is still about 4%, although high indium composition regions are generated by composition inhomogeneity in some regions of the islands.

From Fig. 6(f), it is revealed that most indium-rich regions are in the relaxed layer rather than leaving the compressively strained layer since the 450 nm band originates mainly from the indium-rich regions. This demonstrates that composition inhomogeneity is closely related to the stress relaxation process. The InGaN band edge peak wavelength at 397 nm in the cross section spectrum is shorter than that at 405 nm in the surface spectrum. From Fig. 6(e), it can be deduced that the 397-nm CL peak originates from a lower InGaN layer and it is the band edge peak of the compressively strained lower part of the InGaN layer. The cross section CL measurements show that most electrons are injected into the lower part of InGaN since it is difficult to focus the electron beam onto the surface part. More carriers in the lower layer can be excited. Therefore, the intensity of the CL peak from the lower part is enhanced while the signal of the band edge peak of the upper part is decreased and covered by that of the lower part. Moreover, this behaviour implies that with weak excitation intensity, most carriers are consumed by the radiative recombination at 450 nm in the relaxed part. This demonstrates that high indium composition regions acts as localized states that can capture carriers from lower indium composition regions. This can account for the higher intensity of 450-nm broad band at 300 K than that at 10 K and the lower band edge peak intensity in sample D than that in sample C at 300 K.

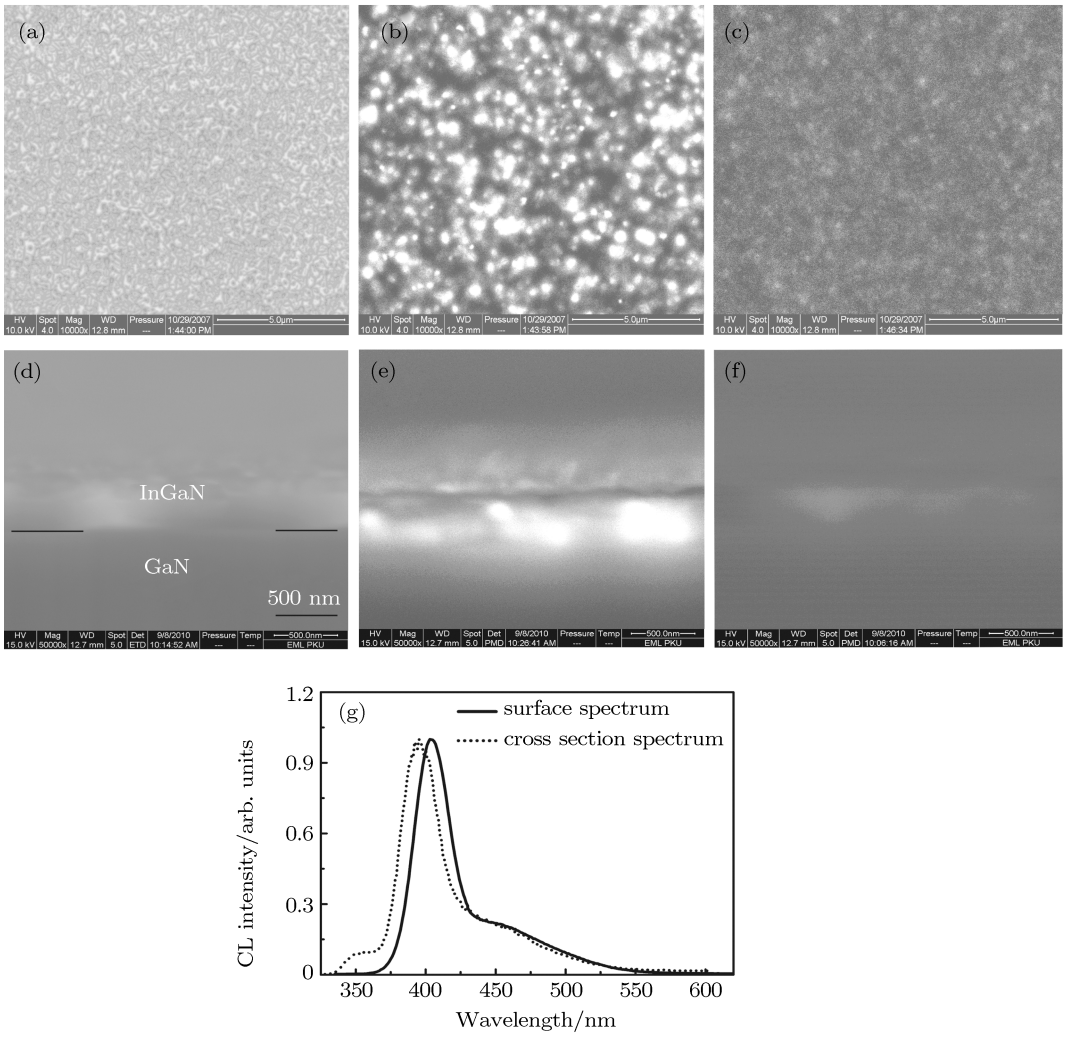


Fig. 6. SEM and CL results of sample D: (a) SEM image of the surface, CL images at (b) $\lambda = 405$ nm and (c) $\lambda = 450$ nm of the surface, (d) SEM image of the cross section, CL images at (e) $\lambda = 397$ nm and (f) $\lambda = 450$ nm of the cross section, (g) surface and cross section CL spectra.

To further confirm the conclusion, we study sample E. The indium composition of sample E is about 4.6%. In Fig. 7(a), it is shown that the InGaN layer is highly tensile-strained by the InGaN buffer grown at low temperature with the same V/III ratio. Therefore, the total indium composition of the InGaN increases to 4.6% by the composition pulling effect, which is closely related to the strain state and can enhance the phase separation.[16,17] Meanwhile, the surface root mean square roughness of sample E is 2.1 nm, which is twice that of sample A. Hence, three-dimensional growth in sample E is also more remarkable than that in sample A, which is caused by the tensile strain. As a result, it is shown in Fig. 7(b) that a broad InGaN peak can be clearly observed beside the GaN peak and the $In_{0.046}Ga_{0.954}N$ peak. This demonstrates that composition inhomogeneity is prominent in sample E.

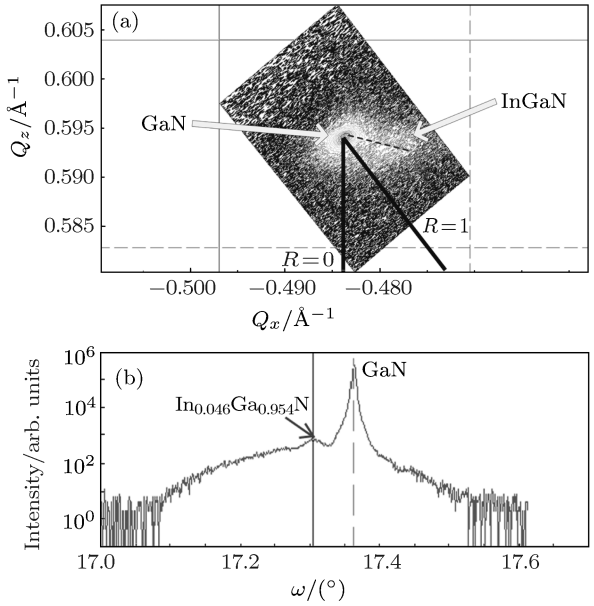


Fig. 7. (a) Reciprocal space mappings of sample E measured around (114) surface reflection, where $R = 0$ and $R = 1$ lines represent the fully compressively strained position and the fully relaxed position of $In_{0.046}Ga_{0.954}N$, respectively; (b) ω–2θ (002) scan of sample E.

PL spectra of sample E is shown in Fig. 8 at 10 and 300 K. The broad peak around 459 nm is the main peak at 300 K. Even at 10 K, the intensity of the broad peak is not weaker than that of the band edge peak of $In_{0.046}Ga_{0.954}N$ epilayer at 401 nm. This behaviour is different from that of the defect-induced PL peak, which is much weaker than the band edge peak of InGaN at low temperature. Considering the prominent composition inhomogeneity detected by XRD, it is proved that the broad peak in the PL/CL spectrum is induced by the indium composition inhomogeneity.

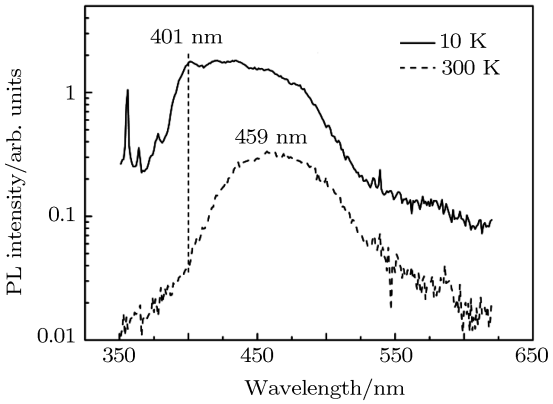


Fig. 8. PL spectra of sample E at 10 K and 300 K.

4. Conclusion

The broad bands in the PL/CL spectra of InGaN films are investigated. The phase separation induced indium composition inhomogeneity in the InGaN layer is demonstrated to be the origin of the broad band in the InGaN luminescence spectrum. The possibility of its origination from impurities is eliminated.

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