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Growth temperature effect on the optical and material properties of $Al_xIn_yGa_{1-x-y}N$ epilayers grown by MOCVD

J.S. Huang[a,*], X. Dong[a], X.D. Luo[a], D.B. Li[a], X.L. Liu[a], Z.Y. Xu[a], W.K. Ge[b]

[a] *Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China*
[b] *Department of Physics, Hong Kong University of Science and Technology, Hong Kong, China*

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Abstract

$Al_xIn_yGa_{1-x-y}N$ epilayers have been grown by metalorganic chemical vapor deposition (MOCVD) at different temperatures from 800 to 870°C. The incorporation of indium is found to increase with decreasing growth temperature, while the incorporation of Al remains nearly constant. The optical properties of the samples have been investigated by photoluminescence (PL) and time-resolved photoluminescence (TRPL) at different temperatures. The results show that the sample grown at 820°C exhibits the best optical quality for its large PL intensity and the absence of the yellow luminescence. Furthermore the temperature-dependent PL and TRPL of the sample reveals its less exciton localization effect caused by alloy fluctuations. In the scanning electron microscopy measurement, much uniform surface morphology is found for the sample grown at 820°C, in good agreement with the PL results. The improvement of $Al_xIn_yGa_{1-x-y}N$ quality is well correlated with the incorporation of indium into AlGaN and the possible mechanism is discussed.
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1. Introduction

Recently, Group-III nitride semiconductors have emerged as a leading material for the fabrication of blue-green light-emitting diodes (LEDs) and laser diodes. Alloys of GaN with InN and AlN can be prepared covering the spectral range from red to vacuum UV (1.9 to 6.2 eV) [1–3]. InGaN has been widely used as an active layer in many device structures mainly for its high luminescence efficiency. However, the large lattice mismatch will result in the device active layer experiencing significant biaxial stress, especially for AlGaN/InGaN or GaN/InGaN heterostructures. Recently, $Al_xIn_yGa_{1-x-y}N$ quaternary alloys have been recognized to have the potential to achieve lattice-matched heterojunctions throughout the entire layered structure. Using AlInGaN film as the barrier for the InGaN

*Corresponding author.
E-mail address: hjs@red.semi.ac.cn (J.S. Huang).

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quantum wells was found to be able to increase the luminescence intensity [4–6]. AlInGaN alloy was also used as the active layer for fabricating LEDs [7]. In spite of the fast development in the device applications, however, the fundamental optical properties of the AlInGaN alloys have not been well exploited.

The growth condition of $Al_xIn_yGa_{1-x-y}N$ alloys is very complicate [8]. The primary concern in the development of high-quality $Al_xIn_yGa_{1-x-y}N$ films lies in the difference of typical growth temperatures for the ternary alloys AlGaN and InGaN. The growth temperature for high-quality AlGaN using metalorganic chemical vapor deposition (MOCVD) can be over 1000°C [9,10], while InGaN growth usually proceeds at much lower temperatures from 700 to 800°C because of the weak In–N bond [11]. Reported values of growth temperature for AlInGaN are much higher than that of InGaN [4,12,13], and then a careful optimization of the growth temperature is very important to achieve high-quality quaternary material.

In this paper, we compare the optical properties of $Al_xIn_yGa_{1-x-y}N$ epilayers grown at different temperatures from 800 to 870°C using photoluminescence (PL) and time-resolved photoluminescence (TRPL). It is found that the sample grown at 820°C exhibits the best optical quality for its largest PL intensity and suppressed yellow band. The results of the temperature-dependent PL and TRPL demonstrate the smaller exciton localization effect in the sample grown at 820°C, reflecting less alloy fluctuations and/or defects in the sample. In the scanning electron microscopy (SEM) measurement, much uniform surface morphology is found for the sample grown at 820°C, in a good agreement with the PL results. The improvement of AlInGaN quality is well correlated with the incorporation of indium into AlGaN and the possible mechanism is discussed.

2. Experimental procedure

The samples studied were grown by low-pressure MOCVD on sapphire (0 0 0 1) substrates. A low temperature (550°C) GaN buffer of $\sim$20 nm thick was first deposited, followed by the deposition of 1 μm of GaN grown at 1030°C.A 0.5-μm-thick AlInGaN layer was then grown on the GaN layer. The growth temperature of AlInGaN layers was in the range of 800–870°C. All other growth conditions were kept unchanged for different samples. The growth pressure was 76 Torr. In the growth, trimethylgallium, trimethylaluminum, ethyldimethylindium and ammonia were used as precursors and SiH_4 was used for n-type doping. The detailed growth procedure will be described elsewhere [14]. The sample compositions were determined by energy dispersive system measurement. High resolution X-ray diffraction, using synchrotron radiation as a light source, was carried out to investigate the strain between GaN layer and AlInGaN layer. In this work we choose three typical $Al_xIn_yGa_{1-x-y}N$ samples to study the growth temperature effect on their optical and material properties. The compositions of the samples are listed in Table 1 along with the basic PL results. As can be seen from Table 1, there is no significant difference in the incorporation of Al in the temperature range from 820 to 870°C, while the incorporation of In decreases rapidly with the increase of the growth temperature. The rapid decrease of the In content with increasing temperature can be attributed to the weak In–N bond [11]. For TRPL measurements, the PL was excited by frequency-doubled ($\lambda = 360$ nm) laser pulses

Table 1
Samples specifications

Samples number	D8	D9	D6
Growth temperature	820°C	850°C	870°C
Composition	$Al_{0.12}In_{0.095}Ga_{0.785}N$	$Al_{0.12}In_{0.033}Ga_{0.847}N$	$Al_{0.11}In_{0.03}Ga_{0.86}N$
E_p ($T = 11$ K)	3.128 eV	3.243 eV	3.251 eV
FWHM ($T = 11$ K)	160 meV	190 meV	236 meV

from a Ti:sapphire mode-locked femtosecond laser and the time-correlated signals were analyzed by a two-dimensional (2D) synchronous streak camera with an overall resolution of less than 15 ps. PL measurement was performed in CW configuration using a combination of a cooled GaAs PMT with a data-link electronic system.

3. Results and discussion

Fig. 1 shows intensity-normalized PL spectra of the three samples, namely D8, D9 and D6 as labeled in the figure, under the excitation power of 3.6 mW at 11 K. The main peak in the PL spectrum has been attributed to a recombination of localized excitons, as often observed in the nitride semiconductor alloys [15,16]. It is generally characterized by a very asymmetric line shape and the blue-shift of the peak energy with the excitation density (not shown). Here we put our stress on the comparison of the optical properties of different samples. It is found that D8 grown at 820°C has the highest PL intensity as well as the narrower full-width at half-maximum (160 meV compared to 190 and 236 meV for D9 and D6, respectively.). The main PL peak intensity of the sample D8 is four times stronger than that of D9, and more than one order of magnitude larger than that of D6. Another striking feature is the absence of yellow luminescence band in D8. In contrast, a strong yellow band about 0.76 eV (0.52 eV) below the main PL peak is observed in D6 (D9). The yellow luminescence band often appears in GaN, which has been considered to stem from the transition from conduction band to deep acceptor centers, possibly gallium vacancy [17] or point defect of nitrogen antisite (N_{Ga}) [18]. These defects could be related to the Ga-poor growth condition [19]. Therefore, we believe that the optical quality of D8 is much better than that of D6 and D9. As the composition of Al is nearly the same for the three samples, it indicates that the increased In composition can significantly improve the optical properties of the quaternary AlInGaN alloys. Similar result has been reported previously that the incorporation of a few percents of indium into AlGaN caused significant smoothening of the band-bottom potential profile in the AlInGaN layers due to improved crystal quality [12].

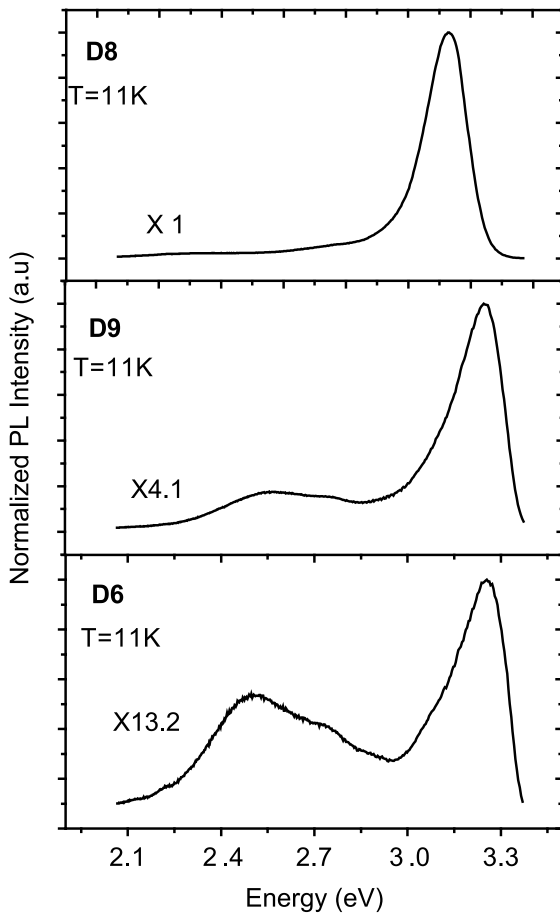

Fig. 1. Normalized PL spectra of AlInGaN samples (D8, D6 and D9) at $T = 11$ K. The normalization factors are indicated in the figure. All the PL spectra are dominated by the localized exciton emission.

As has been discussed, the PL spectrum of the AlInGaN alloy was dominated by the localized exciton emission. The localization was induced by the potential fluctuations caused by either alloy disordering and/or defects. We have performed temperature-dependent PL to study the exciton localization effect in the different samples. As expected the PL intensities in all samples decrease with increasing temperature. Fig. 2 displays the Arrhenius plots of PL intensity vs temperature of the samples. The solid lines in Fig. 2 are the least-squares fit of the data following the equation of

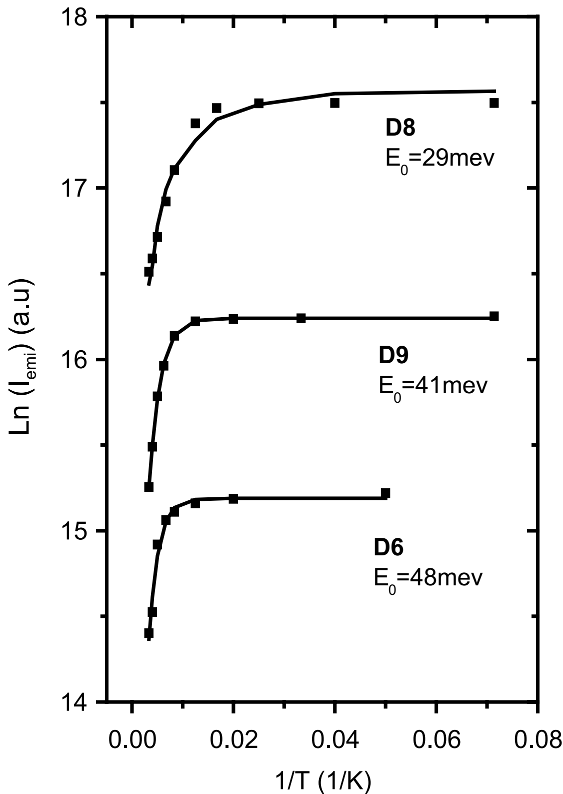

Fig. 2. The Arrhenius plots of PL intensities of the three samples D8, D6 and D9, respectively. The fitted thermal activation energies E_0 are indicated.

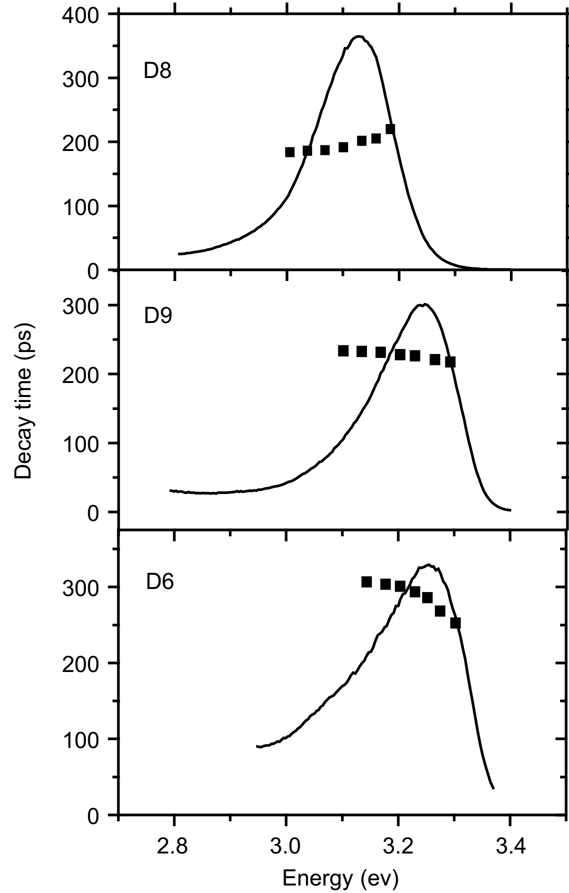

Fig. 3. Energy dependence of the decay lifetime for samples D8, D6 and D9 at 11 K. For references the PL spectra are also shown.

$I(T) = I_0[1 + C\exp(-E_0/kT)]$, where E_0 is the activation energy and C is a fitting constant. The fitted values of E_0 are 29, 41 and 48 meV for D8, D6 and D9, respectively. In general, the measured activation energy can be regarded as a measure of the exciton localization effect in the alloys [20]. Consequently, it reflects the alloy uniformity or the degree of free from defects. The experimental result that E_0 decreases with the increased In composition indicates that the random alloy disordering is reduced with the increase of the In composition in our AlInGaN alloy. This is consistent with the observed narrower line width and less asymmetric line shape in the sample D8.

Further argument about the exciton localization can be found in the TRPL measurements on our AlInGaN samples. Fig. 3 shows the measured decay times of the samples at 11 K monitored at different energies. It is seen that the variation of the decay time with the energy is different for different samples. For D8 the decay time increases slightly with the increase of energy, while the decay times of D6 and D9 decrease with the increase of energy. The latter is a well-known characteristic of the localized excitons and has been attributed to the transfer of excitons from higher to lower energy sites within the band-tail states caused by alloy fluctuation [21]. From the figure it is also noted that the decay time at the low-energy side for D6 is longer than those of D8 and D9. This behavior is qualitatively consistent with pervious theoretical prediction that the radiative lifetime of the bound exciton increases with the binding

energy [22,23]. Within AlInGaN alloys, excitons are energetically and spatially localized due to compositional fluctuations and/or defects. This localization is analogous to the binding of an exciton to an impurity, so that a larger characteristic localization energy (E_0) results in a longer radiative lifetime.

In order to correlate the observed optical properties with the material quality, we have performed the SEM measurement on the $Al_xIn_yGa_{1-x-y}N$ samples. The results are shown in Fig. 4. It is clear that the surface morphology of D8 is much better than that of D6 and D9. While there are many random pinholes on the surfaces of D9 and D6, few pinholes appear on the sample D8. The random pinholes are common defects in AlGaN and GaN films grown on sapphire and are believed to come from the incomplete coalescence of AlGaN or GaN islands during the film growth [24]. As reported previously, the appearance of the pinhole could be related to the growth temperature and the strain between AlInGaN and GaN [25]. It was reported that the pinhole density was significantly reduced with the increase of the growth temperature [26]. Certainly, it is not for our case as the sample D8 experienced the lower growth temperature than others. On the other hand, our XRD measurement indicates that the strain in the sample D8 is the largest among the three samples, as shown in Fig. 5. Fig. 5 is the (0004) $\Theta - 2\Theta$

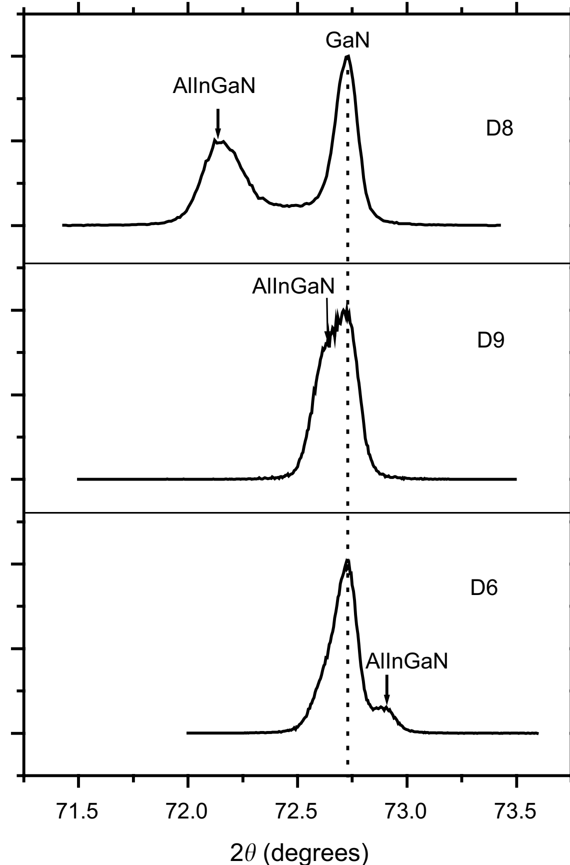

Fig. 5. (0004) $\Theta - 2\Theta$ X-ray spectra of the AlInGaN samples of D6, D8 and D9, respectively.

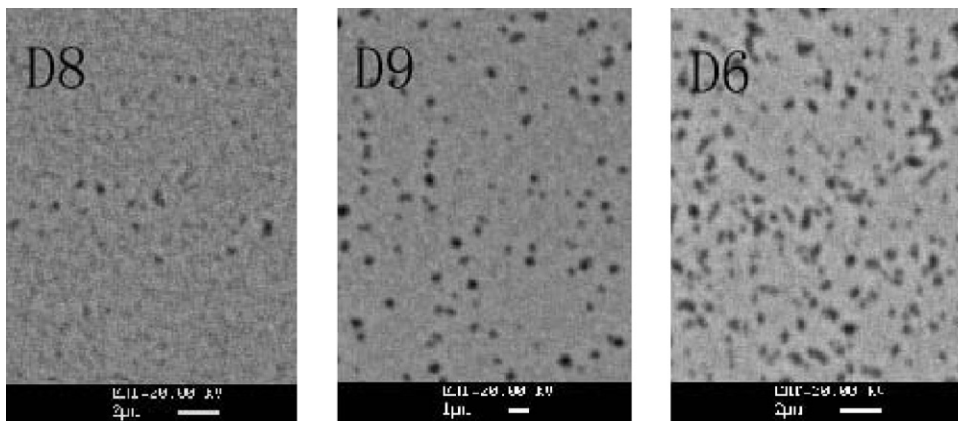

Fig. 4. SEM scanning images for the AlInGaN samples D8, D6 and D9, respectively.

diffraction pattern of our AlInGaN samples. The two peaks in the X-ray pattern are associated with GaN and AlInGaN, respectively. The spacing between two peaks in D8 is found to be the largest among the three samples, indicating the largest lattice mismatch existing in the sample D8. This result rules out the correlation of the pinhole with the strain. Therefore, we conclude that it is the increased indium composition that significantly improves the material quality. As mentioned above, indium is easier to incorporate into the alloys at lower growth temperature due to the weak In–N bond. This will make the indium atoms with a greater possibility to occupy normally vacant Ga sites in the growth. On the other side, the increased indium will saturate the free bond of N atoms allowing Ga atoms to diffuse freely on the surface, with an increased probability of exploring the possible incorporation sites. Thereby, the density of Ga vacancy related defects is lowered leading to suppressed yellow luminescence. In addition, since indium has a surface migration rate higher than that of Ga [27], the increased indium would facilitate 2D growth, which improves material quality by reducing pinholes on the surface of the alloys and making the material more uniform, leading to less localization energy.

4. Conclusion

In summary, we have used the optical spectroscopy to characterize $Al_xIn_yGa_{1-x-y}N$ alloys grown by metalorganic chemical vapor deposition at different temperatures. It is found that the sample grown at lower temperature (820°C) exhibits the best optical quality for its largest photoluminescence (PL) intensity and the absence of the yellow luminescence. Furthermore, the exciton localization caused by the alloy fluctuation and material defects was investigated by the temperature-dependent PL and time-resolved photoluminescence. In the scanning electron microscopy measurement, much uniform surface morphology is found for the sample grown at 820°C, in a good agreement with the PL results. The improvement of $Al_xIn_yGa_{1-x-y}N$ quality is well correlated with the incorporation of indium into AlGaN.

Acknowledgements

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