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Growth and Optical Properties of Double Heterostructure GaN/InGaN/GaN Films with Large Composition

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The double heterostructure GaN/InGaN/GaN films with different thicknesses of the InGaN layer were grown at 780 °C or 800 °C by metal–organic chemical vapour deposition. The samples were investigated using x-ray diffraction (XRD), room-temperature photoluminescence (PL) and Raman scattering. The dependences of the samples on both the growth temperature and the thickness of the InGaN layer were studied. The composition of InGaN was determined by the results of XRD, and the bowing parameter of InGaN was calculated in terms of the PL spectra. When the thickness of the InGaN layer was reduced, the phase separation of InGaN was found in some samples. The Raman frequency of the A_1 (LO) and E_2 (low) modes in all the samples shifted and did not agree with Vegard's law.

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Gallium nitride and related Ⅲ-nitride compound semiconductors are one of the most attractive wide bandgap materials for optoelectronics devices. The high luminescence blue light emitting diodes (LEDs) and InGaN multi-quantum well (MQW) laser diodes (LDs) have been successfully fabricated on sapphire substrates.[1] InGaN is a promising wide bandgap material for LEDs in the visible region from red (InN with $E_g = 1.89$ eV, $\lambda = 650$ nm) to near ultraviolet (GaN with $E_g = 3.39$ eV, $\lambda = 366$ nm) and is used as the active layer in these optical devices, playing a key role in the fabrication of both blue and green LEDs.[2]

It is a difficult task to grow the InGaN alloy. One of the main reasons is the large difference of 11% between the lattice constants of GaN and InN.[3] This large mismatch can give rise to a solid miscibility gap and the highly strained InGaN layer. Another problem is the high equilibrium vapour pressure of nitrogen over InN that is several orders of magnitude higher than that over GaN.[3] Therefore, low temperatures are required for the growth of InGaN. The development of InGaN single and double heterostructures (DH) is very important and a close inspection of InGaN DH has to be carried out. This is necessary for the development of single quantum well (SQW) and MQW devices in a nitride system because of the drastic changes of the growth conditions used for each single layer and in the characteristics of each layer.[4] The growth of the GaN/InGaN heterostructures poses a challenge, because the growth temperatures have to be changed by several hundreds of degrees.

In this Letter, the DH GaN/InGaN/GaN films with InGaN layers of different thicknesses were grown at 780 °C or 800 °C by metal–organic chemical vapour deposition (MOCVD). The growth temperatures have an influence on the quality of InGaN. If the growth temperature of InGaN is more than 800 °C, the concentration of InN will be very low. If the growth temperature of InGaN is lower than 760 °C, Ga droplets will be formed on the surface. The strain state and the degree of the structural perfection of the material have an influence on the performance of devices. Here we investigate the DH of the samples with x-ray diffraction (XRD), room-temperature photoluminescence (PL) and Raman scattering. The dependences of the DH films on the growth temperature and the thickness of the InGaN layer are studied.

The (0001) sapphire substrates were cleaned in a solution of 3:1 H_2SO_4:H_3PO_4 before being introduced into the growth chamber of MOCVD with radio frequency. Trimethylgallium (TMGa), trimethylgalindium (TMIn) and NH_3 were the precursor sources of Ga, In and N, respectively. A GaN buffer layer was deposited at 570 °C whose thickness was nominally 25 nm, followed by a 0.5 μm thick GaN layer grown at 1070 °C. An InGaN layer was grown at 800 °C or 780 °C with the flow ratio of TMIn to TMGa being 200:1.5, then a second GaN layer was grown at 1070 °C, with the ratio of V/Ⅲ being about 10 000. The growth rate of GaN was typically 1 μm/h and that of InGaN was about 1 μm/h. The composition of InGaN was controlled by both the flow ratio of TMI to TMG and the growth temperature. The samples were divided into two groups: one group including N1318, N1319 and N1320 had the InGaN layer deposited at 780 °C and the other group including N1323, N1324 and N1325 had the InGaN layer deposited at 800 °C. Each group had three samples with InGaN thicknesses of 100 nm (N1320 and N1325), 200 nm (N1319 and N1324) and 333 nm (N1319 and N1323). The pressure of the chamber was controlled at 76 Torr during the growth process.

The structural and optical properties were characterized with XRD, PL and Raman scattering. The

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composition of InGaN was determined by the splitting between GaN peaks and InGaN peaks in the 2θ profile of the XRD measurement equipped with a standard Cu K_α radiation source. Raman spectrum were measured in the backscattering geometry (Z(X,X)Z) with the incident light and the scattered light propagating normally to the layer planes. The wavelength 514.5 nm of an Ar^+ ion laser was used for excitation and the Raman scattering measurement was carried out at room temperature with the spectrum resolution of 1.5 cm^{-1}. An ISA JOBIN YOON -SPEX FL-3 spectra-meter was used for the measurement of PL spectra at room temperature and the light wavelength range was from 320 to 600 nm.

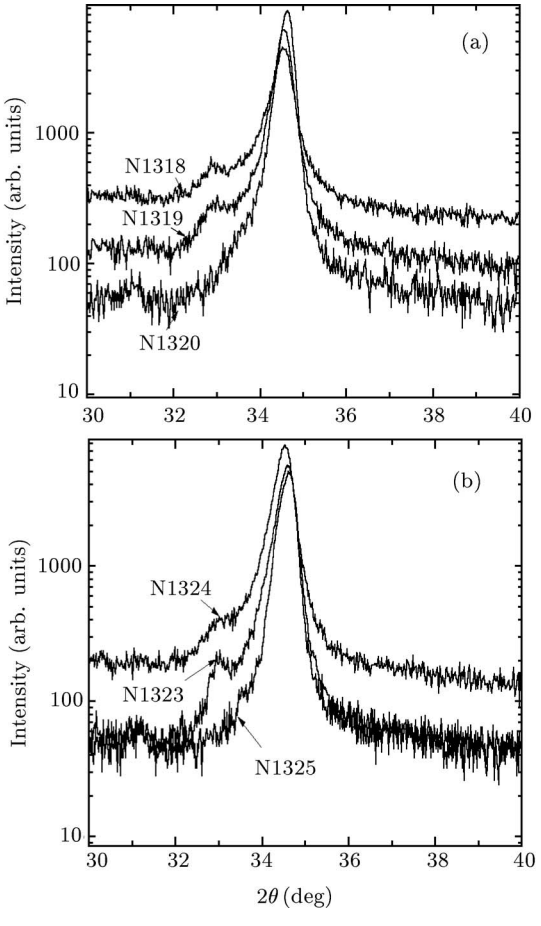


Fig. 1. XRD profiles of (a) 780 °C and (b) 800 °C groups.

Figures 1(a) and 1(b) show 2θ XRD profiles of the two groups, respectively, i.e., the 780 °C group and the 800 °C group. According to the dependence of the composition of InGaN on the position of the (0002) peak of XRD, the composition of InGaN is calculated under Vegard's law.[5] The composition values x of four samples N1318, N1319, N1323 and N1324 are the same at 40.8%. While those of two samples N1320 and N1325 are 36.8% and 25.8%,

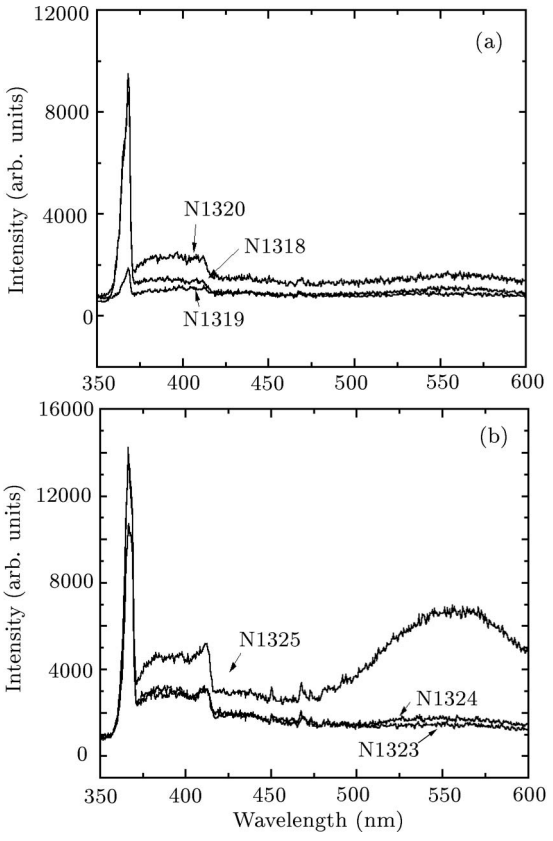


Fig. 2. PL spectra of (a) 780 °C and (b) 800 °C groups.

respectively. The peaks located at 31.2° are found in the $\theta/2\theta$ XRD profiles of both N1320 and N1325 and are attributed to the InN (0002) plane. In view of Figs. 1(a) and 1(b), when the InGaN layer becomes thicker than 200 nm, the composition of InGaN of both groups has no difference. However, when the InGaN layer becomes thinner than 200 nm such as N1320 and N1325 samples, the composition of InGaN is changed into a small value. At the same time, the InN phase appears in these two samples. We can conclude that the phase separation in the DH films is related to the thickness of the InGaN layer. There is a critical thickness of the InGaN layer in the DH, in which the strain energy is just relaxed by the dislocations. When the InGaN layer is kept well below the critical thickness, its entire mismatch in the DH is accommodated by the elastic strain. However, the thicker layers generally accommodate the lattice mismatch by the combination of strains, dislocations and three-dimensional islands. When the thickness of the InGaN layer decreases, the elastic strain is relaxed not only by the dislocations, but also by the phase separation of InGaN. The thin InGaN layer contains the large strain energy that makes the InGaN layer appear as phase separation. Comparing the sample N1320 with the sample N1325, we find that the phase separation of InGaN deposited at 800 °C is more serious than that deposited at 780 °C. The thermal strain en-

ergy also influences the phase separation because the thermal strain energy increases with the growth temperature. Looking up the full width at half maximum (FWHM) of GaN peaks located at 34.6°, we obtain the relation

$$T_{N1318} > T_{N1323} > T_{N1319} > T_{N1324} > T_{N1320} > T_{N1325},$$

where T denotes the value of the FWHM. This relation shows that the quality of the DH films increases with the decrease in thickness of the InGaN layer and increases with the improvement of the growth temperature of the InGaN layer under the same conditions.

The PL spectra of both the 780 °C and 800 °C groups are shown in Figs. 2(a) and 2(b), respectively. The peaks originated from the band-edge emission of GaN are located at the wavelength 368.5 nm in both Figs. 2(a) and 2(b). The emission band from 380 nm to 414 nm is observed in both groups, which have a small peak located at 412 nm (3.01 eV). The emission band near purple can be attributed to the composition fluctuations of InGaN. The yellow emission band with a peak located at 560 nm is only observed in the PL spectra of the sample N1325. Many researchers have even reported that the yellow band of GaN originated from the point defects in the GaN film.[6,7] The intensity of the yellow band of the sample N1325 is strong, which means that there is a large density of point defects in the sample N1325. The profiles in the yellow band zone of the other samples are flat. Both peaks located at 468 nm (2.65 eV) and 451 nm (2.75 eV) in the PL spectra of the 800 °C group are found, but their intensities are small. They originate from the emission of InGaN. The blue emission at 468 nm originating from InGaN is used to calculate the bowing parameter of InGaN. According to Vegard's law, together with the x value of the InGaN composition determined by the result of XRD, the value of the bowing parameter is 1.33 for $x = 0.258$ ($E_{\mathrm{gInGaN}} = 2.75$ eV) and it is 0.50 for $x = 0.408$ ($\mathrm{E_{gInGaN}} = 2.65$ eV). These results show that the values of the bowing parameter depend on the alloy composition. The intensity ratio of the peak at 412 nm to the peak at 368.5 nm depends on the thickness of the InGaN layer, as shown in Fig. 3. The intensity ratio of the InGaN emission (468 nm) to the GaN emission depending on the thickness of the InGaN layer is also shown in Fig. 3. The intensity ratios of both profiles increase with the decrease of the thickness of InGaN. This result indicates that the thickness of the InGaN layer should be decreased in order to improve the efficiency of the blue emission. At the same time, two peaks in the blue emission zone are observed, which shows that phase separation exists in the InGaN layer and this is in agreement with the result of XRD. The emission mechanisms of InGaN/GaN heterostructure are not fully understood yet. Two different radiation recombination mechanisms are generally accepted.[8] One is based on the spatial indium fluctuations leading to indium-rich regions acting as quantum dots. The emission from the InGaN region may be assigned to the recombination of excitons localized at potential minima, i.e., the so-called exciton localization effect. The other model attributes the quantum confined stark effect (QCSE) to the presence of a large piezoelectric field in the active layer, which arises from the strain caused by the lattice mismatch between GaN and InGaN. The QCSE can be ignored due to the large thickness of the InGaN active layer. The phase separation of the InGaN layer from the result of the PL spectrum supports the emission mechanism on the spatial indium fluctuations.

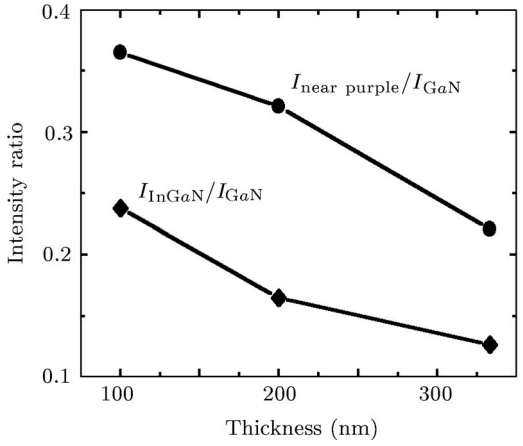


Fig. 3. Emission intensity ratio for the 800 °C group depending on the thickness of the InGaN layer.

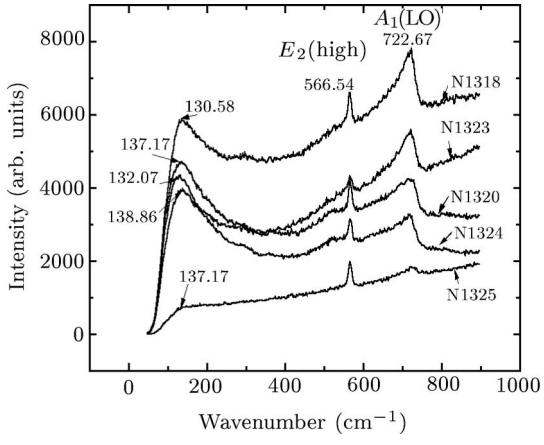


Fig. 4. Raman spectra of DH films.

There are $A_1 + 2B_1 + E_1 + 2E_2$ Raman active modes of the optical phonon at the Γ point of the Brillouin zone in the wurtzite structure of both GaN and InGaN.[9] The A_1 phonon longitudinal optical mode (A_1 (LO)) and the E_2 optical mode are allowed in the spectrum taken in the backscattering geometry at room temperature. The Raman spectrum of the DH is shown in Fig. 4. E_2 (high), E_2 (low) and A_1 (LO) modes are found at 566.54 $\mathrm{cm^{-1}}$, about 137 $\mathrm{cm^{-1}}$ and 722.67 $\mathrm{cm^{-1}}$, respectively. Both E_2 (low) and A_1 (LO)

shift while E_2 (high) does not. The shift value of A_1 (LO) mode is $-12.22\,\mathrm{cm}^{-1}$ and that of E_2 (low) mode is about $-5.8\,\mathrm{cm}^{-1}$. In Fig. 4, the Raman frequency of E_2 (high) and A_1 (LO) modes is not affected by either the growth temperature or the thickness of alloy InGaN. Liu *et al.*[10] reported that the Raman frequency of the A_1 (LO) mode of AlGaN obeyed Vegard's law and was linear with the alloy composition. The Raman frequency of the A_1 (LO) mode of InGaN in the DH films does not agree with Vegard's law for $A_1\ (\mathrm{LO})_{\mathrm{InN}} = 596\,\mathrm{cm}^{-1}$, $A_1\ (\mathrm{LO})_{\mathrm{GaN}} = 734.89\,\mathrm{cm}^{-1}$ and $A_1\ (\mathrm{LO})_{\mathrm{InGaN}} = 722.22\,\mathrm{cm}^{-1}$.[11] There is an unknown mechanism to represent the coupling between $A_1\ (\mathrm{LO})_{InN}$ and $A_1\ (\mathrm{LO})_{GaN}$, so it is necessary to explore the coupling mechanism of the $A_1\ (\mathrm{LO})_{InGaN}$ mode of InGaN in the future.

In conclusion, the composition of InGaN has been determined by the results of XRD, and the bowing parameter of InGaN has been calculated by the PL spectrum. When the thickness of the InGaN layer was reduced, the phase separation of InGaN was found in both groups. According to the results of XRD and PL, the phase separation in the DH films was more serious for the 800 °C group than that for the 780 °C group. The Raman frequencies of A_1 (LO) and E_2 (low) modes in the DH shifted and did not obey Vegard's law that is suitable for the AlGaN alloy. Neither the growth temperature nor the thickness of InGaN affected the Raman frequency of the A_1 (LO) and E_2 (low) modes in all the samples.

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