Effects of H_2/NH_3 Flow-Rate Ratio on the Luminescent, Structural, and Electrical Properties of GaN Epitaxial Layers Grown by MOCVD

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GaN epitaxial layers were grown on sapphire substrates in a separate-flow reactor by metalorganic chemical vapor deposition. The flow-rate ratio of H_2 on the upper stream to NH_3 on the bottom stream is varied from 0.5 to 2. The growth condition and characterization of the GaN epitaxial layers are investigated in detail. The H_2 flow rate of the upper stream strongly affects the reactant gas flow pattern near the substrate surface and thus influences the quality of epitaxial layers. At the optimum H_2/NH_3 flow ratio of 1.0, we can obtain a good quality of GaN epitaxial layers which exhibit a strong near band-edge emis-sion in the 20 K photoluminescence (PL), a full width at half maximum of 66 meV for the 300 K PL, an electron mobility of 266 $cm^2/V\text{-}s$ and concentration of 1×10^{18} cm^{-3} at 300 K.

Key words: GaN, high band-gap energy, photoluminescence (PL), x-ray diffraction (DC-XRD)

INTRODUCTION

The GaN-based materials have long been viewed as promising for optical devices that have applications in the blue and ultraviolet wavelengths.[1–3] These devices are essential to full-color display and pick-up head in high-definition digital-video-disk (HD-DVD) systems.[4] In addition, its wide direct bandgap and excellent thermal conductivity make it a good candidate for the high-temperature field-effect transistors (FETs).[5,6] The performance and reliability of these devices depend on the electronic defect concentration, the native defect density, and the incorporation of intentional and unintentional impurities.[7]

In order to improve the quality of GaN films, the defects in GaN films should be reduced and thus some essential parameters of growth process must be investigated.[8,9] Defects in III-V nitrides can be studied by some measurements including photoluminescence (PL),[10] vibration-mode Raman spectroscopy,[11] deep level transient spectroscopy (DLTS),[12] and magnetic resonance techniques,[13] Among these methods, PL has been extensively used to study the GaN films. The emission peaks at 378 and 550 nm in the 20 K PL spectra have been attributed to the donor-acceptor transitions,[14,15] and the yellow band emission of C or N vacancies,[16,17] respectively. In addition, x-ray diffraction is also an important technique to measure the thin-film structure. It is also important to understand that the x-ray measurements should be done in both the in- and normal-plane directions, because the thin films do not have equal structural properties in both directions.[18,19]

In the GaN growth, many authors studied the surface morphology at various H_2 flow rates previously. Sasaki showed the effect of H_2 flow rate on the GaN layer without buffer layer, where an increase of H_2 flow rate will cause a discontinuous island growth and finally results in no film growth.[20] Also, Nishida et al. reported that the H_2 flow rate of upper stream of 1.0 l/min could obtain the mirror-like surface by a two-flow horizontal reactor.[21] However, the luminescent, crystalline, and electrical properties are strongly influenced by H_2/NH_3 ratio and have not been studied in detail. In this work, we report on the observation of the 369-nm peak of 20 K PL spectra, x-ray diffraction, and the electronic mobility measurements as a function of H_2/NH_3 ratio.

EXPERIMENT

GaN epitaxial layers were grown by metalorganic chemical vapor deposition (MOCVD) with a separate-

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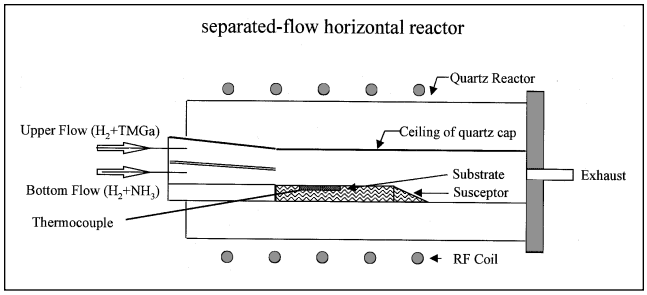

Fig. 1. A schematic drawing of the separate-flow horizontal reactor for GaN growth.

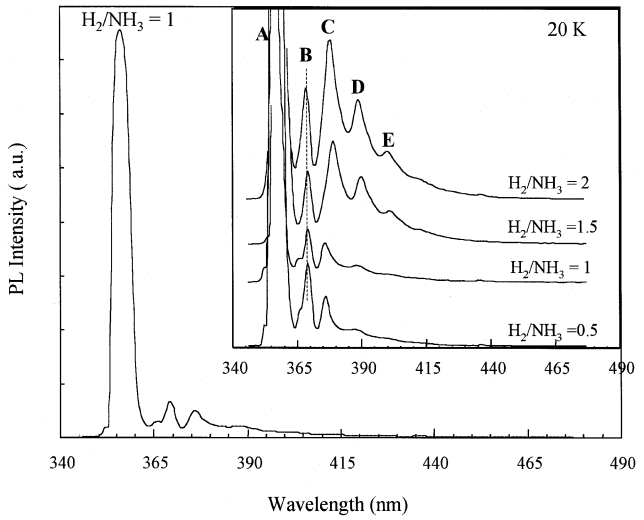

Fig. 2. The 20 K PL spectrum for the GaN layer grown at H_2/NH_3 = 1.0. The inset of this figure shows the 20 K PL spectra of GaN layers grown at different H_2/NH_3 ratios.

flow horizontal reactor (SF-HR), as shown in Fig. 1. The details of SF-HR have been described in our previous work.[22] The main reactant sources were separated by a quartz plate, where the TMGa with a varied amount of H_2 was introduced into the upper stream and the NH_3 with a small amount of H_2 was introduced into the bottom stream. During the experimental process, the flow rate of 60 μ mol/min in TMGa and 5000 cc/min in NH_3 flow into upper and bottom streams which were kept at a constant V/III molar ratio. The H_2 flow rate of the upper stream (F_{H2} up) was varied from 2500 to 10000 cc/min. In other words, the flow-rate ratio of H_2 in the up stream to NH_3 in the bottom stream was varied from 0.5 to 2.0. Prior to loading, the (0001) sapphire substrate was etched by 3 HNO_3: 1 HCl. Before the growth of GaN epitaxial films, the substrate was first pre-cleaned at 1050°C for 10 min in a hydrogen ambient. The substrate temperature was then cooled down to 525°C to grow a 250-Å nucleation layer, followed by raising to 1000°C to grow the GaN epitaxial layer of ~4 μm

Herein, we shall clarify the influence of different flow-rate ratios of the upper-stream H_2 to the bottom-stream NH_3. Photoluminescence at 20 K, a high-resolution x-ray diffraction (XRD), and Hall measurements at 300 K were carried out to characterize the GaN epitaxial layers. The 20 K PL was performed by using an 18 mW/cm² He-Cd (λ = 325 nm) laser as the excitation light source with a spot size smaller than 0.2 mm through a focus lens. A narrow band-pass filter was used to block the laser harmonic lines The high-resolution x-ray diffractometer consists of an 18 kW rotating-anode x-ray generator (Cu target) and a Huber 5042 large diffractometer. A Ge (111) monochromator and a 200-pm precision slit were used to filter out the Cu $K_{\alpha 2}$ and K_β; only $K_{\alpha 1}$ line was used. The different x-ray diffraction methods were employed that include the conventional 2θ/θ scan normal to the epitaxial plane and the grazing incidence of x-ray diffraction to probe the in-plane epitaxial relation with the 20 detector arm of 700 nm long. The 2θ breadth of direct x-ray beam is 0.03^0 after closing the slit, which is 300 μm in front of the detector. Hall mobility and concentration were measured by the van der Pauw method at 300 K with a magnetic field of 5000 G and a current of 1 mA.

RESULTS AND DISCUSSION

Figure 2 shows the 20 K PL spectrum of GaN epitaxial layers grown at H_2/NH_3 = 1.0 and the inset of Fig. 2 shows the 20 K PL spectra of GaN grown at different H_2/NH_3 ratios. These spectra are normalized to the same PL peak intensity. All the samples exhibit a strong peak A located at 357.5 nm (3.468 eV) and four weak peaks B, C, D, and E located at 369 nm (3.360 eV), 379 nm (3.271 eV), 389.5 nm (3.183 eV), and 401 nm (3.090 eV), respectively. The peak A dominates the 20 K PL spectra and is attributed to excitor bound to donor with a binding energy of 8 meV.[23] As shown in the inset of Fig. 2, peaks B and C have the weakest intensity at the case of H_2/NH_3 = 1.0. By increasing H_2/NH_3 ratio, the relative intensity of peaks B and C increases in the 20 K PL spectra. On the other hand, when the H_2/NH_3 ratio is lower than 1.0, the relative intensity of peaks B and C becomes strong again. Therefore, peaks B and C are strongly N-associated transitions. Dai et al. reported that both peaks B and C are due to the neutral donor of the N vacancy and donor-acceptor (DA) pair transitions, respectively.[24] The transitions of peaks D and E are resulted from the longitudinal optical (LO) phonon replica of peak C and are denoted as DA-LO and DA-2LO, respectively.[24] By increasing the H_2/NH_3 ratio higher than 1.0, it will lead to a decrease of the N-atom concentration during growth and thus may result in an N-vacancy ambient. However, for the case of the H_2/NH_3 ratio lower than 1, the reduction in N surface coverage is expected to weaken the Ga adhesion to the surface and to suppress the initial nucleation and the lateral growth on the sapphire surface, as reported by Sasaki.[20]

Figure 3 shows the 20 K PL intensity ratio of peak A to peak B and 300 K PL FWHM as a function of H_2/NH_3 ratio. As mentioned above, the optimized growth condition to obtain the maximum PL intensity ratio of peak A to peak B is at H_2/NH3 = 1.0. The intensity ratio decreases as H_2/NH_3 ratio is higher or lower than 1.0. The narrowest FWHM of 300 K PL is 66 meV at

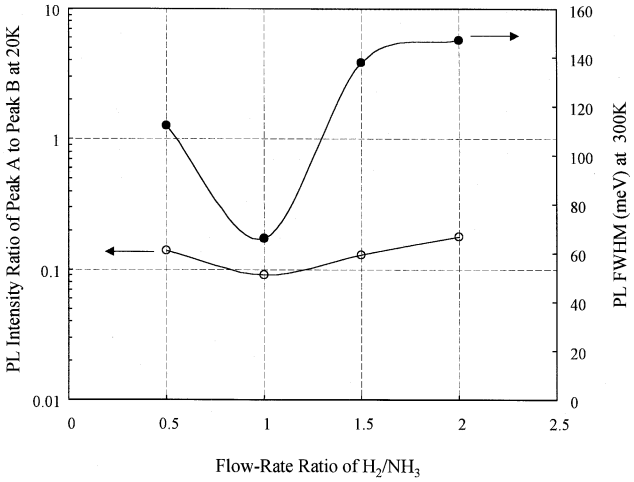

Fig. 3. The 20 K PL intensity ratio of peak A to peak B as a function of H_2/NH_3 flow-rate ratio.

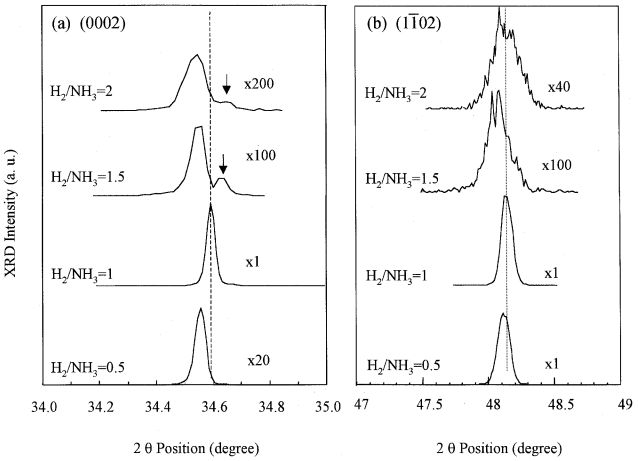

Fig. 4. The 2θ/θ scan of GaN (0002) and GaN(1$\bar{1}$02) diffraction peaks at different H_2/NH_3 flow-rate ratios.

$H_2/NH_3 = 1.0$. Similarly, an increase or decrease of the H_2/NH_3 ratio also leads to a broader FWHM value due to a poor quality of GaN epitaxial layers.

The results of x-ray diffraction are shown in Fig. 4 which consists of the 2θ/θ scan of GaN(0002) peak (Fig. 4a) and GaN(1$\bar{1}$02) peak (Fig. 4b) as a function of H_2/NH_3 ratio. The data of GaN(0002) contains the structure information of GaN on the normalplane direction, while the GaN(1$\bar{1}$02) peak reveals more information on the in-plane structure than the one on the normal-plane direction. From the diffraction intensity, it is clearly observed that the diffraction intensity of peaks is the strongest for the H_2/NH_3 = 1.0. The samples grown at the ratio other than 1.0 result in a very poor epitaxial crystalline quality, so that the diffraction intensity is smaller in one to two orders of magnitude. The coherence length of the crystallization, obtained from the breadth of 2θ/θ peaks (see Fig. 5), is the largest for the sample grown at $H_2/NH_3 = 1.0$. Also, we can see that the 2θ breadth is almost instrument limited. In other words, the coherence length in the normal-plane direction is larger than 3000Å.

Figure 4 also shows that both the d spacings of GaN(0002) and GaN(1$\bar{1}$02) are the smallest for $H_2/NH_3 = 1.0$, which may indicate that the non-stoichiometric of the sample can affect the crystalline structure of GaN in both the normal- and in-plane directions. If we further examine the diffraction data of GaN(0002), we can see an additional weak and broad diffraction peak located at the high-angle side (see arrow signs in Fig. 4a) at the flow-rate ratio of H_2/NH_3 higher than 1.5. The existence of this extra peak indicates the nonhomogeneity of the GaN films. This extra peak cannot be identified as other crystalline orientations of wurtzite GaN, nor the peaks of zinc-blende GaN It may be attributed to a new gallium-rich phase of GaN, which is not known so far. It could be a part of GaN structure under a large compressive stress also.

By comparing the 20 breadth in the 2θ/θ scan of GaN(1$\bar{1}$02) and GaN(0002) (see Fig. 5), the 20 breadth of GaN(1$\bar{1}$02) is seen to be much larger than those measured of GaN(0002), which reveals that all the GaN thin films were grown into columnar structures.[18] Furthermore, if we compare the intensity ratio from Figs. 4a and 4b, we can find the in-plane structure has a better intensity order under low H_2/NH_3 ratios. If we assume that the low H_2/NH_3 ratio leads to easier NH_3 decomposition and nitrogen rich on the surface of as-grown GaN layers, the better structure of in-plane GaN may indicate a quick migration of Ga precursors in the plane. The movement of Ga precursors to the in-plane direction also causes a serious Ga deficit in the normal-plane direction, which gives rise to an extraordinarily low intensity of diffraction peaks along the normaldirection plane of GaN(0002). The surface morphology studied by optical microscopy[25] also showed that when the H_2/NH_3 ratio is around 0.5, a large amount of hole defects are observed on the surface of GaN epitaxial layers. When the H_2/NH_3 approaches 2.0, a large amount of hillock defects appear on the surface. The hole defects may be

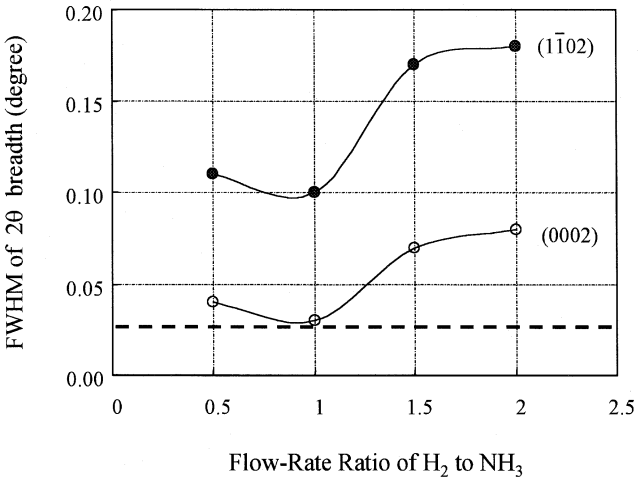

Fig. 5. The measured 2θ breath of high-resolution XRD as a function of H_2/NH_3 flow-rate ratio. The dash line at 0.03° indicates the 2θ breadth of instrument.

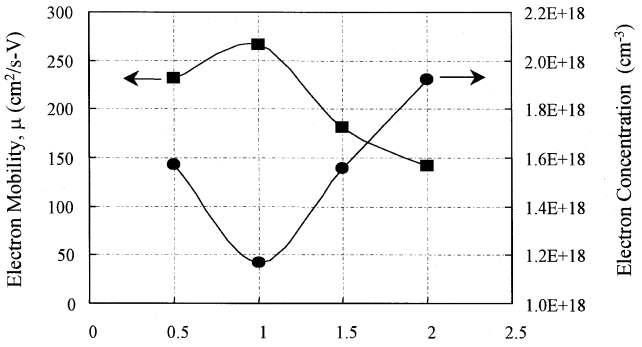

Fig. 6. The Hall electron mobility and concentration as a function of H_2/NH_3 flow-rate ratio at room temperature.

due to the holes created by migrating Ga precusor to the growing plane instead of growing upward, while the hillock formation may be due to the supply of excess Ga. The larger surface tension of the Ga precursors will lead to the nucleation of hillock formation, especially under the compressive stress as an implication from the extra peak formed at the high-angle side of GaN(0002).

Rocking curve measurements (with a fixed 2θ and a 300 μm slit placed in front of the detector) were also performed. The results show that the best crystalline quality is for the flow-rate ratio of H_2/NH_3 = 1.0. However, the difference of rocking-curve widths is small for all the data As we compare it to the PL spectra, the best structure can be grown at H_2/NH_3 = 1.0. All the main peaks grown under the flow ratio other than one are considered as a loose GaN structure with many defects inside. These results consist with the one intensity and peak width of PL measurements.

Figure 6 illustrates the mobility and concentration of undoped GaN layers as a function of H_2/NH_3 flow-rate ratio. The electron mobility is 230 cm^2/V-s at H_2/NH_3 = 0.5 and increases to a maximum value of 266 cm^2/V-s at H_2/NH_3 = 1.0. After passing over this maximum point, with increased H_2/NH_3 ratio, the mobility curve falls again. Similarly, the electron concentration also exhibits a minimum value of 1.1×10^{18} cm^{-3} at H_2/NH_3 = 1.0. These results follow the similar trend of H_2/NH_3-ratio dependent of PL and XRD properties for the GaN epitaxial layers.

From the above results, it is observed that the structural, optical, and electrical properties of GaN layers strongly depend on the H_2/NH_3 ratio during growth. The optimal flow-rate ratio of H_2/NH_3 to obtain a good quality of GaN layers is around one. By increasing the ratio of H_2/NH_3, the total flow velocity will increase and thus lead to decrease the boundary-layer thickness.[26] Increasing the H_2 will suppress the decomposition of NH_3 and cause the Ga-rich solid drops on the epitaxial layers. Also, decrease of H_2/NH_3 ratio will result in many N vacancies in the epitaxial layers due to the excess NH_3. It is in good agreement with the results of surface morphology, as observed previously.[26] At the H_2/NH_3 ratio of 0.5, there are many hole defects on the surface of GaN epitaxial layers. The mirror-like surface morphology can be obtained at optimum ratio of H_2/NH_3 = 1.0. With further increasing the H_2/NH_3 ratio up to 2.0, it appears a large amount of hillock defects on the surface of GaN epitaxial layers Therefore, the H_2/NH_3 ratio can effectively confine the reactant gas onto the substrate surface and thus influence the chemical cooperation of N with Ga atoms during growth.

CONCLUSIONS

We have demonstrated that the luminescent, crystalline, and electrical properties of GaN epitaxial layers can be improved by optimizing the flow-rate ratio of H_2 to NH_3 in our separate-flow MOCVD system. It is observed that the structural, optical, and electrical properties of GaN epitaxial layers strongly depend on the H_2/NH_3 ratio during growth. These samples have the same trends in luminescent, crystalline, and electrical properties. The optimal flow-rate ratio of H_2 to NH_3 to obtain a good quality of GaN epitaxial layer is around one. However, when the H_2/NH_3 ratio is higher or lower than 1.0, the relative intensity of peaks B and C, which are due to the neutral donor of N vacancy and D-A pair transitions, respectively, will become strong. When the H_2/NH_3 ratio is lower than 1.0, the reduction in N surface coverage will weaken the Ga adhesion to the surface and suppress the initial nucleation and lateral growth on the sapphire surface. However, with increasing H_2/NH_3 ratio higher than 1.0, it will lead to a decrease of N-atom concentration or N-vacancy ambient during growth.

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