Growth and characterization of GaN films on (0001) sapphire substrates by alternate supply of trimethylgallium and NH_3

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Received 23 February 1998

Abstract

GaN films were grown on (0001) sapphire substrates in a temperature range of 500–950°C by exposing the substrates to trimethylgallium (TMG) and NH_3 one at a time. High quality GaN films were achieved at 800–900°C with a thin GaN buffer layer predeposited at 500°C. The linewidth of the (0004) double-crystal rocking curve X-ray diffraction (DCXRD) of a 2.0 μm thick GaN film is about 250–500 arcsec. Increment in growth temperature over a temperature range of 800–900°C is helpful to suppress the intensity of yellow luminescence and to enhance the luminescence intensity of the near band-to-band emission. Typically, the room temperature photoluminescence intensity ratio of the near band edge emission to the yellow luminescence for an as-grown high quality GaN film is more than one order of magnitude. The best GaN films with superior optical behavior were achieved at ~900°C with a V/III ratio of 5000. Photoluminescence measurements of these GaN films at 9 K show strong and sharp near band-to-band emission with almost no yellow luminescence. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: GaN films; Sapphire substrates; Trimethylgallium; NH_3

1. Introduction

Gallium nitride has become one of the most promising wide band-gap semiconductor materials for use in high brightness blue/green light emitting diodes (LEDs) [1] and laser diodes (LDs) [2] which are very important devices for applications in full-color outdoor LED displays and optical storage devices. Several growth techniques, like metal–organic chemical vapor deposition (MOCVD) [3], molecular beam epitaxy (MBE) [4], and hydride vapor phase epitaxy (HVPE) [5], have been utilized for GaN growth. Due to the lack of suitable lattice-matched substrates, most of the GaN materials and related devices were prepared on sapphire substrates. However, the large differences in the lattice constant and thermal expansion coefficient between the GaN film and the sapphire make it difficult to obtain high quality GaN films. It has been reported in the literature that a dislocation density as high as $10^8 \sim 10^{10}$

cm^{-2} [6] has been observed in the GaN films grown by conventional techniques. Although high brightness blue/green LEDs can be prepared by MOCVD, high growth temperatures up to 1050°C are required for high quality materials. Growth temperature as high as 1050°C could generate additional issues like high desorption rate of the group III adatoms as well as the corrosion problem in the graphite susceptor. Accordingly, the implementation of low temperature epitaxy on the III-nitride film growth is of great interest.

Previous reports [7,8] show that the sequential supply of metalorganics and hydrides to the substrate is helpful for the preparation of high quality semiconductor thin films at lower temperatures. Heteroepitaxy of GaN thin films by alternate supply of reactants has recently been reported [9]. However, most of the studies focused upon the behavior of saturation growth instead of the material properties. In this paper we report the achievement of high quality GaN films on (0001) sapphire substrates through process optimization by alternate supply of trimethylgallium (TMG) and NH_3 .

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Fig. 1. An SEM micrograph of the surface of a GaN film grown at 800°C.

2. Experimental

Growth of GaN films was carried out in a home-made reactor operated at atmospheric pressure. The reactor and susceptor design is similar to one described previously [8]. TMG and NH_3 were used as Ga and N sources carried by purified H_2 gas. During GaN growth the sapphire substrate was carried to expose it to the space-separated TMG and NH_3 gas streams one at a time. The (0001) sapphire substrates were solvent-cleaned first, followed by hot-etching in $\text{HCl-H}_3\text{PO}_4$ (3:1) solution for 5 min, then rinsed with deionized water, and blow-dried with N_2 . GaN buffer layers of 200 Å in thickness were deposited at 500°C after the

substrate was heated at 1050°C under NH_3 for 1 min nitridation. A series of 2.0 μm thick GaN films were then deposited in a temperature range 500 ~ 950°C with V/III ratios of 2000 ~ 5000.

A Bede Q2a double-crystal X-ray diffractometer was utilized for structural characterization. A Topcon ABT-55 scanning electron microscope (SEM) operated at 10 kV was used to reveal the surface morphology and thickness of the grown films. Photoluminescence (PL) measurements using the 325 nm excitation of a He–Cd laser were carried out to characterize the luminescence properties of the GaN films. Contactless electroreflectance (CER) was used for estimation of the emission energies of the excitons in the GaN films. The transport properties of the as-grown GaN films were characterized by van der Pauw Hall measurements.

3. Results and discussion

For GaN films prepared at low temperatures of 500 ~ 700°C, the crystallinity of the films is poor with broad DCXRD linewidth. GaN films grown at elevated temperatures without a low temperature GaN buffer layer tends to result in a rough surface morphology with a (0004) DCXRD linewidth of 10 ~ 20 arcmin. However, high quality, transparent GaN films having a smooth morphology were achievable in a temperature range 800 ~ 900°C through optimization of the growth parameters like nitridation time, buffer layer thickness,

Fig. 2. A typical (0004) DCXRD curve of a GaN film grown at 850°C.

Fig. 3. The RT PL data of GaN films grown at 800, 850 and 900°C, respectively.

buffer layer deposition temperature, growth temperature, and V/III ratio which have been reported as very critical in the growth of high quality GaN by MOCVD [10,11]. As-grown films are n-type with room temperature carrier concentrations and mobilities falling in low $10^{18} \sim \text{mid } 10^{19} \text{ cm}^{-3}$ and $20 \sim 50 \text{ cm}^2/\text{V}\cdot\text{sec}$, respectively. Fig. 1 shows an SEM micrograph of the surface of a GaN film grown at 800°C with a GaN buffer layer thickness of 200 Å deposited at 500°C. The micrograph shows a smooth surface morphology which is typical for GaN films grown at temperatures of this range. A particle in the micrograph is intentionally chosen for focusing purpose. Most of the GaN films grown at 800 ~ 900 °C show good crystallinity with the linewidth of (0004) DCXRD falling within 250 ~ 500 arcsec. Fig. 2 shows a typical DCXRD curve of a 2.0 µm thick GaN film grown at 850°C with a GaN buffer layer thickness of 200 Å deposited at 500°C. The full width at half maximum (FWHM) of the (0004) diffraction peak is about 300 arcsec which is comparable to the results reported in the GaN films grown by other growth techniques [12]. It has been reported that an alternate supply of the reactants is helpful in enhancing the surface velocities of the adatoms on the grown surface [13]. An alternating supply of TMG and NH_3 thus provides higher surface diffusion velocities of the Ga adatoms to locate themselves at proper atomic sites. Furthermore, growth by alternate supply of reactants is dominated by a surface kinetics limited process rather than a mass transport limited process. In a so called self-limiting process [7], only partially cracked N–H radicals instead of atomic nitrogen are required for the accomplishment of adsorption processes. For NH_3 , the thermal energy for forming partially cracked N–H rad-

icals is less than that for the formation of atomic nitrogens. Consequently, GaN films of high crystallinity are achievable by an alternating supply of TMG and NH_3 at a relatively lower temperature range than that of conventional MOCVD growth.

Increase in growth temperature over the range 800 ~ 900°C results in apparent reduction in the luminescence intensities of the yellow emissions located near 2.25 eV and enhancement in the luminescence intensity of the near band-to-band emission. Fig. 3 shows the room temperature(RT) PL results of the GaN films prepared at 800, 850 and 900°C, respectively, with the same V/III ratio of 3000. For the GaN films grown at 800°C, the RT PL spectrum shows only yellow luminescence with near band-to-band emission being completely quenched. Increment in growth temperature to 850°C tends to enhance near band-to-band emission but the yellow luminescence intensity stays high. For GaN films grown at 900°C, the RT PL spectrum shows very strong near band-to-band emission with greatly reduced yellow luminescence intensity. A further increase in growth temperature up to 950°C, however, tends to cause a deterioration of the morphology of the GaN films although the PL properties of the GaN films prepared at 950°C are pretty much the same as those obtained in the samples grown at 900°C. In this case SEM observations show localized cavities on the surface of GaN films grown at temperatures higher than 95°C. The growth temperature increment tends to result in an increase in thermal energy which is helpful in the promotion of surface mobilities of the adatoms and the cracking efficiency of NH_3 , however, thermal energy at this temperature range may also result in considerable desorption of the Ga and N adatoms at the grown

Fig. 4. Typical RT PL spectrum of the high quality GaN films.

surface. In particular, the desorption rate of Ga becomes prominent at elevated temperatures if the replenishment of reactive N–H radicals is insufficient. Thus, an optimized growth temperature is essential for the growth of high quality GaN film at a given V/III ratio. Based upon the PL results shown in Fig. 3, at the temperatures of 800 ~ 850°C and a V/III ratio of 3000, the amount of reactive N–H radicals may not be high enough to support sufficient overpressure on the grown surface due to the insufficient cracking efficiency of NH_3 at this temperature range. As a result, defects like Ga vacancies as well as complexes between Ga vacancies and impurities may easily be created at this temperature range. These defects have been reported to be responsible for the yellow luminescence near 2.25 eV [14,15]. The observed yellow luminescence dominant PL spectra of the GaN films prepared at 800 ~ 850°C can thus be attributed to the high density of states of these defects. It is known that high quality GaN films can only be achieved by very high V/III ratios at temperatures higher than 1000°C by the MOCVD process because the gas phase decomposition of NH_3 occurs only at very high temperatures [16]. Similarly, a sufficient supply of the reactive N–H radicals is crucial for the growth of high quality GaN films in this study. For a given V/III ratio of 3000, growth temperature increment from 800 to 900°C allows the provision of more reactive N–H radicals which are beneficial in reducing the density of the states of the defects related to Ga vacancies. This gives an interpretation for the change in PL spectra from yellow luminescence dominant to near band-to-band emission dominant when growth temper-

ature increases from 800 to 900°C. A similar tendency was found in the GaN films grown at V/III ratios higher than 3000. Fig. 4 shows a RT PL of a GaN film prepared at 900°C with a V/III ratio of 5000. Note that the PL intensity ratio of the near band edge emission to the yellow luminescence is more than one order of magnitude.

Fig. 5 shows the CER spectra of the GaN films grown at 900°C. The transition energies of free excitons (FX) [17] were estimated by fitting the curves to the first derivative of a Lorentzian lineshape function form [18]. As indicated by the arrows in Fig. 5, blue-shift in the excitonic emission energies of A excitons from 3.422 to 3.484 eV and B excitons from 3.429 to 3.492 eV has

Fig. 5. The 300 K and 15 K CER spectra of a GaN film grown at 900°C.

Fig. 6. A PL spectrum of the best GaN films grown at 900°C with a V/III ratio of 5000.

been observed as the measurement temperature reduces from RT to 15 K. This result is in good agreement with the reported excitonic transition energies of A and B FXs in GaN films grown by MOCVD on (0001) sapphire substrates [17,19]. A biaxially compressive strain of 0.04% for the GaN films grown in this study is estimated accordingly. It is not certain why the signal of the transition energy of C excitons is absent in the 15 K CER spectrum in Fig. 5. Previous report shows that the binding energy of C excitons is lower than that of A and B excitons [17]. Nevertheless, the difference in binding energies between A/B and C excitons is not prominent. Thus, the binding energy difference can only partly explain the CER result even if C excitons are dissociated predominantly due to the high background of n-type dopants of the order of $10^{18} \sim 10^{19} \text{ cm}^{-3}$ in the as-grown GaN films. However, it can not explain the complete disappearance of C excitons in the 15 K CER spectrum. More work is required to elucidate this issue.

It appears that a further increment in V/III ratio is helpful to increase the PL intensity ratio of the near band edge luminescence to the yellow emission. A comparison of the RT PL data of Figs. 3 and 4 shows that the intensity ratio of near band edge luminescence to yellow emission has increased from a ratio of 4 for GaN films grown at 900°C with a V/III ratio of 3000 (as shown in Fig. 3) to a ratio of 20 for GaN films prepared at 900°C with a V/III ratio of 5000. It is believed that NH_3 overpressure helps to cut down the density of yellow luminescence defects. Fig.

6 shows the 9 K PL spectrum of a GaN film grown at 900°C with a V/III ratio of 5000. Note that the 9 K PL intensity of the near band-to-band emission is very strong with a linewidth as narrow as 9 meV and the yellow luminescence is so weak that it can hardly be detected. A careful inspection of the 9 K PL spectrum in Fig. 6 shows that the emission energy of the primary peak is about 3.475 eV which has been identified as the emission of the A free excitons bound to neutral donors associated with nitrogen vacancies [17,20].

4. Conclusion

In conclusion, high crystalline quality GaN films were achieved on (0001) sapphire substrates in the range 800–900°C by an alternate supply of TMG and NH_3 with a thin GaN buffer layer predeposited at 500°C. The structural and optical properties of the GaN films grown in this investigation are comparable to those obtained in the GaN films grown by conventional techniques. The best GaN films were achieved at 900°C with a 9 K PL linewidth of the 3.475 eV emission as narrow as 9 meV. The preparation of high quality GaN films at relatively lower temperatures than that reported in the MOCVD growth has been attributed to the migration enhancement of the Ga adatoms on the grown surface and the easy access of cracked N–H radicals for the growth process implemented in current investigation.

Acknowledgements

This work was supported in part by the National Science Council of Taiwan with contract numbers NSC 83-0404-E-035-001 and NSC 84-2215-E-035-003. The authors would like to thank Professor Y.S. Huang's group at the Electronic Engineering Department, National Taiwan University of Science and Technology, Taipei, Taiwan. and Dr P.T. Chang's group at the United Epitaxy Company, Hsinchu, Taiwan, for assistance in the CER and DCXRD measurements.

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