Study of GaN thin films grown on vicinal SiC (0001) substrates by molecular beam epitaxy

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Abstract

A detailed study of the characteristics of undoped GaN films, grown on either vicinal or nominal flat SiC (0001) substrates by molecular beam epitaxy, has been carried out using photoluminescence and Raman scattering techniques. The 11 K photoluminescence spectra of the GaN film grown on the vicinal SiC (0001) substrate show a strong and sharp near-bandgap peak (full width at half maximum (FWHM) ~ 16 meV). This feature contrasts with that of the GaN film grown on the nominal flat SiC (0001) substrate where the 11 K photoluminescence spectra exhibit the near-bandgap peak (FWHM ~ 25 meV) and the intensity is approximately seven times weaker than that of the vicinal film sample. The redshift of the near-bandgap peak associated with excitons bound to shallow donors is related to the stress caused by both the lattice mismatch and the thermal expansion coefficient difference between GaN and SiC substrates. The measured thermal activation energy of the shallow donor of 33.4 meV is determined by using an Arrhenius plot of the near-bandgap luminescence versus $1/T$ from the slope of the graph at high temperature. The temperature dependence of the FWHM of the near-bandgap luminescence has also been studied. The Raman scattering measurements from the vicinal film reveal that the E_2 phonon peak is strengthened and the $A_1(\text{LO})$ phonon peak is shifted towards the low-frequency side with enhanced intensity, in comparison to that from the nominal flat film, suggesting a reduction in the density of defects and a lower free carrier concentration in the vicinal GaN film.

1. Introduction

GaN is currently attracting much interest, due to its potential applications in the fields of optoelectronics and electronics. Because of the large and direct gap as well as its outstanding chemical and physical stability, this material is a great candidate for the construction of short-wavelength light emitting devices and transistors operating at high temperature [1, 2]. However, the defect density of the GaN material is exceptionally high compared to other conventional

III–V semiconductors. Although the major technique used to grow GaN for optoelectronic devices is metal–organic chemical vapour deposition (MOCVD), the molecular beam epitaxy (MBE) technique allows *in situ* diagnostic observation. Certain microscopic processes related to nucleation and growth, learning from such *in situ* studies, may be applicable to both MBE and MOCVD. Furthermore, MBE-grown films may have better prospects for various photodetectors and electronic devices. These applications essentially rely on the epitaxial film quality. The measurements of optical,

electrical and structural properties of the GaN films are usually employed to assess the crystal quality. For this reason, much of the considerable research effort devoted to GaN has been directed towards its optical, electrical and structural properties. Photoluminescence (PL) has been used extensively for the optical characterization study of the GaN films [3, 4]. The PL spectra of the undoped GaN films generally show a sharp peak close to the energy gap, which is attributed to excitons bound to shallow donors [4]. There is also a broader peak centred at 2.2 eV [5, 6]. Raman scattering spectroscopy is a convenient and nondestructive tool for characterizing semiconductors and, in particular, the epitaxial layer of GaN. The crystal quality can be judged from the peak shape and adherence to the selection rules [7]. Of particular interest to the present study is the fact that the longitudinal optical (LO) phonons interact strongly with a free carrier plasma when the plasma frequency is close to the LO phonon frequency. The coupled LO phonon plasma modes have thereby been created, diminishing the intensity of the LO phonon peak in a systematic fashion, which can be used to determine the donor concentration in Si-doped GaN [8]. In this study, we present experimental data for the undoped GaN films deposited by MBE on both vicinal 4H-SiC (0001) substrates, which are misoriented towards $[1\bar{1}010]$ by 3.5° and on nominal flat 6H-SiC (0001) substrates. The GaN films are called M047 and M051, respectively, and are investigated by means of PL and Raman scattering measurements. The performed measurements demonstrate the importance of PL and Raman scattering to the assessment of the optical, electronic and structural quality of the GaN films. Recently, Xie *et al* [9] have observed a significant reduction of threading dislocations in GaN films grown by MBE on vicinal SiC [0001] substrates using scanning tunnelling microscopy. In good agreement with the results of Xie *et al*, our PL and Raman scattering measurements confirm that the GaN film quality on a vicinal SiC substrate is superior to that on nominal flat substrate.

Undoped n-GaN film samples M047 and M051 were grown by MBE. The GaN layer thicknesses were 1.2 and 1.0 μm , respectively. The substrates of the samples were either 4H-SiC (0001) (Nippon Steel Co.) misoriented towards $[1\bar{1}010]$ by 3.5° (sample M047) or nominal flat 6H-SiC (0001) (Cree Research Inc., sample M051), respectively. Details of the growth conditions have been described elsewhere [9]. The PL was excited by a cw He-Cd laser (325 nm) with an output power of 5 mW, and analysed by a Spex 500M single grating monochromator with a R406 photomultiplier tube. The sample temperature was varied from 11 to 295 K using a closed cycle helium cryostat. The Raman scattering was carried out using Jobin Yvon Raman scattering spectroscopy. The 514 nm line of an Ar⁺-ion laser was focused on the sample at room temperature. The experiments were carried out in the backscattering geometry, denoted as $Z(X, X)\bar{Z}$ and $Z(X, Y)\bar{Z}$, with the Z direction parallel to the (0001) axis of GaN. The allowed modes for the above two configurations are $A_1(\text{LO})$ and E_2 .

2. Results and discussion

2.1. Photoluminescence

Figures 1 and 2 reveal the PL spectra at selected temperatures (11–295 K) for samples M051 and M047, respectively. The

Figure 1. PL spectra obtained from sample M047 at selected temperatures.

Figure 2. PL spectra obtained from sample M051 at selected temperatures.

dominant near-bandgap luminescences at 3.450 and 3.445 eV at 11 K observed in samples M047 and M051, respectively, are due to the recombination of excitons bound to shallow donors of nitrogen vacancies (DBE) [10] with a binding energy of 35.5 meV [11, 12]. Monemar [13] has shown that the temperature dependence of the GaN bandgap is given by

$$E_g(T) = 3.503 \text{ eV} - \frac{5.08 \times 10^{-4} (\text{eV K}^{-1}) T^2}{996 \text{ K} - T}. \quad (1)$$

This gives $E_g(11 \text{ K}) = 3.496 \text{ eV}$. However, Gil *et al* [14] have shown that the strain can change the near-bandgap luminescence position. The strain is due to the lattice mismatch of the substrate and the GaN epitaxial layer, and it depends on the choice of substrate, the properties of the buffer layer, the growth temperature and the thickness of the epilayer. It is noted that the near-bandgap luminescence positions at 11 K for samples M047 and M051 shifted 46 and 51 meV, respectively, below the unstrained bandgap (3.496 eV at 11 K). This suggests that the strain in sample M051 is larger than that in sample M047. An inspection of figures 1 and 2 reveals that, at 11 K, the near-bandgap luminescence intensity of sample M047 is approximately seven times higher than that

Figure 3. The temperature dependence of the intensity of the near-bandgap peak for sample M047. The black square is the experimental data. A thermal activation energy of 33.4 meV was obtained from the slope of the graph at high temperature.

of sample M051, suggesting that sample M047 has a better optical quality. Figures 1 and 2 also show that, at 11 K, for samples M047 and M051 the near-bandgap luminescence intensity is approximately 50 times higher than that at 295 K, indicating temperature activated non-radiative processes. Also, we see no evidence of the obvious difference in intensity of yellow luminescence between samples M047 and M051.

On the basis of the temperature dependence of the near-bandgap luminescence position, the energy gap temperature dependence is usually described by the equation

$$E_g(T) = E_g(0) - \frac{\alpha_c T^2}{T_0 - T} \quad (2)$$

where $E_g(0)$ is the energy gap at 0 K, T_0 is somehow associated with the Debye temperature, and α_c is an empirical constant. This form of the temperature dependence of the energy gap was proposed by Varshni [15] and later successfully applied to describe $E_g(T)$ in many semiconductors. We can fit the bandgap temperature dependence (M047) neglecting the DBE binding energy according to equation (2) and we obtain $E_g(0) = 3.4501$ eV, with $\alpha_c = 1.24 \times 10^{-3}$ eV K⁻¹ and $T_0 = 1559.23$ K. These values are very close to $E_g(0) = 3.503$ eV, $\alpha_c = 5.08 \times 10^{-4}$ eV K⁻¹ and $T_0 = 996$ K reported by Monemar [16]. Figure 3 shows an Arrhenius plot of the near-bandgap luminescence intensity for sample M047 versus $1/K$. A thermal activation energy of 33.4 meV was obtained from the slope of the graph at high temperature. This value is very close to 35.5 meV [11], the binding energy of the assumed shallow donor (nitrogen vacancies). These data, combined with the near-bandgap luminescence position (3.45 eV, at 11 K) suggest that the near-bandgap luminescence is due to DBE transition.

Figure 4 shows the temperature dependence of the full width at half maximum (FWHM) of the near-bandgap luminescence for samples M047 and M051. The near-bandgap luminescence is broadened from 11 to 295 K and its energy positions (3.45 eV for sample M047 and 3.445 eV for sample M051 at 11 K) are below the unstrained bandgap (3.496 eV at 11 K); this is consistent with the assignment of the DBE transition. It is concluded from figure 4 that the FWHM of sample M051 is larger than that of sample M047, suggesting

Figure 4. The temperature dependence of the FWHM of the near-bandgap peak for samples M051 and M047.

Figure 5. Raman spectra of sample M051 in selected configurations.

a better optical quality of sample M047 in comparison to that of sample M051.

2.2. Raman scattering

Typical Raman scattering spectra of samples M051 and M047 are shown in figures 5 and 6, respectively, for comparison. Since the light penetration depth of 514 nm is longer than the thickness of the GaN films, two signals SiC $A_1(TO)$ and SiC E_2 from the silicon carbide substrate have also been observed in the $Z(X,X)\bar{Z}$ and $Z(X,Y)\bar{Z}$ configurations. In the above backscattering geometries, the selection rules were almost satisfied. However, the $A_1(LO)$ mode that is forbidden in the $Z(X,Y)\bar{Z}$ configuration was observed in these experiments (figure 6) because the incident light was not exactly normal to the surface of the sample.

In figure 5 for sample M051, 145 cm⁻¹ E_2 (low), 567 cm⁻¹ E_2 (high), and 737 cm⁻¹ $A_1(LO)$ modes are observed, in addition to 789 cm⁻¹ SiC $A_1(TO)$ and 767 cm⁻¹ SiC E_2 [17]. The other three observed modes, 149, 503 and 505 cm⁻¹, are not identified. In GaN single crystals grown at high pressure and high temperature without strain, the E_2 (high) mode is located at 568 cm⁻¹ [8]. However, the redshift of the E_2 (high) mode of sample M051 (at 567 cm⁻¹) indicates that there is a biaxial stress induced

Figure 6. Raman spectra of sample M047 in selected configurations.

by a change of the elastic constant with strain [18]. This is the result of the thermal expansion coefficient difference and the lattice mismatch between GaN and SiC. Hence, the GaN epitaxial layer is compressed in the plane of the layer when the temperature is reduced from the growth temperature. In the $Z(X, X)\bar{Z}$ configuration, we notice that the signal of the $A_1(\text{LO})$ mode at 737 cm^{-1} is very weak, and its peak is broadened for sample M051.

In figure 6 for sample M047, the E_2 (low) at 143 cm^{-1} , E_2 (high) at 567 cm^{-1} and $A_1(\text{LO})$ at 734.5 cm^{-1} modes can be seen, in addition to 777 cm^{-1} SiC $A_1(\text{TO})$ and 790 cm^{-1} SiC E_2 [17]. Three unidentified Raman peaks at 201.7 , 202.4 and 610 cm^{-1} are also observed. In comparison with the E_2 (high) mode at 567 cm^{-1} for sample M051 (figure 5), although the E_2 (high) mode peak position of sample M047 (567 cm^{-1}) is the same, its intensity is significantly enhanced. The much weaker intensity of the E_2 (high) mode for sample M051 may be related to the high defect density in typical heteroepitaxial GaN films grown on nominal flat 6H-SiC (0001) substrates, as reported by Xie *et al* [9] based on scanning tunnelling microscopy. This is also consistent with the PL results. Kozawa *et al* [8] have concluded that the LO phonon band is shifted towards the high-frequency side and broadened with an increase in carrier concentration, especially when the carrier concentration exceeds 10^{18} cm^{-3} . They have further pointed out that the carrier concentrations obtained from Raman data and Hall measurements agree well, which demonstrates that the Raman measurement is a suitable technique to determine the free carrier concentrations in GaN. In the $Z(X, X)\bar{Z}$ configuration (figures 5 and 6) one can observe that the $A_1(\text{LO})$ mode peak position (737 cm^{-1}) for sample M051 appears in the high-frequency side in comparison to that for sample M047 (734.5 cm^{-1}). Also, the width and intensity of the $A_1(\text{LO})$ mode peak in sample M051 is broadened and reduced, compared with that of sample M047, suggesting that the background free carrier concentration of sample M051 should be higher than that of sample M047. It is then estimated that the free carrier concentration in sample M051 is of the order of magnitude of 10^{18} cm^{-3} and in sample M047 below 10^{18} cm^{-3} .

3. Summary

The performed PL and Raman scattering measurements in GaN films deposited on either vicinal or nominal flat SiC (0001) substrates have enabled us to demonstrate the improvement in the quality of GaN films grown on the vicinal SiC (0001) substrate. The PL spectra confirm that the GaN film quality on the vicinal SiC substrate is superior to that on the nominal flat substrate. The redshift of the near-bandgap PL exciton peak is related to the stress caused by both the lattice mismatch and the difference in the thermal expansion coefficient between the GaN film and the SiC substrate. The temperature dependence of the FWHM of the near-bandgap luminescence has been studied. From this, we have calculated the shallow donor binding energy E_A to be 33.4 meV . In good agreement with the PL data, our Raman scattering spectra from the GaN film deposited on the vicinal SiC (0001) substrate reveal that the E_2 phonon peak intensity is strengthened and the $A_1(\text{LO})$ phonon peak is shifted towards the low-frequency side with enhanced intensity, in comparison to the GaN film deposited on the nominal flat SiC (0001) substrate. The results of Raman measurements suggest that the GaN film deposited on the vicinal SiC (0001) substrate has a reduced defect density and a lower free carrier concentration.

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