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Control and improvement of crystalline cracking from GaN thin films grown on Si by metalorganic chemical vapor deposition

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Abstract

A series of GaN thin films were grown on Si substrate under different conditions using metalorganic chemical vapor deposition (MOCVD) and characterized by Nomarski microscopy (NM), optical reflectance (OR), high-resolution X-ray diffraction (HRXRD), Raman scattering (RS) and photoluminescence (PL). NM showed different patterns for GaN/Si grown under different growth and source flow parameters. XRD, RS and PL measurements confirmed their wurtzite crystalline GaN structures, and the corresponding line shape analyses revealed their difference corresponding to the NM observations. The control and improvement of the crystalline cracking in GaN/Si are discussed.

Keywords: GaN; Si; MOCVD; Optical reflectance; X-ray diffraction; Raman scattering; Photoluminescence

1. Introduction

Research and development on GaN-based materials and structures have been greatly enhanced in recent years and remarkable breakthroughs have been achieved in their growth and applications in visible–UV light emitting diode (LED), laser diode (LD) and other optoelectronics/electronic devices. [1–5]. Metalorganic chemical vapor deposition (MOCVD) is currently a major technique for the industry mass production of these materials and device wafers with sapphire as the main substrate. SiC is the secondary commonly used material as substrate. However, the insulating nature of sapphire and high costs of SiC have limited their further wider use. Various other substrate materials have been explored. Silicon is an attractive one among them because of its high crystal quality, large area size, low manufacturing cost and the potential application in integrated devices. GaN and related materials/structures grown on Si are promising for developing new generation of devices by combining Si and III-N based materials and technologies in the 21st century.

Due to a large lattice mismatch (17%) and a big difference in thermal expansion coefficients (37%) between GaN and Si [6], which are both larger than that between GaN and sapphire, it is even more difficult to grow high-quality GaN films and structures on Si substrates than on sapphire. In order to realize good quality of GaN films grown on Si, buffer layers with composite structure have been inserted and grown between the GaN epilayer and Si substrate, such as AlN [7], carbonized silicon [8], nitridized GaAs [9], oxidized AlAs [10], γ-Al_2O_3 [11], and intermediate superlattice [12,13]. Recently, to grow GaN on Si(111), Kim et al. [6] used a five-step graded $Al_xGa_{1-x}N$ ($x=0.87-0.07$) interlayer between AlN buffer layer and GaN epilayer, and Dadgar et al. [14] employed a method to reduce tensile stress and improve GaN layer quality in the early stage of buffer layer growth by an in situ masking of the AlN seed layer with a thin SiN mask. Lee et al. [15] reported the high-quality GaN by MOCVD using a Si_xN_y inserting layer between the 1.5 μm GaN overlying layer and the 1.0 μm underlying layer, which was grown on Si(111) with a high-temperature AlN buffer.

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In this paper, we report the growth and characterization for a series of GaN thin films on Si under different conditions by metalorganic chemical vapor deposition (MOCVD). They were characterized by Normarski microscopy (NM), optical reflectance (OR), high-resolution X-ray diffraction (HRXRD), Raman scattering (RS) and photoluminescence (PL). The control and improvement of cracks in GaN/Si have been realized by MOCVD growth.

2. Experimental details

GaN epitaxial layers were grown on n-type Si(111) substrates by low pressure (LP) MOCVD in a vertical reactor with a high speed rotation disk holder for multiple wafers. Trimethylgallium (TMGa), trimethylaluminum (TMAI) and high purity ammonia (NH_3) were used as Ga, Al and N precursors, respectively. After a chemical cleaning process, the Si(111) substrate was heated to 1030 °C under hydrogen ambient for 10 min to produce a clean, oxide-free surface. To prevent the melt back etching of Si substrate by TMGa subsequently injected, the high-temperature AlN layer was first deposited at 1050 °C. For the samples NS1295, NS1296, NS 1347, the AlN layer is 50 nm thick without Si-doping while in the samples NS 1691 and NS 1692, the AlN layer is 100 nm thick with Si-doping. Finally, the temperature was adjusted to 1000 °C and about 1–2 μm thick unintentionally doped GaN epitaxy layer was grown. For samples NS1691 and NS1692, the Si-delta doping was also performed during the GaN growth. More details of growth will be published elsewhere.

After the growth, a series of material characterization techniques, including Nomarski microscopy (NM), X-ray diffraction (XRD), optical reflectance (OR), Raman scattering (RS) and photoluminescence (PL) spectroscopy, were used to assess the GaN films. XRD was measured using a Philips X'pert five-crystal diffractometer with a Cu Kα radiation (1.54 Å). OR was measured using a UV–Visible FilmMeter, F20UV. RS was performed by a J-Y microscope under the excitation of 633 nm from a HeNe laser. PL was measured with a Renishaw UV-2000 microscope with the He–Cd laser 325 nm line for excitation. All measurements were performed at room temperature (RT).

3. Results and discussion

Some data summary from characterization are listed in Table 1 for the five experimental GaN/Si samples. Detailed description can be seen from the following sections.

3.1. Normaski microscopy

Fig. 1 shows the Normaski microscopy photos of five MOCVD-grown GaN/Si. All graphs are recorded under a magnification of 500 and with an inserted ruler length of 0.2 mm. The variation of cracks with samples grown under different conditions is clearly revealed. Many groups have reported the appearance of cracks along the {1-100} in the GaN layers grown on the Si substrate [6,15–17]. Cracks in GaN on Si are known to be formed during the cooling stage due to a large tensile stress caused by the large difference in thermal expansion coefficients [6]. Our present work has shown the variation of cracks with the growth conditions, and the control and optimization of the cracking patterns. The reduction of cracks in some samples (NS1691, NS1692) is caused by the Si-delta doping process. They correspond to the features revealed from structural and optical measurements.

3.2. Film thickness

The film thicknesses were measured by optical reflectance (OR). Fig. 2 shows such an example for the sample NS1347. The arrow in the left side of the figure indicates the band gap of the epitaxial GaN film, which is close to 360 nm. The simulation on the OR spectrum in the wavelength range of 400–850 nm gives the film thickness of d=778 nm, and also the values of refraction index, n, and the extinct coefficient, k, vary with wavelength.

3.3. High-resolution X-ray diffraction

All films were characterized by high-resolution X-ray diffraction (HR-XRD). A typical $2\theta-\omega$ wide scan (20–130°) for a GaN/Si sample, NS1691, is shown in Fig. 3. It exhibited only the dominant wurtzite (w-) GaN crystalline (0002), (0004) and (0006) peaks plus two peaks from Si substrate. This indicates the grown GaN layer with the normal orientation along the c-axis of wurtzite crystalline structure [18]. The narrow value of 0.18° of the full width at

Table 1
Characterization summary for MOCVD-grown GaN/Si samples

Sample	Cracking overview	Thickness (nm)	PL peak (eV)	PL FWHM (meV)	XRD (0002) FWHM	Raman E_2 (cm^{-1})	E_2 FWHM (cm^{-1})	RamanA_1 (LO) (cm^{-1})
NS1691	Best	2142	3.403	44.7	0.177°	564.5	3.3	731.0
NS1692	2nd best	1747	3.398	48.5	0.171°	565.3	3.5	732.5
NS1295	Middle	2048	3.411	48.7	0.178°	566.4	4.5	733.2
NS1296	Worse	2001	3.404	48.6	0.177°	565.6	4.3	732.4
NS1347	Worst	778	3.382	64.2	0.180°	563.1	5.2	731.5

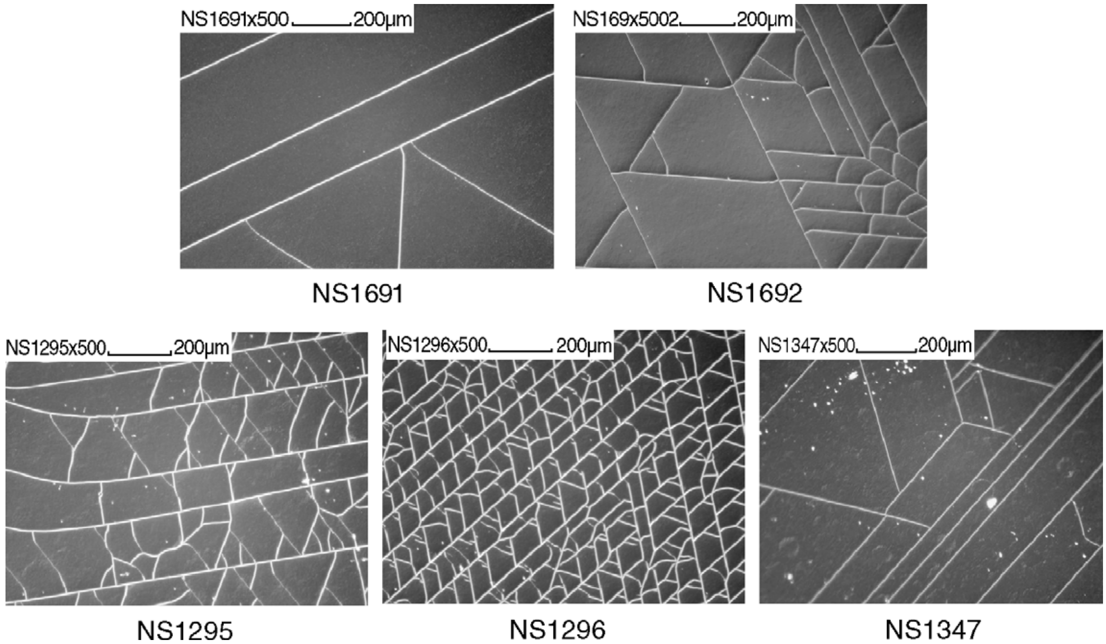

Fig. 1. Normaski microscopy pattern of five MOCVD-grown GaN/Si. All graphs are with a magnification of 500 and an inserted ruler length of 200 μm.

half maximum (HWFM) on the (0002) GaN peak, as shown in the bottom plot of the figure, indicates the high degree of crystalline perfection of the grown sample. FWHM values

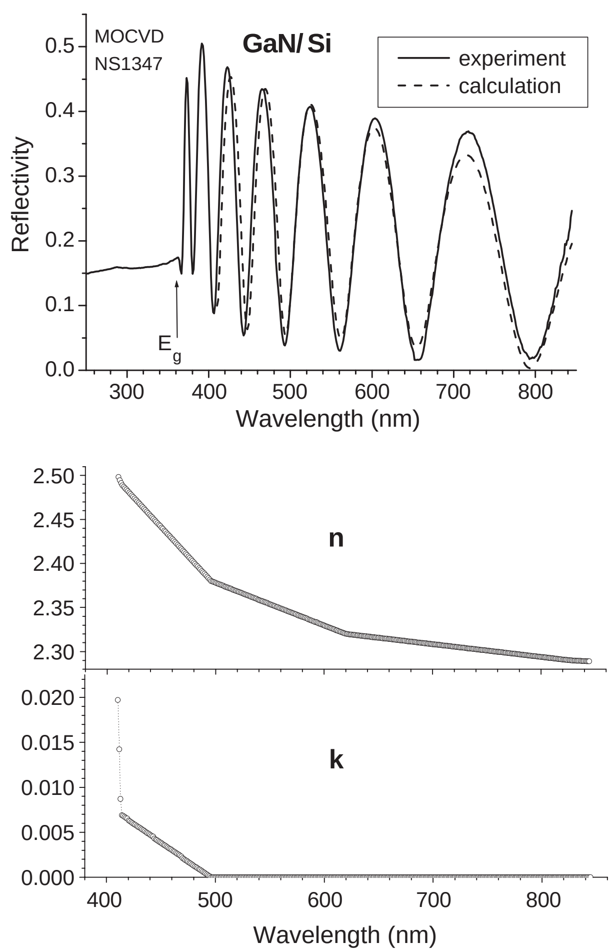

Fig. 2. The optical reflectance spectrum for a GaN/Si sample, NS1347, measured in 250–850 nm (solid line) with simulated data in 400–850 nm (dash line). The deduced values of the refraction index, n, and the extinct coefficient, k, are plotted in the bottom side graph.

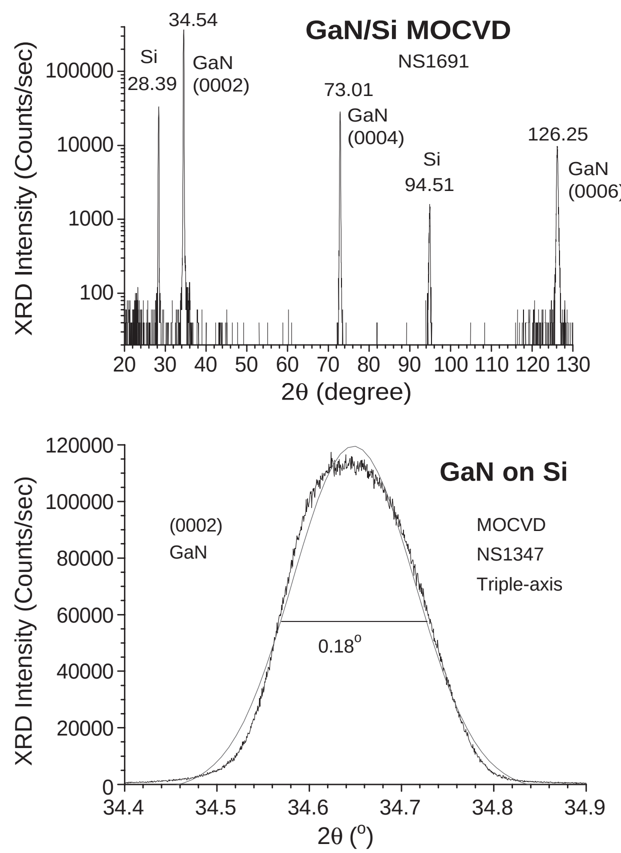

Fig. 3. The HR-XRD wide (20–130°) $2\theta-\omega$ scan for a GaN/Si sample, NS1691 (top graph), and a typical GaN (0002) peak/Gaussian fit for a GaN/Si, NS1347 (bottom graph).

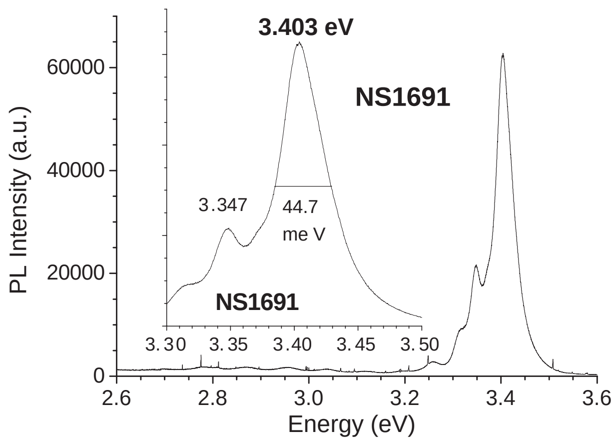

Fig. 4. The RT PL spectra for a GaN/Si, NS1691, with the insert for expansion.

of the GaN (0002) peak for other samples are also listed in Table 1. It can be seen that other samples even show even smaller FWHM values than NS1347, indicating better crystalline quality.

3.4. RT photoluminescence

Fig. 4 shows the RT PL spectra for a GaN/Si sample, NS1291, with the insert for the expanse of the main peak area. It shows a strong PL emission band at 3.403 eV due to the near band edge emission from wurtzite GaN. It possesses a small FWHM value of 44.7 meV, also indicating a high quality of w-GaN material. The PL peak and FWHM values for five experimental samples are all listed in Table 1.

3.5. Raman scattering

Fig. 5 exhibits the RT Raman spectra of five MOCVD-grown GaN films on Si, and a reference Si (111) bare substrate. Fig. 6 is a typical Raman spectrum with two inserts for the w-GaN characteristic E_2 and A_1 (LO) modes [19] as well as their curve fits. The peak frequencies and the

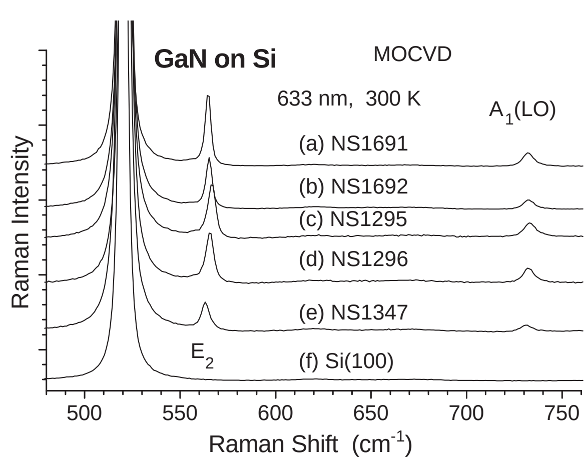

Fig. 5. Raman spectra of five MOCVD-grown GaN films on Si, and a Si (111) bare substrate, measured under 633 nm from a He–Ne laser at RT.

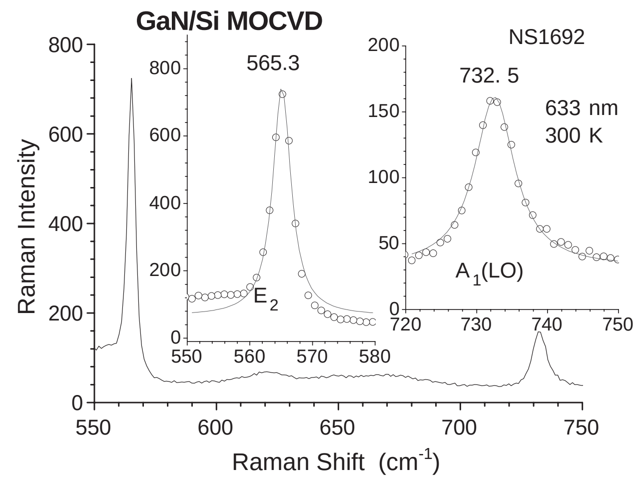

Fig. 6. A typical Raman spectrum for a MOCVD GaN/Si, with details and Gaussian curve fits shown in two inserts for the E_2 and A_1(LO) modes.

FWHM values of the E_2 mode for all samples are listed in Table 1.

4. Conclusions

In this study we have employed MOCVD to grow a series of GaN thin films on Si under different conditions and films were characterized by a variety of techniques. Nomarski microscopy showed different cracking patterns for GaN/Si depending on growth and source flow parameters. Film thicknesses were determined from optical reflectance. High-resolution XRD, Raman scattering and photoluminescence measurements confirmed their wurtzite crystalline GaN structures, and the corresponding line shape analyses revealed their difference corresponding to the NM observations. It was found that NS1691 has the best shape of widest cracking distribution, the narrowest PL and Raman band, NS 1692 takes the 2nd position while NS1295 is the 3rd one with poor surface morphology. NS1296 and NS1347 have the high density of cracks. The high-temperature AlN buffer growth with Si-doping and the Si-delta doping during the GaN layer growth are useful to realize the control and improvement of cracking in GaN/Si.

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