The influence of an Si_xN_y interlayer on a GaN film grown on an Si(111) substrate*

Peng Dong-Sheng(彭冬生)†, Chen Zhi-Gang(陈志刚), and Tan Cong-Cong(谭聪聪)

Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, Shenzhen University, Shenzhen 518060, *China*

(Received 1 April 2012; revised manuscript received 8 May 2012)

A method to drastically reduce dislocation density in a GaN film grown on an Si(111) substrate is newly developed. In this method, the Si_xN_y interlayer which is deposited on an AlN buffer layer *in situ* is introduced to grow the GaN film laterally. The crack-free GaN film with thickness over 1.7 micron is successfully grown on an Si(111) substrate. A synthesized GaN epilayer is characterized by X-ray diffraction (XRD), atomic force microscope (AFM), and Raman spectrum. The test results show that the GaN crystal reveals a wurtzite structure with the ⟨0001⟩ crystal orientation and the full width at half maximum of the X-ray diffraction curve in the (0002) plane is as low as 403 arcsec for the GaN film grown on the Si substrate with an Si_xN_y interlayer. In addition, Raman scattering is used to study the stress in the sample. The results indicate that the Si_xN_y interlayer can more effectively accommodate the strain energy. So the dislocation density can be reduced drastically, and the crystal quality of GaN film can be greatly improved by introducing an Si_xN_y interlayer.

Keywords: Si_xN_y interlayer, silicon substrate, GaN film, Raman scattering

PACS: 81.05.Ea, 81.15.Kk, 61.72.–y **DOI:** 10.1088/1674-1056/21/12/128101

1. Introduction

Because of the large direct energy band-gap and good thermal stability properties, GaN and relevant materials have attracted much attention. They are found to have their numerous optoelectronic and electronic applications, such as laser diodes (LDs), visible-blind ultraviolet (UV) detectors, and short-wave light emitting diodes (LEDs).[1–4] However the lack of a suitable substrate makes its application in the above fields more difficult,[5] and the threading dislocations (TDs) with a density of $10^8/cm^2$–$10^9/cm^2$ remain in the GaN film due to the large differences in lattice constant and thermal expansion coefficient between the GaN epilayer and the substrate,[6] so the choice of suitable substrate is very important. Silicon, due to its low cost, high thermal conductivity, and potential integration with a mature Si-based electronic process, and serving as a substrate for GaN growth, has attracted more and more attention. But the cracking and high defect density problems are still very serious when the GaN is grown on Si. This is due to the large lattice mismatch and the difference in thermal expansion coefficient between the GaN epilayer and Si substrate.[7–9] In the past few years the quality of GaN film grown on the Si substrate has been greatly improved due to the progress of the buffer layer technologies and some important devices have been implemented.[10] The high-quality GaN layer on Si substrate can also be achieved by an interlayer structure between the GaN and Si substrate. The defect-free GaN grown on an Si substrate was realized by using an Si_xN_y interlayer in hot wall chemical vapour deposition via the metal–organic chemical vapour deposition (MOCVD) growth technique. In the present paper, the high-quality GaN film is grown on the silicon substrate with an Si_xN_y interlayer, and the influence of the Si_xN_y interlayer on the GaN film is investigated. The Raman spectroscopy can be used to nondestructively and accurately measure the optical properties of GaN films.[11] The paper also shows how the Raman modes of GaN thin film grown on an Si substrate may be distinguished from the Raman fea-

*Project supported by the National Natural Science Foundation of China (Grant No. 60806017), the Science and Technology Program of Shenzhen, China (Grant No. JC201005280455A), the Shenzhen University Research and Development Program, China (Grant No. 201128), the Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, China (Grant No. 201208), and the Rising Industry Development Foundation of Shenzhen, China (Grant No. JCYJ20120613162522373).

†Corresponding author. E-mail: pengdongsheng@163.com

© 2012 Chinese Physical Society and IOP Publishing Ltd

tures of the silicon substrate. The wavenumber shift about the Raman mode of the GaN film is explained theoretically, which is very consistent with the XRD results.

2. Experimental procedure

GaN film is grown in the vertical Thomas Swan LP-MOCVD on an N-type (111)-oriented 2″ Si substrate at a pressure of 13.33 kPa. Prior to the growth process, the substrate is cleaned as follows: firstly the substrate is washed by acetone for 10 min to remove the grease from the surface, and then immersed in the aqua regia for 5 min to remove the metal ions. Secondly, the substrate is etched by the H_2SO_4:H_2O_2(1:1) solution for 10 min to eliminate organic contamination from the surface and to oxidize the surface. Finally, the HF (49%) is used to extract the previous thin oxide layer. After rinsing with deionized water and drying with nitrogen, the substrate is loaded into the reactor.

At the beginning of the growth of the AlN buffer, the substrate is baked in H_2 ambient at 1100 °C for 10 min in order to eject the native oxide, then the temperature is reduced to 1060 °C to grow the AlN buffer and undoped GaN layer. In the course of the growth of the undoped GaN layer, two LT-AlN interlayers are inserted. The thickness of the LT-AlN interlayer is 15 nm and the growth temperature is 600 °C. Following thermal etching, an Si_xN_y interlayer on the AlN buffer surface is grown, of which the substrate is nitridated by exposing it to the NH_3 flow of 0.8 slm at 1020 °C. The nitridation times are 0 (without nitridation) and 120 s for samples A and B, respectively. In all the above cases, trimethylgallium (TMGa), trimethyaluminum (TMAl), and ammonia (NH_3) are used as Ga, Al, N precursors, with N_2 and H_2 as carrier gases.

The crystalline quality of the GaN layer is examined by high resolution X-ray diffraction (HRXRD) using a four-crystalline Philip DCXRD system, in which the scanning step is 0.02°/s. The Raman spectra are obtained using the T64000 micro-Raman system (Jobin Yvon Inc.) excited with 325-nm continuous light and the spectral resolution is better than 1.0 cm^{-1}.

3. Results and discussion

In order to compare the crystal quality, (0002) XRD measurements are carried out on samples A and B, in which the full-width at half-maximum (FWHM) of the diffraction peak can show the magnitude of dislocation. The XRD spectra of samples A and B are shown in Fig. 1.

The formulation of the Bragg diffraction is shown in Eq. (1)

$$2d\sin\theta = \lambda, \tag{1}$$

$$2d = c, \tag{2}$$

$$e = (c - c_0)/c_0, \tag{3}$$

where λ is the wavelength of the X-ray, θ is the angle of diffraction, d is the distance of adjacent (0002) plane, e is the out-of-plane strain, c_0 is the lattice parameter of bulk GaN.

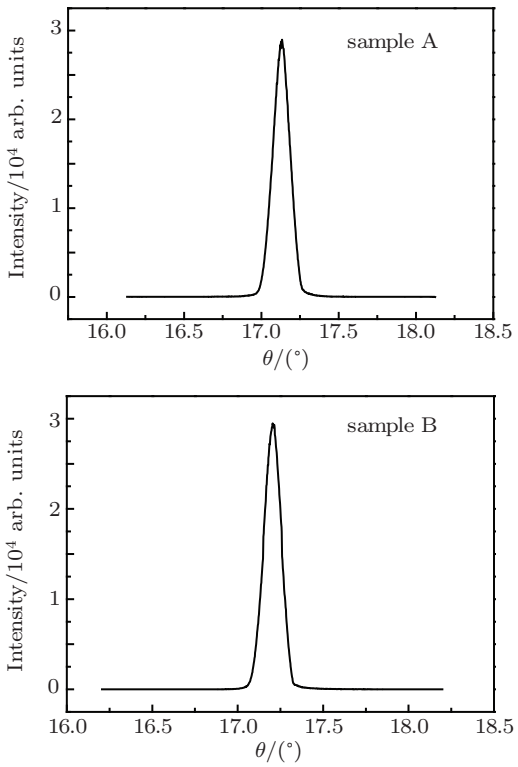


Fig. 1. The XRD spectra of samples A and B.

Based on Eq. (1) and the XRD experimental results (Fig. 1), Table 1 gives the quantitative XRD analysis results of samples A and B.

Table 1. Quantitative XRD analysis results of samples A and B.

GaN film	(0002) FWHM/arcsec	c/nm	e/%
Sample A	465	0.5227	0.8100
Sample B	403	0.5207	0.4243

The full width at half maximum (FWHM) of the XRD rocking curve is used to quantify crystalline imperfection.[12] The lower the FWHM of the XRD, the more perfect the crystal quality is. The FWHM of

sample A in (0002) plane is 465 arcsec, while that of sample B is reduced to 403 arcsec. So the dislocation density of the GaN epilayer can be reduced greatly in the case of using an Si_xN_y interlayer. Both samples A and B are of tensile stress, and compared with sample A, sample B has a low strain, so the crystal quality of sample B is superior to that of sample A.

Raman spectrum can provide the structural information of material, which is sensitive to the microscopic disorder and residual stress in material. GaN normally has a wurtzite structure, with the space group of $P_{63}mc$ (no. 186), in which all atoms occupy the position of C_{3v}. The wurtzite structure consists of alternating biatomic close-packed (0002) planes of Ga and N pairs stacked in an ABABAB sequence. Atoms in the first and third layers are directly aligned with each other. The analysis of the group theory shows that the symmetric species has the optical mode as

$$\Gamma_{\rm opt} = A_1(z) + 2B_1 + E_1(x,y) + 2E_2. \tag{4}$$

Here, x, y, z represent the orientation of the polarization of phonons. In the case of H–GaN, E_1 and A_1 denote Raman and infrared activity respectively, E_2 is the Raman activity, B_1 is the Raman inactivity. Raman scattering frequencies of wurtzite GaN are as follows:[13]

$$\begin{aligned} A_1({\rm TO}) &= 533\ {\rm cm}^{-1}, \quad E_1({\rm TO}) = 559\ {\rm cm}^{-1}, \\ A_1({\rm LO}) &= 738\ {\rm cm}^{-1}, \quad E_1({\rm LO}) = 743\ {\rm cm}^{-1}, \\ E_2({\rm high}) &= 568\ {\rm cm}^{-1}, \quad E_2({\rm low}) = 145\ {\rm cm}^{-1}. \end{aligned}$$

The Raman spectra of samples A and B are shown in Fig. 2. The scattering bands between 500 $\rm cm^{-1}$ and 800 $\rm cm^{-1}$ can be assigned to the vibration of silicon and A_1(LO) mode of GaN. The GaN epilayer is transparent to the green light, so the Raman band of silicon also appears in Fig. 2. The Raman peak of E_2(high) mode indicates that the GaN film has a hexagonal wurtzite structure. Moreover, there is no Raman scattering of bulk cubic GaN in Fig. 2, which indicates that the epitaxial film is of pure hexagonal wurtzite structure GaN.

The Raman peaks of Si:TO are located at 523.4 $\rm cm^{-1}$ and 521.8 $\rm cm^{-1}$ for samples A and B, respectively, each of which has an obvious blue-shift compared with the eigenfrequency of 520 $\rm cm^{-1}$, which is most likely to be due to compressive strain in the layers. Furthermore, compared with the Raman spectra of wurtzite GaN, the Raman peaks of E_2(high) and A_1(LO) in GaN films for samples A and B each have an obvious red-shift, which indicates a tensile stress existing in the GaN epilayer. According to the empirical formula of Kisielowshi[14] the relationship between wavenumber shift and the stress is related by

$$\Delta\omega = k\sigma_{xx}, \tag{5}$$

where $\Delta\omega$ is the shift of the frequency of phonon and it is in unit $\rm cm^{-1}$, k is the Raman stress coefficient, and σ_{xx} is the biaxial stress originating from strain energy and it is in GPa. For backscattering from Si(111) plane, k is 2.3, while for E_2(high) in the GaN film, k is 4.3.[15]

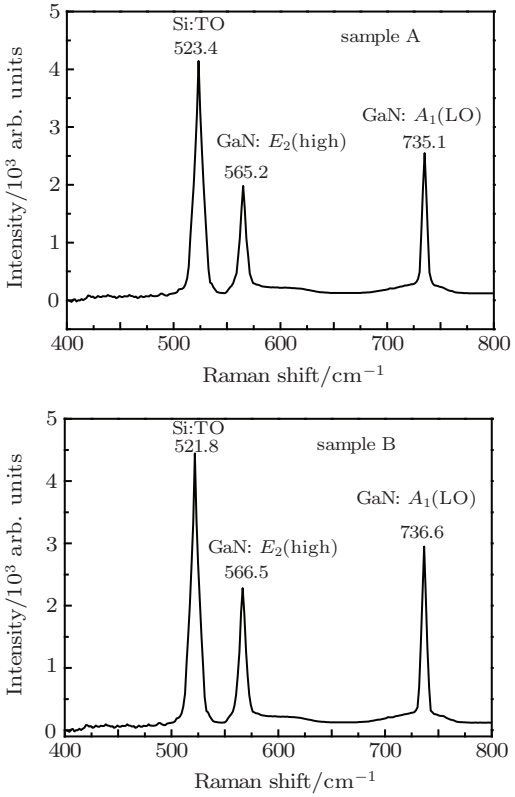


Fig. 2. Raman spectra of samples A and B.

Based on the calculated stress, the strain can be expressed as[16]

$$\sigma_{xx} = \left(C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}}\right) \times \varepsilon_{xx}, \tag{6}$$

where ε_{xx} is the biaxial strain; C_{ij} is the elastic constant of GaN material; C_{11}, C_{12}, C_{13}, and C_{33} are 390 GPa, 145 GPa, 106 GPa, and 398 GPa, respectively.[17]

Based on the σ_{xx} and the wavenumber shift of A_1(LO) of GaN films, the $\Delta\omega$ can be calculated as[18]

$$\Delta\omega = (0.8 \pm 0.4)\,\sigma_{xx}. \tag{7}$$

Using Eqs. (5), (6), and (7), we can easily calculate the maximum stress based on the Raman spectrum. The results are shown in Table 2.

Table 2. Quantitative Raman analysis results of samples A and B.

	σ_{xx} in silicon substrate/GPa	σ_{xx} in GaN film/GPa	ε_{xx}/%	$\Delta\omega$ of A_1(LO)/cm^{-1}
Sample A	1.48	0.65	0.1358	0.52 ± 0.26
Sample B	0.78	0.35	0.0731	0.28 ± 0.14

Based on Table 2, the stresses of the silicon substrate are 1.48 GPa and 0.78 GPa for samples A and B, respectively. The maximum tensile stresses of samples A and B are 0.65 GPa and 0.35 GPa, respectively. Compared with sample A, sample B has a low tensile stress, so the crystal quality of sample B is superior to that of sample A.

From Fig. 2, the wavenumber shifts of A_1(LO) are 2.9 cm^{-1} and 1.4 cm^{-1} for samples A and B, respectively, and the values are much larger than those calculated from Eq. (7), so the reason for the wavenumber shift of A_1(LO) is due to not only the strain energy originating from lattice mismatch but also the difference in coefficient of thermal expansion between GaN and Si. The another reason may be the change of polarization ratio originating from the variety of free carrier concentrations. The wavenumber shift of A_1(LO) for sample A is lower than that for sample B, so the quality can be greatly improved because of the Si_xN_y interlayer. This result is in good consistence with the X-ray results, which disclose the lower XRD FWHM for sample B.

AFM images are given in Figs. 3(a) and 3(b) for samples A and B, respectively. The scanned area is 30 μm×30 μm. The values of root mean squared (RMS) surface roughness are assessed to be 18.7 nm and 3.4 nm for samples A and B respectively. The surface morphology of GaN film with an Si_xN_y interlayer is superior to that without an Si_xN_y interlayer.

A very thin Si_xN_y interlayer is deposited "*in situ*" in MOCVD system by flowing NH_3 and diluting SiH_4. The introduction of SiH_4 and NH_3 gases results in the appearance of amorphous Si_xN_y interlayer, which perhaps enhances the lateral growth of the next GaN layer. Tentatively, we propose a similar mechanism that is involved in the Si_xN_y interlayer to that of the epitaxial lateral overgrowth (ELO). The solid-phase epitaxy starts from the nanometer holes and then spreads laterally. So, part of dislocations bending in the consequent process of lateral growth cannot reach the GaN film surface. The differences between the present technique and the ELO lie in the size and the density of the window opening. Since the spacing between the holes is small, the GaN film thickness does not have to be so thick as ELO in order to obtain coalescence. In addition, the larger surface coverage (about 90%) by Si_xN_y in the new technique makes the dislocation-free area larger than that of the ELO. So the dislocation density can be reduced drastically, the crystal quality of GaN film can be greatly improved by introducing an Si_xN_y interlayer.

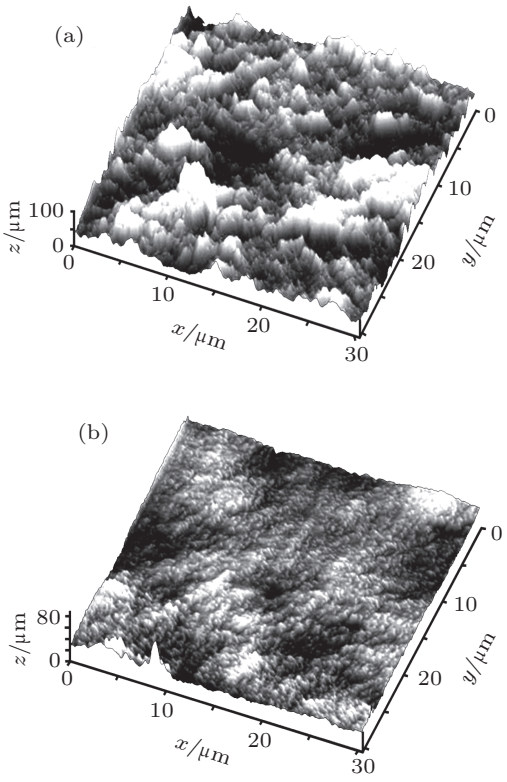


Fig. 3. AFM images of samples A (a) and B (b).

4. Conclusion

In this paper, high-quality GaN film with a low dislocation density is grown on the silicon substrate with an Si_xN_y interlayer. The introduction of the Si_xN_y interlayer results in the appearance of nanoholes, which enhances the lateral growth of the GaN layer. Using this method, the threading dislocation density is dramatically reduced. The XRD measurements indicate that the full-width at half-maximum (FWHM) on (0002) plane of the GaN film is reduced to 403 arcsec, and the surface quality is improved. In addition, the Raman peaks of E_2(high) and A_1(LO)

phonon mode in the GaN film each have an obvious redshift compared with bulk GaN eigenfrequency, which is most likely to be due to tensile strain in the GaN layer. However the TO phonon mode of Si has a blueshift which shows that the Si substrate is subjected to a compressive strain, the wavenumber shifts of the GaN film and Si substrate with the Si_xN_y interlayer are lower than that without it. According to the Raman spectrum analysis results, it is suggested that the Si_xN_y interlayer can more effectively accommodate the strain energy, and the Si_xN_y interlayer plays a role in releasing the residual stress in GaN film. We believe that the Si_xN_y interlayer is more helpful for growing crack-free GaN film on an Si(111) substrate.

References

[1] Sun W, Shatalov M, Deng J, Hu X, Yang J, Lunev A, Bilenko Y, Shur M and Gask R 2010 *Appl. Phys. Lett.* **96** 061102

[2] Kim K S, Kim J H, Jung S J, Park Y J and Cho S N 2010 *Appl. Phys. Lett.* **96** 091104

[3] Bayram B, Jean C, Stefan E, Romain Q and Ekmel O 2007 *Photon. Nanostruct.* **5** 86

[4] Serkan B, Mutlu G, HongBo Y and Ekmel O 2006 *Appl. Phys. Lett.* **89** 073503

[5] Zhang W, Hao Q Y, Liu C C and Feng Y C 2008 *J. Alloys Compd.* **456** 368

[6] Huang X H, Liu J P, Fan Y M, Kong J J, Yang H and Wang H B 2012 *Chin. Phys.* B **21** 037105

[7] Weng X, Raghavan S, Acord J D, Jain A, Dickey E C and Redwing J M 2007 *J. Cryst. Growth* **300** 217

[8] Dadgar A, Veit P, Schulze F, Bläsing J, Krtschil A, Witte H, Diez A, Hempel T, Christen J, Clos R and Krost A 2007 *Thin Solid Films* **515** 4356

[9] Liu Z, Wang X L, Wang J X, Hu G X, Guo L C, Li J P, Li J M and Zeng Y P 2007 *J. Cryst. Growth* **298** 281

[10] Xiong J J, Tang J J, Liang T, Wang Y, Xue C Y, Shi W L and Zhang W D 2010 *Appl. Surf. Sci.* **257** 1161

[11] Xue X Y, Xu S R, Zhang J C, Lin Z Y, Ma J C, Liu Z Y, Xue J S and Hao Y 2012 *Chin. Phys.* B **21** 027803

[12] Peng D S, Feng Y C and Niu H B 2009 *J. Alloys Compd.* **476** 629

[13] Dobos L, Pécz B, Tóth L, Horváth Z J, Horváth Z E, Beaumont B and Bougrioua Z 2008 *Vacuum* **82** 794

[14] Pan X, Wei M, Yang C B, Xiao H L, Wang C M and Wang X L 2011 *J. Cryst. Growth* **318** 464

[15] Kucheye S O, Bradby J E, Williams J S and Jagadish C 2000 *Appl. Phys. Lett.* **77** 3373

[16] Dadgar A, Schulze F, Zettler T, Haberland K, Clos R, Straßburger G, Bläsing J, Diez A and Krost A 2004 *J. Cryst. Growth* **272** 72

[17] Polian A, Grimsditch M and Grzegory I 1996 *J. Appl. Phys.* **79** 3343

[18] Gleize J, Demangeot F, Frandon J, Renucci M A, Widmann F and Daudin B 1999 *Appl. Phys. Lett.* **74** 703