



Synthesis and characterization of heteroepitaxial GaN films on Si(111)

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ABSTRACT

We report crack-free and single-crystalline wurtzite GaN heteroepitaxy layers have been grown on Si (111) substrate by metal-organic chemical vapor deposition(MOCVD). Synthesized GaN epilayer was 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 XRD ω -scans showed a full width at half maximum (FWHM) of around 583 arcsec for GaN grown on Si substrate with an HT-AlN buffer layer. In addition, the Raman peaks of E_2^{high} and $A_1(\text{LO})$ phonon mode in GaN films have an obvious redshift comparing to bulk GaN eigen-frequency, which most likely due to tensile strain in GaN layers. But the AO phonon mode of Si has a blueshift which shows that the Si substrate suffered a compressive strain. And we report that the AlN buffer layer plays a role for releasing the residual stress in GaN films.

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1. Introduction

GaN, the representative of the III–V generation semiconductor, which has a direct and wide band gap, possesses many excellent properties, such as mechanical functions, heat and chemical stability, strong atomic-bond, high thermal conductivity and better resistance to radiation and corrosion[1–6]. Recently, GaN is the preferred material to make devices such as high-temperature devices, anti-radiation devices, etc[7–10]. Piezoelectric and spontaneous polarizations in strained AlGaIn/GaN hetero-structure induce two-dimensional electron gas (2DEG) at the AlGaIn/GaN hetero-interface which is extremely sensitive to stress. But only a few basic studies have been published in respect to AlGaIn/GaN hetero-structure based MEMS devices which can work in the nuclear reactors, drilling bits, turbines engines, interplanetary exploration or other harsh environments[11–13].

Most of the GaN-based materials and devices are grown on sapphire or SiC substrates due to the lack of high quality native bulk substrates[14]. But sapphire substrates are too stable and difficult to micromachining and SiC substrates are too expensive to fabricate large-area MEMS devices or integrated circuits.

However, with the rapid improvement of Si-micromachining technology, GaN/Si-based MEMS devices have revealed more and more advantages in a broad range of fields[15–18]. In this paper, we

report that GaN epitaxial films on Si(111) with AlN buffer layer were fabricated by MOCVD. This growth method produces a high quality of single-crystalline GaN films at relatively high purity and low cost. So it is probably used for commercial scale production of MEMS devices or integrated circuit(IC) chips based GaN/Si.

2. Experimental procedure

A 1.5 μm -thick Si-doped GaN epilayer was grown on Si (111) substrate by MOCVD in the 13th Research Institute of CETC. The MOCVD system is Aixtron 200/4 HT-S. At the beginning of fabricating n-type GaN epilayer, cleaned the Si substrate as the following steps: (1)Washed Si substrate in an ultrasonic bath of acetone and then rinsed with deionized (DI) water for 5–10 min (to remove the organics on the surface). (2)Putted the Si substrate into H_2SO_4 : HNO_3 mixing solutions at 90 °C (to remove heavy metals). (3)Immersed the Si substrate in HCl : H_2O_2 : H_2O (5:3:3) mixing solutions at 70 °C for oxidation about 5 min. At last, then soaked the Si substrate in HF : H_2O (1:10) solutions for 2 min (to remove oxides) and rinsed with DI water for 5–10 min.

Then using trimethyl gallium (TMGa), trimethyl aluminum (TMAI) and ammonia (NH_3), respectively, as sources of Ga, Al and N, using H_2 and N_2 as the carrier gas during AlN and GaN growth, and maintain the gas pressure in reaction chamber at 2×10^4 Pa. The growth of GaN epitaxial films has three steps: firstly, growing AlN films about 60 nm on Si substrate at 950 °C as buffer layer; then, Si-doped GaN films with dopant concentration of about $1 \times 10^{19} \text{ cm}^{-3}$

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Fig. 1. Schematic view of GaN/Si(111) with the HT-AlN buffer layer.

was grown on AlN buffer layer at 1100 °C; lastly, annealing the sample in N₂ ambient at 650 °C for 20 min. Fig. 1 is schematic diagram of our sample.

The surface morphology of our sample was investigated by optical microscopy, scanning electron microscope (SEM, Model No S-320) and contact-mode atomic force microscopy (AFM, Model No 5500 of Benyuan GZ.)[19]. The crystalline orientation of the layers and the quality of GaN epilayer have been analyzed by X-ray diffraction (XRD) measurements using a Bruker D-8AVANCE diffractometer system which uses Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$)[20]. Raman spectroscopy (RENISHAW inVia) was carried out with 30-mW Ar + green light ($\lambda = 514 \text{ nm}$) laser as an excitation source [21].

The experimental steps were as follows.

Washing samples with acetone and ethanol, and dried them with high-purity nitrogen (N₂). At the beginning, observing the

sample under SEM and AFM. Then using XRD which set the scanning step was 0.02°/s and the range of intensity was 30 W to detect our sample. Finally, putting our sample in the laser Raman spectrometer with the exposure time of 30 s and the grating of 1800 l/mm(vis) for testing residual stress.

3. Results and discussion

3.1. Morphology observation

The surface morphologies of the samples were studied by optical microscopy. Fig. 2(a)–(c) show the microscopy photographs of our sample from edge to center at the magnification of 50 times. These figures show a nearly crack-free surface was achieved on sample with a 60 nm HT-AlN buffer layers GaN grown on the silicon substrate. Cracks in GaN on Si are known to be formed during the cooling stage due to a large tensile stress that is caused by the large difference in the thermal expansion coefficients. These indicate that it is successful to grow crack-free GaN films by using above process.

Fig. 3 shows the cross-sectional SEM image of our sample observed at the magnification of 2000 times. The sample is composed of GaN film and Si substrate, and the GaN films can be observed clearly with about 1.5- μm -thick in Fig. 3. And from Fig. 2 we find that the stress exists in the GaN epilayers and Si substrates, but it would be the greatest near the epilayers–substrate interface between GaN and Si for which the cross-section of Si substrates will gradually be plainness away from the epilayers–substrate interface.

Fig. 4 shows the two-dimensional(2D) surface roughness and three-dimensional(3D) morphology characteristics images of GaN epitaxial films in an area of 8.6 $\mu\text{m} \times 8.6 \mu\text{m}$. Using the software of

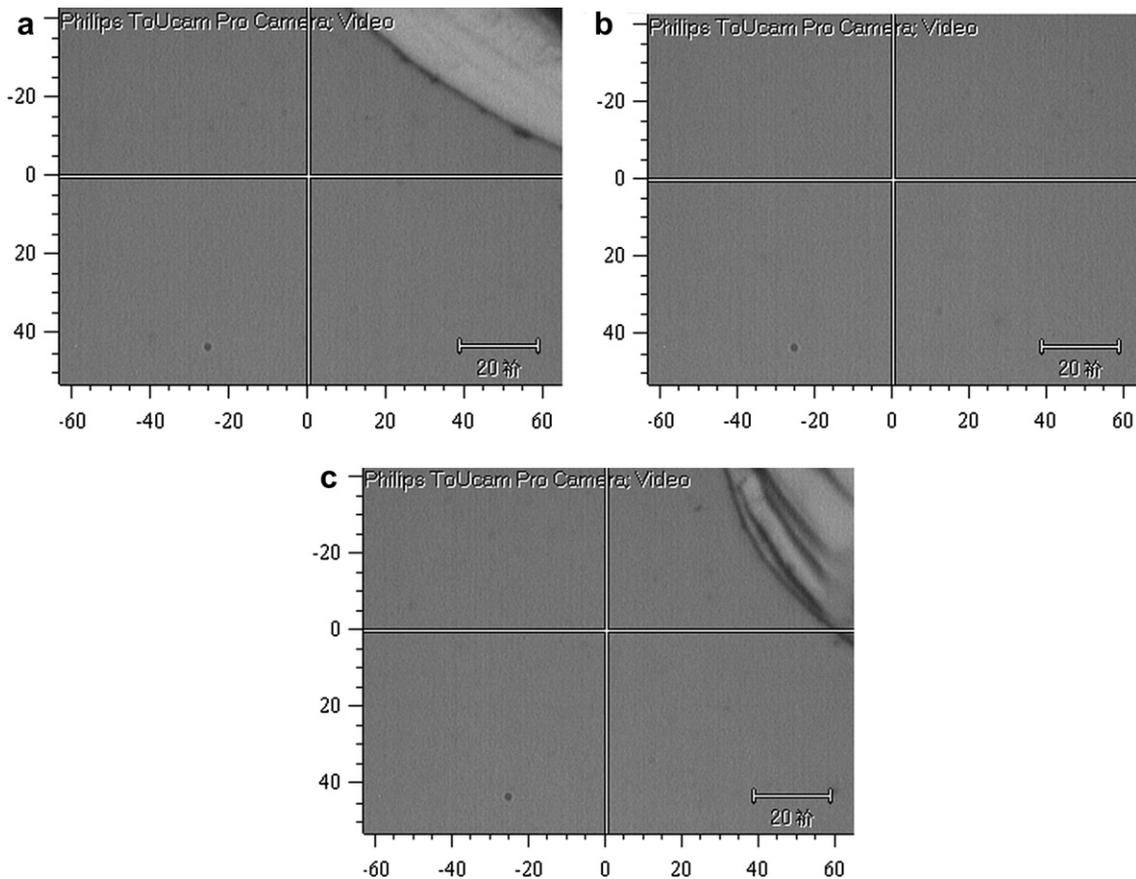


Fig. 2. Optical microscopy views of sample, (a) and (c) are in the edge, (b) is in the center.

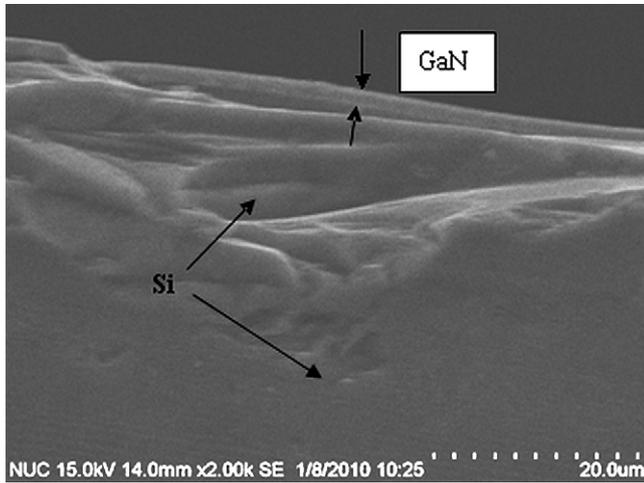


Fig. 3. The cross-sectional SEM image of the sample.

CSPM Imager 4.60 for data processing and surface roughness analysis, (1) We observed that the GaN epilayers growth on Si substrate with a AlN buffer layer are very flat and smooth on the surface, and the steps are not clear, which indicates that the quality of GaN films is excellent. (2) According to the surface roughness analysis of GaN epitaxial films, we can obtain that the surface roughness (Ra) reach 0.75 nm, the surface slope is 1.54 and the maximum peak-to-valley is 100 nm. These results demonstrated that it is possible to grow high-quality GaN film on Si by MOCVD.

3.2. Composition and phase analysis

XRD was performed for all the samples to investigate the crystal phase of the GaN on Si (111). According to Fig. 5(a), three strong peaks are found attributed to Si(111) at a 2θ angle of 28.76° , GaN(0002) at an angle of 34.86° and GaN(0004) at an angle of 73.14° according to JCPDS PDF. NO.52-0791, respectively [22,23]. No diffraction peaks of C-GaN or other impurities are found in any of our sample, suggesting that the GaN epilayers is the single wurtzite GaN phase. These results of XRD spectrum suggest that the GaN films were grown with a highly preferred orientation along the $\langle 0001 \rangle$ direction.

An XRD ω -scan of the (0002) reflection for a 1.5 μm -thick GaN layer grown at high temperature directly on an HT-AlN buffer layer is shown in Fig. 5(b). The linewidth of the (0002) reflection is

around 583 arcsec. Ref. [24] have reported that the symmetric (0002) reflection is notably sensitive to the presence of dislocations with screw component and the minimal width achieved is around 600 arcsec for growth temperatures above 1100 $^\circ\text{C}$. But our sample's value is less approximate 17 arcsec than Ref. [24] vales for GaN on Si. These values are comparable with other literature vales for GaN on Si [25,26]. In summary, growth of a high temperature GaN epitaxial films directly on the HT-AlN buffer layer led to a significant improvement in both crystal quality and surface morphology.

3.3. Raman spectrum analysis

Laser Raman scattering spectrum can provide informations of the molecular vibration of GaN, and the spectrum is sensitive to the microscopic disorder and residual stress in materials. According to the shapes and selection rules of the vibration band, Raman spectrum can be used to measured the material crystallinity. GaN normally has a wurtzite structure, with the space group of P63mc(no.186), in which all atoms occupy the position of C3v. 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. According to the analysis of the group theory shows that the optical phonons as:

$$\Gamma_{\text{opt}} = A_1(z) + 2B_1 + E_1(x,y) + 2E_2 \quad (1)$$

Here, x, y, z express the orientation of the polarization of phonons. In the case of H-GaN, A_1 mode is Raman activity and E_1 mode is infrared activity, respectively, two modes of E_2 are only Raman activity and two modes of B are both Raman and infrared inactivity. The peaks are as follows: $A_1(\text{TO}) = 533 \text{ cm}^{-1}$, $E_1(\text{TO}) = 559 \text{ cm}^{-1}$, $A_1(\text{LO}) = 736 \text{ cm}^{-1}$, $E_1(\text{LO}) = 743 \text{ cm}^{-1}$ and $E_2^{\text{high}} = 568 \text{ cm}^{-1}$ and $E_2(\text{low}) = 145 \text{ cm}^{-1}$ [27,28].

Fig. 6 shows the Raman spectrum of three samples fabricated under the same conditions. Fig. 6(a) shows that the intensities of all these Raman peaks observed from GaN films are normalized. The peaks of $500\text{--}800 \text{ cm}^{-1}$ results from the superposition of three normalized peaks of Si(AO), E_2^{high} and $A_1(\text{LO})$ of GaN, respectively. GaN epilayer is transparent to the green light, so we can see the Raman peak of Si in Fig. 6(a). The Raman peak of E_2^{high} mode indicates the GaN films has a hexagonal wurtzite structure. Moreover, in the Raman spectrum of GaN thin films we found no peaks belonging to the spectrum of the bulk C-GaN which shows that the epitaxial films are pure hexagonal wurtzite structure GaN [29].

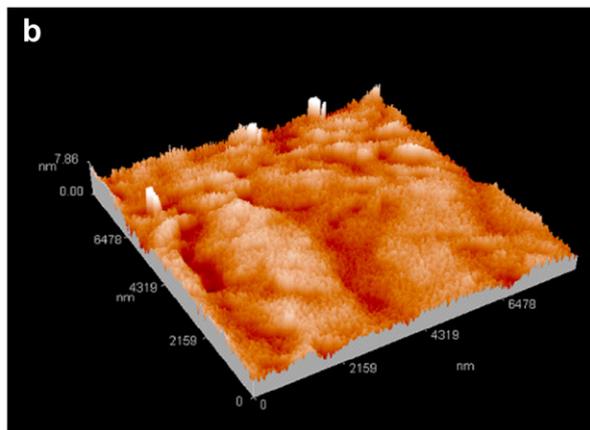
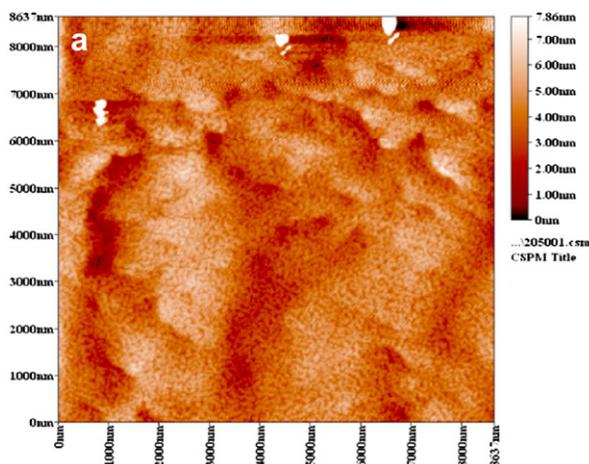


Fig. 4. 2D surface(a) and 3D morpholog feature (b) images by AFM.

properties, which is obviously advantageous for the applications of integrated circuit(IC) chips.

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