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The Influence of Graded AlGaN Buffer Thickness for Crack-Free GaN on Si(111) Substrates by using MOCVD *

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GaN films with different thicknesses of Al composition graded AlGaN buffer are grown on substrates of Si(111) by metal-organic chemical vapor deposition (MOCVD). The thicknesses of graded AlGaN buffer are fixed at 200 nm, 300 nm, and 450 nm, respectively. Optical microscopy, atomic force microscopy, x-ray diffraction, and Raman spectroscopy are employed to characterize these samples. We find that the thickness of the graded AlGaN buffer layer plays a key role on the following growth of GaN films. The optimized thickness of the graded AlGaN buffer layer is 300 nm. Under such conditions, the GaN epitaxial film is crack-free, and its dislocation density is the lowest.

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Owing to their superior intrinsic properties, GaN-based materials are very promising semiconductor materials for applications in optoelectronic devices, as well as in high power, high frequency and high temperature electronic devices. However, a lack of suitable substrate hampers their application in these fields. Generally, sapphire, SiC and Si are the most used as substrates.[1−3] Due to its low cost, large-size, high electrical, thermal conductivities, and potential applications in optoelectronic integrated circuits, Si has attracted more and more attention for use as a substrate for GaN growth. However, compared with sapphire and SiC, the growth mechanisms of GaN films grown on Si(111) substrates are less well understood. Many groups have attempted to grow crack-free GaN films in the past few decades. Chen *et al.*[4] firstly reported the pre-seeding of Al on the Si surface to suppress the formation of SiN_x. Amano *et al.* introduced thin low-temperature AlN interlayers to improve the surface morphologies and GaN layer quality.[5] Huang *et al.*[6] and Wu-Yih Uena *et al.*[7] used NH_3 flow for Si substrate nitridation. Hageman *et al.*[8] introduced AlN/GaN superlattices (SLs) to grow high quality GaN films. Using a graded AlGaN interlayer is also proved to be an effective method to control the strain in GaN epilayers. It is believed that a graded AlGaN buffer with a small lattice constant can provide the upper GaN layer with compression stress, which is helpful to relieve the tension stress in the GaN layer produced by the Si substrate and thus to eliminate the crack in GaN films. However, only few researchers have studied the influence of the graded AlGaN interlayer thickness, which is found to be quite critical to achieve high quality and crack-free GaN on Si substrates.

In this study, GaN films with graded AlGaN buffers of various thicknesses are grown under the same condition on Si(111), which are labeled as samples A, B, and C. The AlGaN layer thicknesses are 200 nm, 300 nm, and 450 nm, respectively. All the samples are prepared by metal-organic chemical vapor deposition (MOCVD) and characterized by optical microscopy, atomic force microscopy, Raman spectroscopy, and x-ray diffraction (XRD).

GaN epitaxial films were grown on 2-inch Si(111) substrates by MOCVD (Aixtron 2400HT). Trimethylgallium (TMGa), trimethylaluminum (TMAl), and ammonia (NH_3) were used as Ga, Al, and N precursors, respectively. Nitrogen (N_2) and hydrogen (H_2) were used as carrier gases. Firstly, TMAl was introduced for 20 s to avoid the formation of SiN_x. Secondly, a 100-nm–thick AlN buffer was grown at 1010 ℃ under mixed ambient N_2 and H_2. Then under the pressure of 70000 Pa followed by the growth of a graded AlGaN buffer layer, where the flow rates of TMGa and TMAl were gradually varied from 0 to 15 μmol/min and from 100 μmol/min to 0 while NH_3 flow rate was kept at 4000 sccm. Lastly, a 2-μm GaN film was grown under the pressure of 110000 Pa with 30 μmol/min TMGa and 4000 sccm NH_3. An in-situ interferometer was used to estimate the thickness of the graded AlGaN buffer layer.

High-resolution x-ray diffraction (HRXRD) ω and ϕ scans were carried out by using a Bede D1 high resolution XRD device to evaluate the quality of the GaN epitaxial films. Optical microscopy and atomic force microscopy (AFM) were used to characterize GaN surface morphologies. Raman spectroscopy was em-

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ployed to compare the strain states in the GaN layers.

Due to the large mismatches in the lattice parameter (−16.9%) and thermal expansion coefficients (approximately 57%) between the GaN film and Si substrate,[9−11] cracking occurs along the equivalent {1−100} GaN plane during the cooldown stage after the film growth. This fact has been reported by many groups.[12,13] The optical microscopy pictures for the three samples are shown in Fig. 1. The results show that only sample B is crack-free, while cracks can be clearly observed in GaN films for sample A with smaller AlGaN thickness and for sample C with larger AlGaN thickness. From the optical microscopy images, we can note that the cracks of GaN on Si are seriously affected by the thickness of the AlGaN buffer. There is an optimum thickness of the graded AlGaN buffer layer (around 300 nm) for reducing the crack density.

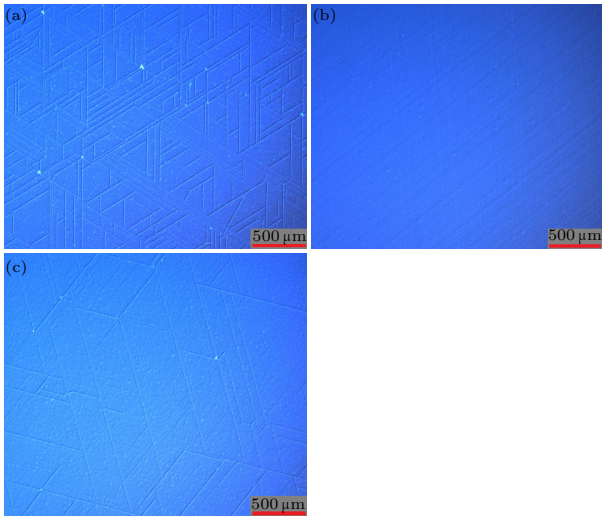


Fig. 1. Optical microscopy views of (a) sample A, (b) sample B, (c) sample C.

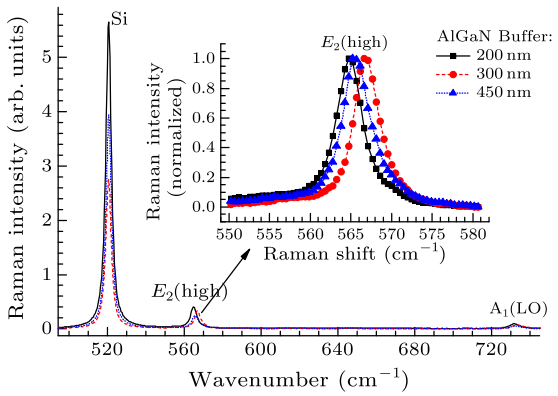


Fig. 2. Raman spectra for the GaN epitaxial layers on Si with different AlGaN buffer layers.

In Raman scattering measurements, the state of stress in GaN layers is analyzed based on the shift of the E_2 phonon mode. As we know, the E_2 mode is sensitive to biaxial stress,[14] and the E_2 mode in bulk GaN is located at 567.6 cm^{-1}.[15] Figure 2 shows the Raman spectra for the GaN epitaxial layers on Si with different AlGaN buffer layers. For samples A, B and C, the E_2 phonon mode for GaN is located at 564.8 cm^{-1}, 566.8 cm^{-1} and 565.5 cm^{-1}, respectively. As is shown, there appears to be 2.8 cm^{-1} shift towards low frequency of E_2 phonon mode occurs in sample A; similarly, 2.1 cm^{-1} shift towards low frequency of E_2 phonon mode in sample C. Therefore, large tensile stress still remains in samples A and C. At the same time, E_2 phonon mode in sample B shows 0.8 cm^{-1} shift towards low frequency. Therefore, there is relatively much less tensile stress in sample B.

Generally, cracks of GaN films on Si substrates occur under biaxial tensile stress, which results from the large difference in the thermal expansion coefficients between GaN and Si. From the Raman results, the graded AlGaN buffer layer with the optimum thickness has the smallest biaxial tensile stress. There are two reasons for this fact. One of the reasons is that, when the thickness of AlGaN buffer is smaller than the optimum thickness, the islands have not completely coalesced and the crystalline quality is poor. The initial GaN growth on such a rough surface may follow a 3D growth mode and release the compression stress. Consequently the AlGaN buffer has little influence on the thermal stress of the latter GaN epilayer. On the other hand, if the thickness of the AlGaN buffer is larger than the optimum thickness, the AlGaN buffer would relax due to the lattice mismatch between AlN and GaN. It also has little influence on the thermal stress of the latter GaN epilayer.

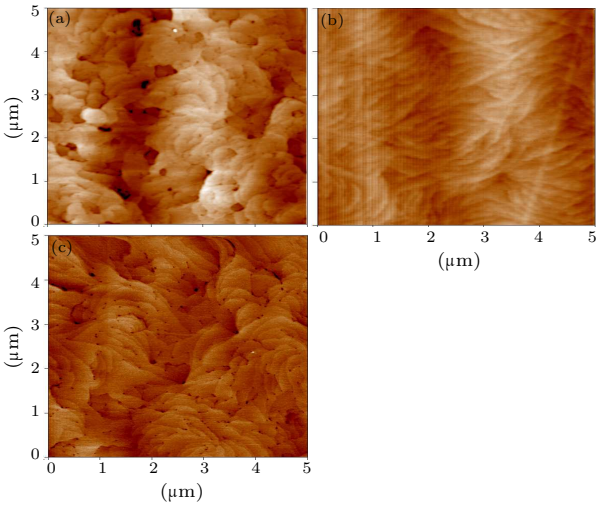


Fig. 3. The AFM of (a) sample A, (b) sample B, and (c) sample C.

As shown in Fig. 3, the surface morphology of the GaN layers was investigated by AFM. The samples were scanned on an area of 5 × 5 μm^2 and the rms roughnesses of samples A, B, and C are 0.700 nm, 0.353 nm, and 0.614 nm, respectively. Sample B shows

a smoother surface than A and C. In addition, samples A and C have more defects, such as surface pits, which are caused by threading dislocations.[16]

The high-resolution XRD ω and ϕ scans were performed to evaluate the dislocation density of the GaN epitaxial films. The GaN (002), (004) and (006) crystal faces were measured to calculate the screw dislocation density of GaN films. Meanwhile, the GaN (121) crystal face was also measured in order to calculate the edge dislocation density.

The (002), (004), (006) crystal faces of the three samples were measured in ω scans and their full width at half maximum (FWHM) values are listed in Table 1.

Applied to the (002), (004) and (006) scans, the lateral correlation length $L_{||}$ and the tilt angle $\alpha_{\rm tilt}$ were determined from a plot analogous to Williamson–Hall plot. In the Williamson–Hall plot method theory, the a following formula is used to calculate the parameter $\alpha_{\rm tilt}$,[17,18]

$$\alpha_\omega^2\left(\frac{2\sin\theta}{\lambda}\right)^2 = \alpha_{\rm tilt}^2\left(\frac{2\sin\theta}{\lambda}\right)^2 + \frac{H^2}{L_{||}^2}, \qquad (1)$$

where α_ω is the FWHM in angular unit, $\alpha_{\rm tilt}$ is the tilt angle; θ is the Bragg reflection angle; λ is the x-ray wavelength; $H{\approx}0.51$ is related to the almost cylindrical shape of GaN columns, and $L_{||}$ is the coherence length parallel to the substrate surface.

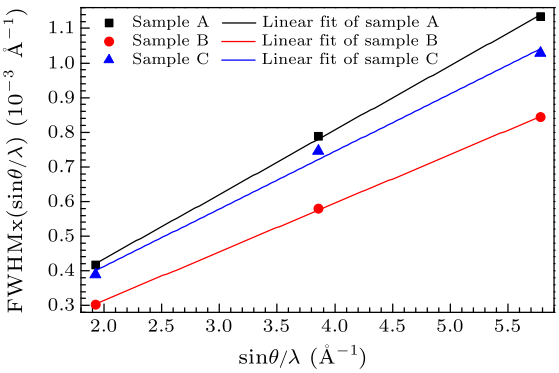


Fig. 4. Williamson–Hall plot for GaN layers for all the samples. Triple-axis ω scan was measured for the (00l) ($l = 2, 4, 6$) reflections. The lines result from a linear fit of the data.

Figure 4 shows the W–H plots for (00l) ω scans. The straight lines are linear fits of the experimental data. From the y-intersection ($y_0 = H^2/L_{||}^2$) of the fitted line, we can estimate the lateral correlation length $L_{||}$. The $L_{||}$ values of samples A, B, and C are 205 nm, 279 nm, and 179 nm, respectively. Here $\alpha_{\rm tilt}$ is obtained from the slope of the liner dependence. The $\alpha_{\rm tilt}$ data of samples A, B, and C are 0.18612°, 0.14042° and 0.16598°, respectively. According to the formula[19–22]

$$N_{\rm s} = \frac{\alpha_{\rm tilt}^2}{4.35|\boldsymbol{b}_c|^2}, \qquad (2)$$

where $N_{\rm s}$ is the screw dislocation density and $|\boldsymbol{b}_c| = 0.5185$ nm.

We can calculate the screw dislocation of the three samples as follows: for sample A, $N_{\rm s} = 8.7\times10^8\,{\rm cm}^{-2}$; for ample B, $N_{\rm s} = 4.9\times10^8\,{\rm cm}^{-2}$; for ample C, $N_{\rm s} = 7.2\times10^8\,{\rm cm}^{-2}$.

In the (121) reflection, when the inclination angle is at 78.6°, the FWHM of ω scan and ϕ scans are almost equal. The twist angles $\alpha_{\rm twist}$ can be taken as the average of the FWHM of ω scan and ϕ scans of $\chi = 78.6°$.[23,24] Therefore, we can calculate the edge dislocation by the formula[19–22]

$$N_{\rm e} = \frac{\alpha_{\rm twist}^2}{4.35\times|\boldsymbol{b}_{\rm e}|^2}, \qquad (3)$$

where ($N_{\rm e}$ is the edge dislocation density $|\boldsymbol{b}_{\rm e}| = 0.3189$ nm)

From the calculation of the dislocation density, sample B with the optimal thickness of graded AlGaN interlayer has a much lower dislocation density than the other two samples.

As mentioned above, the stress state of the graded AlGaN buffer layer is a critical factor affecting whether the GaN film cracks or not. It would be expected that the stress state can be eliminated completely by optimizing the V/Ⅲ ratio, growth pressure, growth rate or H_2/N_2 ratio of AlGaN buffer. On the other hand, we can also introduce superlattices, LT–AlN interlayer and a PSS substrate to further improve the stress state and the crystalline quality.

In conclusion, we have investigated the influence of AlGaN buffer layer thickness on the characteristics of GaN epitaxial films grown on Si(111) substrate. Optical microscopy and AFM are employed to study the surface morphology, and the GaN film is crack-free when the thickness of the AlGaN buffer is 300 nm (sample B). From the Raman spectra, sample B also has the smallest tensile stress. The FWHM of the symmetrical and asymmetrical facets are both measured, and the screw and edge dislocation density are calculated. Sample B has the best results, its screw dislocation density is $4.9\times10^8\,{\rm cm}^{-2}$, and its edge dislocation density is $7.0\times10^9\,{\rm cm}^{-2}$. All these comparisons indicate that the thickness of the graded AlGaN buffer is one of the critical parameters in GaN growth on silicon substrates. There is an optimum thickness of the graded AlGaN interlayer (300 nm) to achieve crack-free GaN films with superior crystal quality.

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