# Influence of double AlN buffer layers on the qualities of GaN films prepared by metal–organic chemical vapour deposition*

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In this paper we report that the GaN thin film is grown by metal–organic chemical vapour deposition on a sapphire (0001) substrate with double AlN buffer layers. The buffer layer consists of a low-temperature (LT) AlN layer and a high-temperature (HT) AlN layer that are grown at 600 °C and 1000 °C, respectively. It is observed that the thickness of the LT-AlN layer drastically influences the quality of GaN thin film, and that the optimized 4.25-min-LT-AlN layer minimizes the dislocation density of GaN thin film. The reason for the improved properties is discussed in this paper.

**Keywords:** GaN, AlN buffer layer, metal–organic chemical vapour deposition, threading dislocations

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## 1. Introduction

The achievement of GaN-based light-emitting diodes (LEDs) has basically caused a revolution in LED technology and opened up economically a new market that was previously inaccessible. Owing to difficulty in fabricating bulk GaN, nearly all GaN films are heteroepitaxially grown on lattice mismatched substrates, sapphires, for example. Because of the lattice constant mismatch and the difference in thermal expansion coefficient between GaN and sapphire substrate, threading dislocations (TDs) occur greatly in GaN ($10^8$ cm$^{-2}$–$10^{12}$ cm$^{-2}$).[1] For reducing the number of TDs, typically, a thin buffer layer of GaN or AlN is used, which, however, can reduce the interfacial energy between the main GaN layer and the substrate as reported in Ref. [2]. Although the growth condition and influence of buffer layers have been extensively studied,[3−11] there are few reports dealing with the buffer layer which grows in combined conditions, such as LT and HT.[12] Since different growth conditions can give rise to different influences on the performance of GaN, the combined-condition-buffer-layer may be able to eliminate the TDs and so improve the quality of GaN.

In this paper, we study the influence of double AlN buffer layers on crystal quality, morphology and stress of GaN grown by metal–organic chemical vapour deposition (MOCVD). Double AlN buffer layers consist of an LT-AlN buffer layer and an HT-AlN buffer layer, whose growth temperatures are 600 °C and 1000 °C, respectively. It is found that the thickness of the LT-AlN layer has a huge effect on the quality of GaN thin film, and that the optimized LT-AlN layer with a growth time of 4.25 min minimizes the density of TDs in the GaN thin film.

## 2. Experimental procedure

GaN thin film was grown on a *c*-plane sapphire substrate in a home-made MOCVD system. Hydrogen was used as carrier gas and triethylgallium (TEG), trimethylaluminum (TMA), and ammonia ($NH_3$) were used as Ga, Al, and N source compounds, respectively. Prior to the epitaxial growth, the sapphire substrate

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was annealed at 1000 °C. For the GaN thin film with double AlN buffer layers, a thin LT-AlN buffer layer was initially grown at 600 °C using flow rates of TMAl and $NH_3$ of 5 sccm and 1000 sccm, respectively, and the growth rate was estimated to be 0.625 nm/min. The growth times of the LT-AlN buffer layers were 2.5 min, 3.5 min, 4 min, 4.25 min, 4.5 min, and 5.5 min, respectively, and the thickness values of the LT-AlN buffer layers were 1.56 nm, 2.19 nm, 2.50 nm, 2.66 nm, 2.81 nm, and 3.43 nm, respectively. Then a 150-nm thick HT-AlN buffer layer was formed at 1000 °C for 40 min. The flow rates of TMA and $NH_3$ were 30 sccm and 300 sccm respectively. After the double AlN buffer layers were formed, a 1.3-μm GaN layer was grown at 950 °C. For comparison, conventional GaN thin film without an LT-AlN buffer layer with a similar HT-AlN buffer layer was grown under identical growth conditions. Figure 1 shows the schematic diagrams of GaN thin films without and with LT-AlN buffer layers.

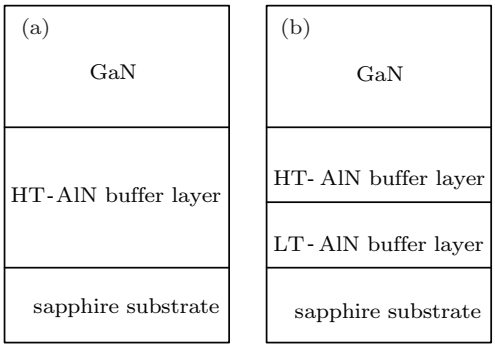



**Fig. 1.** Schematic diagrams of GaN films (a) without and (b) with LT-AlN buffer layers.

The structural quality of the sample was determined by high resolution X-ray diffraction (HRXRD) using a D8/Bruker diffractometer, equipped with a Cu source and a Ge (022) monochromator, which consists of a four-reflection channel-cut (220) oriented Ge crystal in the (+n, −n, −n, +n) mode. Atomic force microscopy (AFM) images were taken with an Agilent 5400 3100 instrument in tapping mode. The root-mean-square (RMS) surface roughness was calculated using the AFM software. The micro-Raman measurement was carried out in backscattering geometry with the Raman spectrometer Jobin Yvon LavRam HR800 for investigating the strain state of the sample. An argon laser of 514-nm wavelength was used as an excitation light source and a 50× objective was used to focus the incident laser light of a power of 14.2 mW on the sample.

## 3. Results and discussion

The structural properties of the 1.3-μm-thick GaN films were examined by HRXRD recording the on-axis symmetric and off-axis symmetric skew XRD rocking curves. Whereas the full width at half maximum (FWHM) of the symmetric (002) rocking curve correlates with the number of threading dislocations (TDs) with screw component, the off-axis (102) measured in a skew symmetric geometry is sensitive to the presence of pure edge TDs in the sample.[13] As seen in Fig. 2, the FWHMs of GaN films without an LT-AlN buffer layer at the (002) and (102) diffraction peaks are 362 arcsec and 770 arcsec, respectively. The FWHM of the (002) diffraction peak first decreases to about 100 arcsec when an LT-AlN buffer layer is adopted, which suggests that the LT-AlN buffer layer can reduce the density of screw TDs markedly, and then increases to 220 arcsec as the LT-AlN growth time increases to 5.5 min. On the other hand, the FWHM of the (102) diffraction peak is the lowest for the sample with the 4.25-min LT-AlN buffer layer, implying that the density of pure edge TDs is sensitive to the thickness of the LT-AlN buffer layer.

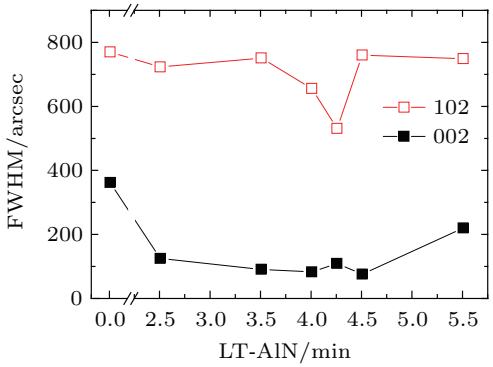



**Fig. 2.** (colour online) FWHMs of the HRXRD rocking curves measured for the (002) and (102) diffraction peaks of 1.3-μm-thick GaN films grown on HT-AlN buffer layers with different LT-AlN buffer layers.

The AFM images taken from the GaN layers with 0 min, 4.25 min, and 4.5 min LT-AlN buffer layers (denoted as samples A, B, and C, respectively) are shown in Fig. 3. The RMS values are calculated using the AFM software to be 0.32, 0.24, and 0.27 nm for sample A, B, and C, respectively. For sample B, the growth steps are clear and the surface is quite smooth, while the surfaces of samples A and C are rough and the growth steps are interrupted by surface undulation. Clear steps demonstrate the 2D growth mode in sample B, which is helpful for wiping out TDs in GaN

material. The surface undulations of samples A and C are caused by the degradation of GaN material, which is consistent with the result of HRXRD measurement.

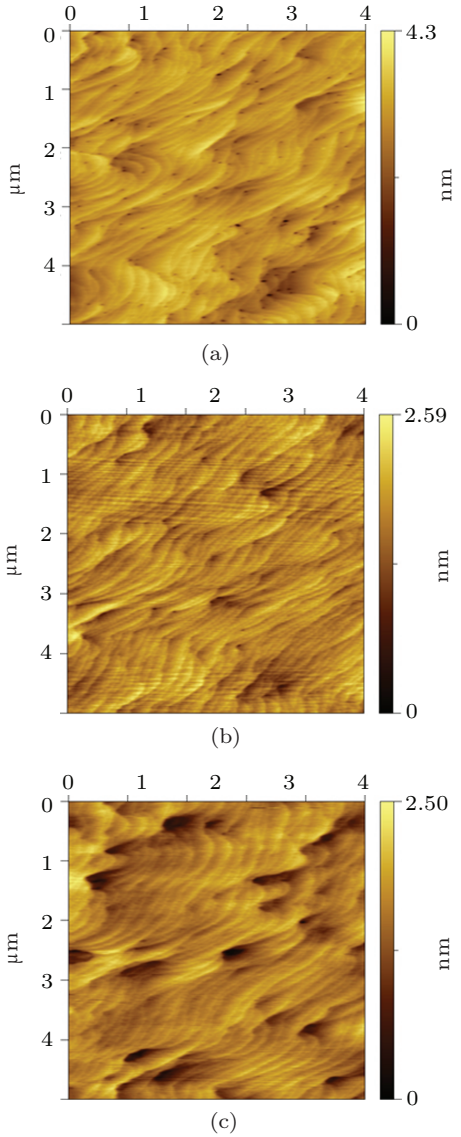



**Fig. 3.** (colour online) AFM images of the surfaces for GaN samples with 0 min (A) / 4.25 min (B) / 4.5 min (C) LT-AlN buffer layers, respectively.

There is evidence to show that the generation of film stress as a natural consequence of epitaxial constraint is due to the mismatch between the lattice parameters of a thin film and those of its substrate, and the stress associated with the elastic strain acts as a driving force for the formation and growth of structural defects, TDs.[14] From this point of view, it is necessary to investigate the strain states of GaN thin films. The Raman spectra of samples A, B, and C are shown in Fig. 4. With the increase of LT-AlN buffer layer thickness, Samples A, B, and C present blue shifts of the GaN E2 (high) mode of 4.1, 4.5, and 2.9 $cm^{-1}$, respectively, relative to the intrinsic value of 567.2 $cm^{-1}$.[15] The blue shift of the GaN E2 (high) mode corresponds to the compressive stress in GaN film, which is caused by differences in the thermal expansion coefficient and lattice mismatch between the film and the sapphire substrate.[16] On the other hand, the E2 (high) values of AlN for samples A, B, and C are 648.1, 643.4, and 645.0 $cm^{-1}$ respectively, implying that all the AlN of the samples are under tensile stress, as the intrinsic value of E2 (high) value of AlN is 657.4 $cm^{-1}$.[17] Considering that the lattice constant, $a$ of AlN (0.3112 nm) is smaller than that of GaN (0.3189 nm), the tensile stress might result from the lattice mismatch between AlN and GaN epilayers. The intensity of A1 (TO) peak of GaN (around 562 $cm^{-1}$) is strongest for sample A, meaning that the angle included between incident light and $c$ axis of GaN in sample A is biggest. This coincides with the theory proposed by Ning *et al.*[18] that edge dislocations arise from the coalescence of islands with different numbers of twist and screw dislocations resulting from coalescence of islands that are tilted, which is confirmed by the result of HRXRD measurement.

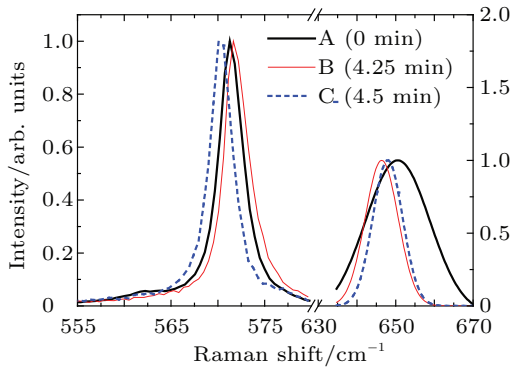



**Fig. 4.** (colour online) Raman spectra of the E2 (high) phonon mode of GaN and AlN for samples A, B, and C respectively.

It was reported that the higher the temperature, the longer the migration length of the adatom would be.[19] With the LT-AlN buffer layer, the migration ability of the Al adatom is weak, and V/III ratio is high, leading to three-dimensional (3D) growth mode. Re-evaporation could not take place at lower temperatures,[20] so the longer the growth time of the LT-AlN, the larger the size of the AlN nucleation island is.

During the growth of the HT-AlN buffer layer, the migration ability of the Al adatom is enhanced due to high temperature and low V/III ratio, which leads

to two-dimensional (2D) growth mode. The change from 3D mode to 2D mode gives rise to the bending of TDs, thus reducing the density of TDs as seen in Fig. 5. This is the reason why the density of TDs is smaller in sample B than that in sample A. At high temperatures, the effect of re-evaporation is strengthened. Based on the ripening theory of crystal growth, the local equilibrium vapour pressure around small islands is higher than that around large islands. The concentration gradient between different islands results in lateral evaporation from small islands to large ones, which is in favour of forming larger islands.[21] Therefore, the growth rate of larger islands is much faster than that of smaller ones at high temperatures. As the growth time of the LT-AlN buffer layer becomes longer, the size of larger islands increases, the size difference between larger islands and smaller ones increases, and the difference in growth rate between larger islands and smaller ones is enhanced. If the growth time of LT-AlN is too long, some of the AlN nucleation islands become too large to impede the growth of small islands. In consequence, the number of AlN nucleation islands declines sharply and the gap between them is too huge to be filled in. The coalescence of HT-AlN is not completely realized, so the surface of the AlN buffer layer is rough while the strain in it is small. The rough surface of AlN is detrimental to the growth of GaN, and the quality of GaN film becomes degenerate as the density of TDs increases and the stress relaxation appears. This is the reason why the density of TDs is bigger in sample C than that in sample B. The measurement results of HRXRD, AFM, and Raman support the above explanations.

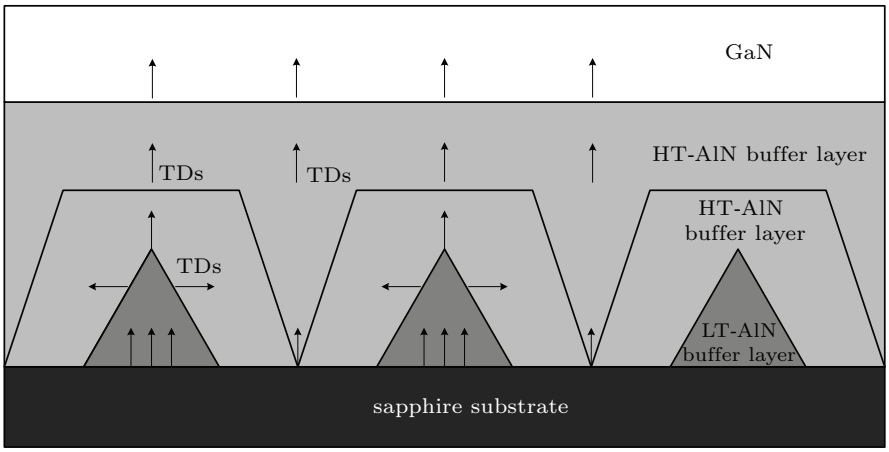



**Fig. 5.** (colour online) Schematic diagram of TD bending due to the change of AlN buffer layer growth mode from 3D case to 2D case.

Compared with on sapphire substrates, GaN-based devices on SiC substrates are very suitable for microwave applications, so it is of importance to control the density of TDs in GaN on SiC substrates. However, the growth of AlN on SiC substrate in a range of 500 °C–1050 °C results only in random polycrystalline material. Subsequently deposited GaN films are also polycrystalline.[22] Therefore, only an HT-AlN buffer layer can be adopted during the growth of GaN on SiC substrates, which means that the growth mode of the AlN buffer layer cannot be adjusted by changing the growth temperature. In order to realize the growth mode of AlN on SiC substrate, the growth parameters such as V/III ratio and the pressure of the chamber should be designed carefully, which requires further investigation.

# 4. Conclusion

In this paper, the thickness of the LT-AlN layer has a great influence on the quality of GaN thin film with double AlN buffer layers, which is confirmed by both HRXRD measurements and AFM ones. The optimized 4.25-min-LT-AlN layer minimizes the dislocation density of GaN thin film. The change from LT-AlN to HT-AlN brings about the bending of TDs, which is responsible for the improvement of GaN thin films' quality.

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