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Formation of AlN and GaN nanocolumns on Si(111) using molecular beam epitaxy with ammonia as a nitrogen source*

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We have demonstrated growth of AlN and GaN nanocolumns using molecular beam epitaxy with ammonia as a nitrogen source. The appearance of the columnar structure is correlated with the use of a low-temperature AlN buffer layer, grown at about 650 ºC. Field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) indicate that the column diameters range from 12 to 30 nm. Layers were grown on Si(111) substrates with a variety of AlN buffer layer growth conditions. The AlN columns are distinct though tightly packed, and the tips of the columns are separated. Large, platelet-like protrusions are observed for low growth temperatures. Results from X-ray diffraction (XRD) and low-temperature photoluminescence (PL) are also discussed.

1 Introduction

In this paper we show that the AlN buffer layer growth conditions have a strong influence on the growth morphology of subsequent GaN layers for ammonia-source molecular beam epitaxial growth on Si (111) substrates. AlN is widely used as a buffer layer for growth of group III nitrides on Si because it aids in preventing reactions between the Si and Ga [1–3] and also helps relieve strain [4]. Our observations of both AlN buffer layers and GaN/AlN layered structures indicate that nanocolumn formation is dominant when the AlN buffer layer is grown near 650 °C. Changes in specimen morphology for growth at higher and lower temperatures appear to be related to increased surface atom mobility and less effective ammonia decomposition, respectively.

2 Experimental details

The epitaxial layers examined in this study were grown by gas-source molecular beam epitaxy (MBE) using ammonia as a nitrogen source. Growth temperatures were measured with an estimated uncertainty of 5 °C using an optical pyrometer set for the emissivity of the Si substrate. The substrates for this experiment were prime grade silicon wafers with (111) ± 0.5° orientation. They were prepared for growth by etching in 10% HF:H_2O solution for 3 min, rinsing about 1 min in deionized water, and blowing dry. The wafers were loaded and placed under vacuum within 5 min of the final rinse. The wafers were also heated in a preparation chamber to approximately 750 °C before transfer into the growth chamber. The bare Si surface produced a reflection high-energy electron diffraction (RHEED) pattern with strong streaks with a 1 x 1 reconstruction pattern. The 7 x 7 reconstruction was not observed, possibly because of the presence of As in the growth chamber from previous GaAs growths. The Al beam equivalent pressures for the buffer layers in Figs. 2 and 3 were from 8 to 9 x 10^{-6} Pa, which yielded a growth rate of 0.03 nm/s.

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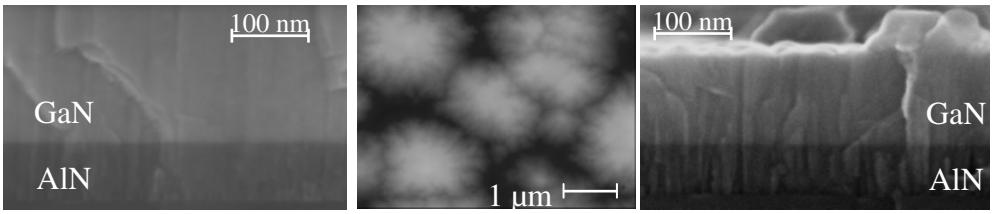

Fig. 1 FESEM edge-view and AFM surface images of GaN layers grown on AlN buffer layers. The AlN on the left was grown at 766 °C, resulting in the GaN surface illustrated in the center AFM image (grey scale corresponding to a 30 nm range in feature height). The AlN layer on the right was grown at 650 °C, resulting in nanocolumn formation that persists through to the GaN surface.

As in previous work, [5, 6] the AlN layers were initiated with a thin layer (0.3 to 0.5 nm) of pure Al before the surface was exposed to ammonia and AlN growth began.

The ammonia was injected into the chamber through a ceramic tube heated slightly (around 300 °C) to avoid condensation. The total flow rate of ammonia was 2.8 μmole/s (4.0 sccm) for specimens depicted in the figures. In order to avoid excessive condensation of ammonia on the MBE cryopanels, the flow of liquid nitrogen was periodically stopped and restarted, introducing some variability in the background pressure of ammonia. The specimens were examined by FESEM with an accelerating voltage of 5 kV, and by AFM in tapping mode. A HeCd laser and liquid helium cryostat were used to acquire PL data.

3 Results

The relationship between the AlN buffer layer morphology and the overlying GaN layers is illustrated above (Fig. 1) for two characteristic regimes of overgrowth. When grown on high-temperature (700 °C to 760 °C) AlN buffer layers, the GaN surface structures consisted of shallow, irregular mesa structures with lateral dimensions of roughly 1 to 2 μm, as shown in the center panel of Fig. 1. When the AlN buffer layer was grown between 600 and 650 °C, nanocolumns formed in the AlN layer that persisted into the overlying GaN. In order to examine this phenomenon further, four single layers of AlN were grown at different temperatures, with the resulting FESEM cross-sections given in Fig. 2.

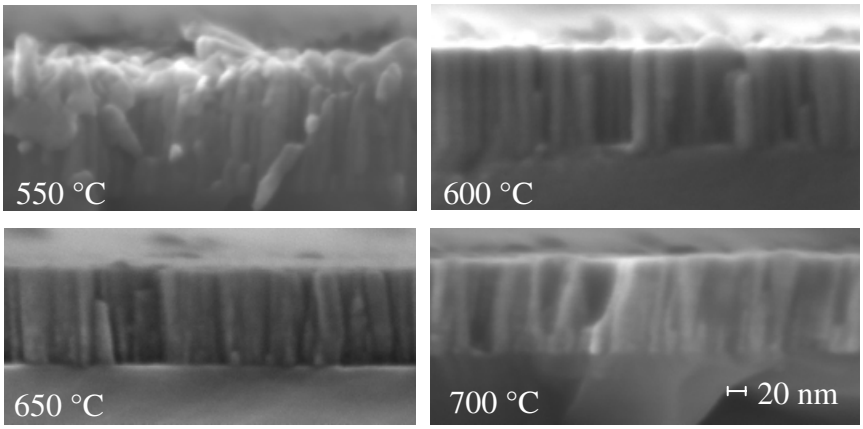

Fig. 2 FESEM micrographs of AlN buffer layers grown at different temperatures, as indicated.

As shown in Fig. 2, the nanocolumns were visible for all layers grown and had a typical diameter of 12 to 25 nm. However, the columns were correlated with surface features only in the temperature range of 600 to 650 °C. At 700 °C, the columns began to expand and coalesce as the growth progressed, and the surface features were frequently larger than the undulations observed in the cross-section FESEM images. Below 600 °C, the nanocolumns continued to form but were increasingly interrupted by irregular platelet-like protrusions.

These changes in surface morphology are illustrated in more detail in Fig. 3. The 550 °C buffer layer had some nanocolumn tips visible, but the surface was mostly covered by large, thin platelets. Although a few small, oblong platelets were still observed for growth at 600 °C, most of the surface consisted of nanocolumn tips. Nanocolumn tips also dominated the surface of the 650 °C layer, but a new surface structure began to appear at an areal density of about 6 μm^{-2}. This structure was a mesa about 10 nm in height and much larger in diameter than the nanocolumns. The edges of the structure were often corrugated. By 700 °C, these mesa structures dominated the surface.

Our observations are consistent with a nanocolumn growth mode that depends on lower surface mobility of both atomic species while still maintaining adequate N supply. Furthermore, the absence of pits and deep facet edges in the films suggests that N from partially cracked ammonia has higher surface mobility than atomic N produced by plasma sources. The GaN films we have grown with ammonia are more uniform in coverage and morphology over a broader range of N flux than typical surfaces of GaN grown by plasma-source MBE. [7] In particular, the dislocation mediated pits [8] seen for both plasma-source MBE and organometallic vapor phase epitaxy did not appear even when we varied the N:Ga ratio by a factor of ten. Finally, while GaN and AlN are known to form isolated columns under conditions of high N to Ga (Al) ratio with a plasma-assisted N source [9], we did not see those types of structures under any of the growth conditions used in this study.

The AlN buffer layers were effective in accommodating the lattice mismatch between Si and AlN. The AlN films have *c* lattice parameters within 0.001 nm of the bulk value of 0.4982 nm. The rocking curves of these films were broad, and there is evidence of specimen warp in the XRD. The RHEED patterns for films grown at 650 °C and below contained hints of cubic phases. [10] Because there were no XRD peaks from cubic AlN, we interpret the RHEED as an indication of stacking faults [11] rather than large volumes of cubic phase formation.

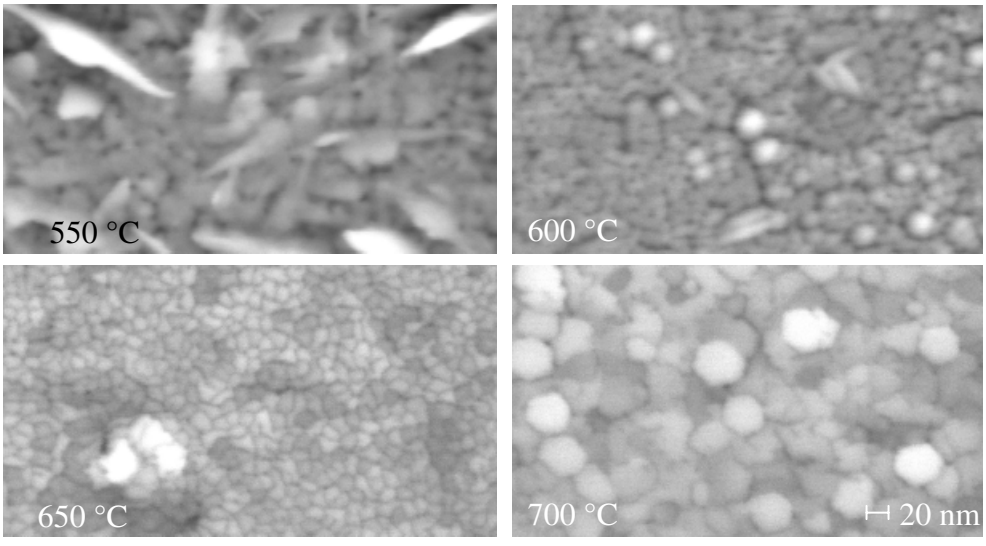

Fig. 3 FESEM micrographs of the surfaces of AlN buffer layers grown at different temperatures.

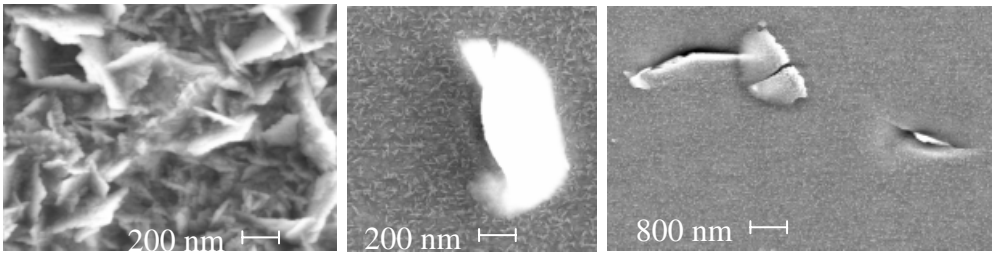

Fig. 4 FESEM micrographs of the surfaces of GaN grown at 705 °C (left) and thick AlN grown with 600 °C buffer layer and 770 °C overlayer (center and right), showing large platelet protrusions. The fine structure in the AlN layer consisted of smaller triangular platelets. Some of the large platelets in the right figure may have broken during handling.

As shown in Fig. 4, the protrusions observed in AlN specimens grown at low temperature were similar to those formed at growth temperatures below 750 °C for GaN. This morphology change appears to be related to the inability of the ammonia to fully decompose into available N at the lower substrate temperature. The lower onset temperature for AlN protrusion formation is consistent with previous observations that ammonia decomposed more readily on an AlN surface than on a GaN surface. [6] The platelets were so large that a reduction in surface species diffusion length is unlikely to explain their formation. No new material phases were observed either by XRD or energy dispersive X-ray spectroscopy for the platelet structures. The RHEED patterns acquired during growth showed diffraction rings at distinct radial positions when these structures formed, which is an indication that they were crystalline but randomly oriented. Photoluminescence at 5 K for the GaN specimen in Fig. 4 was similar in integrated intensity (although broader) to that for smooth GaN films.

4 Summary

AlN buffer layer growth temperature has been shown to have a strong influence on nanocolumn formation in both the buffer layer and overlying GaN layers. Optimal nanocolumn formation occurred at growth temperatures between 600 and 650 °C. Growth at lower temperature led to large, randomly oriented platelets, while growth at higher temperature produced larger columns with irregular heights.

References

[1] H. Ishikawa, K. Yamamoto, T. Egawa, T. Soga, T. Jimbo, and M. Umeno, J. Cryst. Growth **190**, 178 (1998).
[2] D. D. Koleske, M. E. Coltrin, A. A. Allerman, K. C. Cross, C. C. Mitchell, and J. J. Figiel, Appl. Phys. Lett. **82**, 1170 (2003).
[3] R. Liu, F. A. Ponce, A. Dadgar, and A. Krost, Appl. Phys. Lett. **83**, 860 (2003).
[4] A. Reiher, J. Bläsing, A. Dadgar, A. Diez, and A. Krost, J. Cryst. Growth **248**, 563 (2002).
[5] M. C. Luo, X. L. Wang, J. M. Li, H. X. Liu, L. Wang, D. Z. Sun, Y. P. Zeng, and L. Y. Lin, J. Cryst. Growth **244**, 229 (2002).
[6] S. Nikishin et al., J. Vac. Sci. Technol. B **19**, 1409 (2001).
[7] B. Heying, I. Smorchkova, C. Poblenz, C. Elsass, P. Fini, S. Den Baars, U. Mishra, and J. S. Speck, Appl. Phys. Lett. **77**, 2885 (2000).
[8] B. Heying, E. J. Tarsa, C. R. Elsass, P. Fini, S. P. DenBaars, and J. S. Speck, J. Appl. Phys. **85**, 6470 (2003).
[9] M. A. Sanchez-Garcia, E. Calleja, E. Monroy, F. J. Sanchez, F. Calle, E. Munoz, and R. Beresford, J. Cryst. Growth **183**, 23 (1998).
[10] H. Okumura, K. Balakrishnan, H. Hamaguchi, T. Koizumi, S. Chichibu, H. Nakanishi, T. Nagatomo, and S. Yoshida, J. Cryst. Growth **190**, 364-369 (1998).
[11] T. Araki, Y. Chiba, and Y. Nanishi, J. Cryst. Growth **210**, 162 (2000).