High Quality AlN and GaN Grown on Si(111) by Gas Source Molecular Beam Epitaxy with Ammonia.

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ABSTRACT

We describe the growth of high quality AlN and GaN on Si(111) by gas source molecular beam epitaxy (GSMBE) with ammonia (NH_3). The initial nucleation (at 1130-1190K) of an AlN monolayer with full substrate coverage resulted in a very rapid transition to two-dimensional (2D) growth mode of AlN. The rapid transition to the 2D growth mode of AlN is essential for the subsequent growth of high quality GaN, and complete elimination of cracking in thick (> 2 μm) GaN layers. We show, using Raman scattering (RS) and photoluminescence (PL) measurements, that the tensile stress in the GaN is due to thermal expansion mismatch, is below the ultimate strength of breaking of GaN, and produces a sizable shift in the bandgap. We show that the GSMBE AlN and GaN layers grown on Si can be used as a substrate for subsequent deposition of thick AlN and GaN layers by hydride vapor phase epitaxy (HVPE).

INTRODUCTION

There have been numerous recent attempts to prepare AlGaN-based heterostructures on Si (111) substrates [1-4]. The achievements of plasma assisted MBE (PAMBE) of AlN and GaN on Si(111) have been summarized in [5, 6]. GSMBE, with direct decomposition of NH_3 on the substrate surface,[7] can also be used to grow high quality AlN [8] and GaN [7, 9-11]. In the present paper we describe growth of AlN and GaN by GSMBE with NH_3 on Si(111) substrates.

We use *in situ* reflection high-energy electron diffraction (RHEED), low energy electron diffraction (LEED) and *ex situ* triple-crystal x-ray diffraction (XRD), transmission electron microscopy (TEM), RS, and PL to study structure and optical properties. XRD results from AlN and GaN layers, grown by HVPE on the GSMBE AlN and GaN layers are also reported.

EXPERIMENTAL DETAILS AND DISCUSSION

All growth experiments were carried out on 2 and 3-in oriented Si (111) substrates prepared by wet chemical etching [12]. The procedure used results in a hydrogen terminated Si surface. Substrates prepared by this process showed the (7×7) surface structure, observed by RHEED, after heating to 920 K for few minutes. The well known

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Si(111) surface reconstruction transition, from (7×7) to (1×1), which occurs at T_t=1100 K [13, 14], provided a convenient temperature calibration point [9].

It is well known that once the growth chamber is used for the growth of nitrides, the residual nitrogen at the temperature range of 1100-1200 K induces formation of Si-N bonds on the substrate surface [4-6, 15]. The exposition of Si under the active nitrogen flux during PAMBE results in formation of thick SiN layers (down to ~1.5 nm) [16]. The formation of amorphous SiN islands leads to disordered growth of AlN and GaN on Si [6, 17]. Different initial treatments have been tried during MBE to eliminate SiN formation. These are mostly based on the use so-called Al/Si γ-phase as starting surface for AlN growth [5, 6, 9, 18, 19]. However, above 1100K Al/Si γ-phase does not completely protect the Si surface. Approximately 34% of the total substrate area remains bare Si [5] when the AlN growth is initiated. This situation deteriorates at higher temperatures (> 1190 K) where the best AlN crystal perfection can be achieved [6, 20].

The background pressure of NH_3 in our Riber-32 was ~ $5x10^{-8}$ torr. Since the efficiency of NH_3 decomposition at the 1100 K is less than a few percent [21], we estimate the background beam-equivalent pressure (BEP) of the potentially active NH_3 ~ 10^{-10} torr. We have shown [8, 22] that under these conditions the formation of Al/Si γ-phase is inhibited by SiN_x or SiNH [23] islands. These islands form due to the presence of active nitrogen from the background ammonia in the growth chamber.

In order to control the process of silicon nitridation by background NH_3, high growth temperature (1130-1190 K), combined with carefully controlled alternating pulses of Al and NH_3 [24], have been employed [8, 10, 22]. The onset of epitaxy thus suppresses formation of SiN_x and results in very rapid transition to 2D growth mode of AlN [8]. But, the *in situ* RHEED control of Si nitridation by background NH_3 is a very complicated task. Figure 1 (a) shows a typical RHEED pattern resulting from partial nitridation of Si (111) surface by background NH_3, which happens at temperatures above 920 K. To confirm that this pattern is related to the N-Si bond formation, the surface was exposed to higher NH_3 flux (up to BEP ~10^{-6} torr) and for different durations. The symmetry of the pattern does not change with exposure time up to 2 min. (920-1200 K, NH_3 BEP ~10^{-6} torr). Beyond 2 min., discrete RHEED reflections disappear suggesting full surface coverage SiN_x. The pattern in figure 1 (a) also did not change with temperature (down to 300 K) or with different electron energy of ~ 5-9 keV.

In contrast, LEED measurements provide important details about the Si surface due to the shallower region it probes. Figure 2 shows room temperature LEED patterns of Si

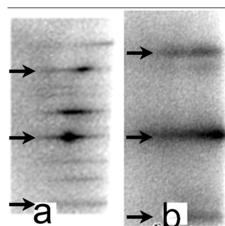

Figure 1. *RHEED patterns along the Si [110} azimuth: (a) partially nitrided Si (111). Position of the (01), (00), and (-01) reflection from the (1x1) structure are indicated from top to the bottom; the extra reflection arise from partial nitridation with NH_3; (b) (1x1) surface structure of the first monolayer of AlN.*

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(111) surface after NH_3 exposure at AlN growth temperature. The pattern, corresponding to an ordered surface, only arises after exposure under background NH_3 for the 1–15 min. or under NH_3 flux with BEP~10^{-6}torr for 1-2 s. We observe extra reflections in the LEED images at different electron energies (20-110 eV), i.e., over the range most sensitive to surface structure. The extra reflections vanish under high or prolonged NH_3 exposure. The presence of the extra reflections in the LEED pattern signal a well ordered surface of the Si substrate, which is found to be best suited for high quality AlN growth.

We grew AlN at 1160 ± 30 K. The formation of the (1x1) surface structure could be seen both by RHEED (figure 1 (b)) and LEED after deposition of 2-3 nm of AlN. The growth was started by turning on both Al and NH_3 after deposition at least one monolayer of AlN. Growth rates of 90-400 nm/h were obtained. A completed 2D growth mode could be seen, by RHEED, after about 5-7 nm. The rapid transition to 2D growth is of interest for several reasons. First, it results in complete relaxation of AlN [25] by the formation of a coincidence lattice at AlN/Si interface [19]. Second, the rapid transition results in a decrease in both the defect density [8, 22] and in the strain energy of AlN layer [26]. From RHEED images we have found the $\{b_{Si(111)}=(a_{Si}/\sqrt{2})\}/a_{AlN(0001)}$ ratio of ~1.233 [8]. This compares to 1.235 obtained from standard values of lattice constants of Si (a_{Si}=0.542 nm) and AlN (a_{AlN}=0.311 nm). Thus the condition 4:5 along [110] azimuth of Si is evident. A similar effect of matching has been observed for c-GaN/GaAs(001) interface [27].

The growth of GaN was started after AlN buffer layer completed the transition to the 2D growth mode. GaN layers were grown at a temperature of 1000±30 K and growth rates of 0.4-1.5 μm/h. Formation of a (2x2) surface structure could be seen by RHEED after deposition of 20-100 nm of GaN. The fastest 3D-2D transition of growth mode was reached at the highest growth rate, possibly due to the high value of lateral growth rate reported for GaN [28]. We also prepared structures incorporating several (1-4) short period AlN/GaN and AlGaN/GaN superlattices (SLs). The effectiveness of such SLs, in controlling defect propagation from the AlN/Si and AlN/GaN interfaces, is demonstrated in the TEM cross section of figure 3. We stress that the third GaN layer and SL (figure 3) were grown in a 2D growth mode with (2x2) surface structure. Recently, similar SLs has been used to improve crystal quality of GaN grown on Si(001) by metal-organic chemical vapor deposition (MOCVD) [29].

From XRD measurements the full width at half maximum (FWHM) of the (0002) AlN peak in triple-crystal ω-2θ scan was less than 100 arc sec. This is the best value reported for ~200 nm thick AlN grown on Si(111). In GaN samples 1.5-2 μm thick the FWHM of the (0002) peak was as narrow as 14 arc sec. The GaN layers were free of cracks.

The layers of GaN grown on silicon are known to crack during the cool-down cycle

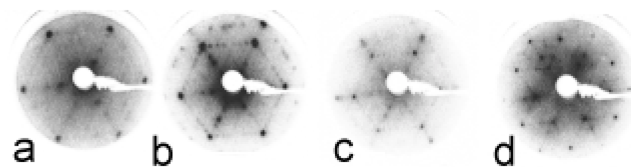

Figure 2. *LEED patterns of an ordered partially nitrided Si (111) surface at different energy of electron beam: (a) E_e=23 eV; (b) E_e=35 eV; (c) E_e=53 eV; (d) E_e=108 eV. All the RHEED and LEED patterns are displayed as negative images for clearness.*

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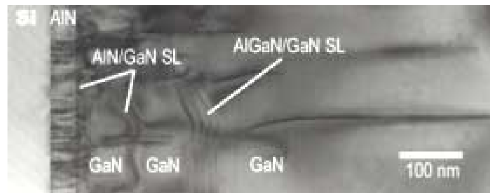

Figure 3. *TEM cross-section of GaN/(buffer layer)/Si structure.*

(see references in [8]). Cracking is believed to occur due to the thermal expansion coefficient mismatch between GaN and Si. Based on the result present both in this article and [10, 19, 22, 24-26], we can assume that cracking of GaN can be completely eliminated by assuring uniform growth of AlN at the Si-N-Al interface. From Raman measurements [10] we found the value of a residual tensile stress of < 0.2 GPa in our GaN with the thickness of 0.4-2.3 μm. This low stress is important because it is well below the ultimate strength of breaking of 0.4 GPa, under tensile stress, for GaN [31].

PL spectra at temperatures ranging from 77K to 495K were excited by a 2 kW pulse (10ns, 100Hz) nitrogen laser. Above 100 K, the PL spectra are dominated by the free exciton (FE) recombination [32, 33]. The red shift of the FE peak, due to the bandgap shrinkage, as well as usual quenching were observed with increasing temperature. The room temperature PL spectra of GaN show a FE peak position at 3.408 eV with the FWHM of less than 40 meV. The temperature dependence of the bandgap energy calculated from PL data for our GaN/Si crystals is presented in figure 4. Experimental data were fitted with both Passler's model [34] and Varshni's empirical approximation [35]. The PL results will be reported in detail in a later paper [36]. Also presented in figure 4 is the temperature dependence of the bandgap energy for a GaN layer grown by MOCVD on 6H-SiC substrate [37] and for a stress-free bulk GaN crystal grown HVPE [38]. Comparison of the $E_g(T)$ dependence for GaN grown on Si(111) and on SiC

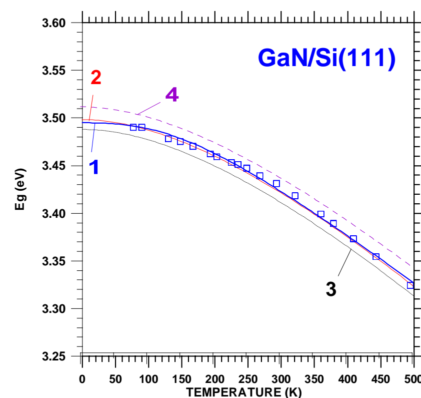

Figure 4. *The temperature dependence of the bandgap. Squares – this work; 1 - Passler's model [34] fit; 2 – Varshni's model [35] fit; 3 – GaN layer grown by MOCVD on SiC (recalculated data from [37]; 4 – Strain free bulk GaN grown by HVPE [38].*

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substrates, with that of bulk GaN indicates residual tensile mechanical stresses in epilayers on both substrates. For GaN/SiC this has a value of about 0.5-1.0 GPa, which is primarily due to differences in values of the thermal expansion coefficients of GaN and SiC. This is at twice as large as what we see in our GaN/Si samples. That is why the $E_g(T)$ dependence is closer to that for strain free bulk GaN as shown in figure 4. Our estimation of the tensile stresses in our GaN/Si samples, based on the PL measurements, ranges from 0.08 to 0.3 GPa. These values are in a good agreement with the results of our Raman measurements.

The AlN and GaN layers grown by MBE on Si were used as substrate materials for growth of thick AlN and GaN layers by HVPE. The FWHM of the AlN (0002) ω-2θ-scan peak in the structure AlN(50 µm thick, HVPE)/GaN-AlN(MBE)/Si was 93 arcsec. For a 50 µm thick AlN layer grown by HVPE directly on Si, a FWHM value of 61 arcsec was obtained. FWHM of (0002) GaN peak in the structure GaN(1.5 µm thick, HVPE)/GaN-AlN(MBE)/Si at ω-2θ-scan was 48 arcsec. The ***c*-**axis lattice constant of HVPE GaN was higher than that of MBE grown GaN. We are currently performing experiments to understand this phenomenon.

CONCLUSIONS

This study shows how to grow high quality of GaN and AlN by GSMBE with NH_3. We can conclude that cracking of GaN grown on Si (111) can be completely eliminated by assuring uniform growth of AlN at the Si-N-Al interface.

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REFERENCES

1. K. S. Stevens, M. Kinniburgh, and R. Beresford, Appl. Phys. Lett. **66**, 3518 (1995).
2. S. Guha, N. A. Bojarczuk, Appl. Phys. Lett. **72**, 415 (1998).
3. D. Kuksenkov, H. Temkin, R. Gaska, and J. W. Yang, IEEE Electron. Device Lett., **19**, 222 (1998).
4. H. Marchand, N. Zhang, L. Zhao, Y. Golan, S. J. Rosner, G. Girolami, Paul T. Fini, J. P. Ibbetson, S. Keller, Steven DenBaars, J. S. Speck, and U. K. Mishra, MRS Internet J. Nitride Semicond. Res. **4**, 2 (1999) and references therein.
5. K. Yasutake, a. Takeuchi, H. Kakiuchi, and K. Yoshii, J. Vac. Sci. Technol., **A 16**, 2140 (1998).
6. E. Calleja, M. A. Sánchez-García, F. J. Sánchez, F. Calle, F. B. Naranjo, E. Muñoz, S. I. Molina, A. M. Sánchez, F. J. Pacheco, R. García, J. Cryst. Growth, **201/202**, 296 (1999) and references therein.
7. M. Godlewski, J. P. Bergman, B. Monemar, U. Rossner, A. Barski, Appl. Phys. Lett. **69**, 2089 (1996).
8. S. A. Nikishin, V. G. Antipov, S. Francoeur, N. N. Faleev, G. A. Seryogin, V. A. Elyukhin, H. Temkin, T. I. Prokofyeva, M. Holtz, A. Konkar and S. Zollner, Appl. Phys. Lett., **75**, 484 (1999).
9. E. S. Hellman, D. N. E. Buchanan, and C. H. Chen, MRS Internet J. Nitride

https://doi.org/10.1557/S1092578300004658 Published online by Cambridge University Press

Semicond. Res. **3**, 43 (1998).
10. S. A. Nikishin, N. N. Faleev, V. G. Antipov, S. Francoeur, L. Grave de Peralta, G. A. Seryogin, H. Temkin, T. I. Prokofyeva, M. Holtz, and S. N. G. Chu, Appl. Phys. Lett. **75**, 2073 (1999).
11. N.-E. Lee, R. C. Powell, Y.-W. Kim, and J. E. Greene, J. Vac. Sci Thechnol, **A 13**, 2293 (1995).
12. V. G. Antipov, S. A. Nikishin, and D. V. Sinyavskii, Tech. Phys. Lett. **17**, 45 (1991).
13. J. J. Lander, Surf. Sci., **1**, 125 (1964).
14. N. Osakabe, Y. Tanishiro, K. Yagi, and G. Honjo, Surf. Sci., **109**, 353 (1981).
15. V. G. Antipov, S. A. Nikishin, A. S. Zubrilov, D. V. Tsvetkov, and V. P. Ulin, *Proceedings of the Sixth International Conference on silicon Carbide and Related Materials,* Kyoto, Japan, 18-21 Sept. 1995, Inst. Phys. Conf. Ser. No 142 (IOP, London, 1996), Vol. XXV+1120, p.847 and references therein.
16. Y. Nakada, I. Aksenov, and H. Okumura, Appl. Phys. Lett., **73**, 827 (1998).
17. A. Ohtani, K. S. Stevens, and R. Beresford, Appl. Phys. Lett., **65**, 61 (1994).
18. A. Bourret, A. Barski, J. L. Rouvière, G. Renaud, and A. Barbier, J. Appl. Phys. Lett. **83**, 2003 (1998).
19. H. P. D. Schenk, G. D. Kipshidze, V. B. Lebedev, S. Shokhovets, R. Goldhahn, J. Ktäußlich, A. Fissel, Wo. Richter, J. Cryst. Growth, **201/202**, 359 (1999);
20. E. Calleja, M. A. Sánchez-García, E. Monroy, F. J. Sánchez, E. Muñoz, A. Sanz-Hervás, C. Villar, and M. Aguilar, J. Appl. Phys. **82**, 4681 (1997).
21. R. C. Powell, N.-E. Lee, and J. E. Greene, Appl. Phys. Lett., **60**, 2505 (1992).
22. S. A. Nikishin, N. N. Faleev, H. Temkin, and S. N. G. Chu, *State-of-the-Art Program on Compound Semiconductors (SOTAPOCS XXXI), Honolulu, Hawaii, 1999, October 17-22,* Electrochemical Society Proceedings Volume 99-17, p. 238 (1999).
23. *Silicon Nitride in Electronics,* edited by A. V. Rzhanov; Novosibirsk, Nauka (1982).
24. S. A. Nikishin, and H. Temkin, unpublished.
25. A. Bourret, A. Barski, J. L. Rouvière, G. Renaud, A. Barbier, J. Appl. Phys. **83**, 2003, (1998).
26. G. D. Kipshidze, H. P. Schenk, A. Fissel, U. Kaiser, J. Schulze, Wo. Richter, M. Weihnacht, R. Kunze, J. Ktäusslich, Semiconductors, **33**, 1241 (1999)
27. A. Trampert, O. Brandt, H. Yang, and K. H. Ploog, Appl. Phys. Lett., **70**, 583 (1997).
28. T. D. Moustakas, Mater. Res. Soc. Symp. Proc. **395**, 111 (1996).
29. X.Zhang, S.-J.Chua, P.Li, K.-B.Chong, Z.-C.Feng, Appl. Phys. Lett. **74**, 1984 (1999).
30. H. Tang and J. B. Webb, Appl. Phys. Lett., **74**, 2373 (1999).
31. Semiconductors and Semimetals, Vol. 57, Gallium Nitride (GaN) II, edited by J. I. Pankove and T. D. Moustakas (Academic Press, San Diego, 1999), p.294.
32. B.Monemar, J.P.Bergman, I.A.Buyanova, W.Li, H.Amano, I.Akasaki. MRS Internet Journal: Nitride Semiconductor Research **1**, 2 (1996).
33. M. Smith, G.D.Chen, J.K.Lin, H.X.Jiang, M.Asif Khan, C.J.Sun, Q.Chen, J.W.Yang, J.Appl. Phys.**79**, 7001 (1996).
34. R. Passler, Phys. Stat. Sol.(b), **200**, 155 (1997).
35. Y. P. Varshni, Physica, **34**, 149 (1967).
36. A. S. Zubrilov, S. A. Nikishin, and H. Temkin (unpublished).
37. A. S. Zubrilov, V. I. Nikolaev, D. V. Tsvetkov, V. A. Dmitriev, K. G. Irvine, J. A. Edmond, and C. H. Carter, Jr. Appl. Phys. Lett. **67**, 533 (1995).
38. A. S. Zubrilov, Yu. V. Melnik, A. E. Nikolaev, M. A. Jakobson, D. K. Nelson, V. A. Dmitriev, Semiconductors **33**, 1067 (1999).

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