



ELSEVIER

Journal of Crystal Growth 225 (2001) 150–154

JOURNAL OF
**CRYSTAL
GROWTH**

www.elsevier.nl/locate/jcrysgro

Growth of high quality GaN layers with AlN buffer on Si(1 1 1) substrates

P. Chen^{a,*}, R. Zhang^a, Z.M. Zhao^a, D.J. Xi^a, B. Shen^a, Z.Z. Chen^a,
Y.G. Zhou^a, S.Y. Xie^a, W.F. Lu^b, Y.D. Zheng^a

^aDepartment of Physics, Nanjing University, Nanjing 210093, People's Republic of China

^bDepartment of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Abstract

High quality GaN layers were grown on Si(1 1 1) substrates using high-temperature-grown AlN as buffer layer by rapid thermal process low-pressure metalorganic chemical vapor deposition. The growth and characteristics of AlN buffer layer and the GaN layers were investigated by using scanning electron microscope, X-ray diffraction, photoluminescence (PL), Raman scattering, and Hall measurements at room temperature. It was found that pre-seeding Al to Si surface is a critical condition for AlN growth on Si. Two-dimensional growth of AlN was achieved under optimized conditions. Raman scattering shows a narrow GaN E_2 peak and broad AlN E_2 , E_1 peaks. At room temperature, the investigated films are unintentionally doped n-type. The carrier concentration is about $1.3 \times 10^{17} \text{ cm}^{-3}$ and the Hall mobility is about $210 \text{ cm}^2/\text{Vs}$. Metal–semiconductor–metal photoconductive detectors were fabricated on the GaN/Si(1 1 1) films. These detectors show a sharp cut-off wavelength at 363 nm. A maximum responsivity of 6.9 A/W was achieved at 357 nm under a 5.0 V bias. These results indicate that high quality GaN films on Si(1 1 1) can be obtained using the AlN buffer layer, and the potential application of GaN films based on Si substrates. © 2001 Published by Elsevier Science B.V.

PACS: 81.15H; 68.55; 61.05J; 07.62

Keywords: A3. Metalorganic chemical vapor deposition; B1. Nitrides

1. Introduction

Recently, GaN-based optoelectronic devices on Si substrates have made great progress. Such devices as LEDs [1] and ultraviolet (UV) photo-detectors [2] have been reported. The performance of these devices is seriously affected by the quality of the GaN films. In order to obtain high quality GaN and related nitride epilayers on Si substrates,

the two-step growth method has been proposed, in which various types of buffer layers such as 3C-SiC [3], AlN [4,5], GaAs [6], AlO_x [7] and Si_3N_4 [8] are used between epilayer and substrate. The large lattice and thermal mismatch between GaN and Si substrates is one of the main impediments for heteroepitaxial growth of GaN on Si. Another impediment is the poor wetting of GaN on Si(1 1 1), which impedes the direct nucleation and frequently results in poor quality and morphology of GaN film if we use similar growth methods on sapphire substrates. Using AlN as buffer layer is

*Corresponding author. Fax: +86-25-3328130.

E-mail address: ydzheng@nju.edu.cn (P. Chen).

one of most promising ways to achieve high quality GaN on Si [9]. The lattice and thermal mismatch between AlN and GaN are much smaller than those between Si and GaN, and AlN has good wetting properties on Si. In addition, the nitridation of the Si surface during growth of nitrides is also a serious impediment. The nitridation of Si surface can be greatly suppressed if Al is firstly deposited on Si surface when using AlN as buffer layer. In 1999, Nikiskin grew the high quality GaN on Si(111) with AlN or AlGaIn/GaN superlattices buffer in gas-source molecular-beam epitaxy (GSMBE) [13]. The X-ray linewidth and PL results of the GaN films might be comparable with those typical of ones on sapphire. However, such high quality Ga(Al)N films were mostly achieved by MBE; the Ga(Al)N growth, especially AlN two-dimensional growth by MOCVD on Si(111) is still almost unknown.

In this paper, we report the growth of high quality GaN epilayers on Si(111) substrates using high-temperature-grown AlN as buffer layer by rapid thermal process low-pressure metalorganic chemical vapor deposition (RTP/LP-MOCVD). GaN-based metal–semiconductor–metal photoconductive detectors were also successfully fabricated on the GaN films. The results indicate that high quality GaN films on Si(111) can be obtained using the AlN buffer layer.

2. Experimental procedure

Si(111) wafers off-cut $\sim 3^\circ$ $13\ \Omega\text{cm}$ resistivity with *n*-type were used as the substrates. The substrates were cleaned by the RCA method. The growth was carried out in a RTP/LP-MOCVD equipped with a horizontal quartz reactor. Trimethylaluminum (TMA), trimethylgallium (TMG) and ammonia (NH_3) were employed as sources of Al, Ga and N, respectively. H_2 was used as the carrier gas. Before growing AlN, the substrate was annealed under H_2 ambient at 1100°C for 15 min to clean the surface. For AlN growth at high temperature, pre-seeding Al to Si surface is very important. In our experiments, three durations of pre-seeding Al, 0, 5 and 10 s, were used just before introducing NH_3 into the reactor, respectively. All

AlN layers were grown at 1070°C for 20 min, to about 150 nm. After AlN growth, the temperature was decreased to 900°C to grow GaN layer. The thickness of GaN film was about $0.8\ \mu\text{m}$. For AlN growth, the flow rates of TMA and NH_3 were $12.5\ \mu\text{mol/min}$ and $1.8\ \text{sl/min}$, respectively. The reactor pressure was 20 Torr. For GaN growth, the flow rates of TMG and NH_3 were $18.5\ \mu\text{mol/min}$ and $1.8\ \text{sl/min}$, respectively. The reactor pressure was 76 Torr. SEM, XRD, PL, Raman scattering, and Hall measurements at room temperature were used to characterize the surface and crystal structures of the samples. GaN-based metal–semiconductor–metal photoconductive detectors have also been fabricated on the GaN films. Details of the fabrication procedure will be published elsewhere.

3. Results and discussions

3.1. Morphology and structure of AlN buffer layer

The morphology of AlN layers is shown in Fig. 1. For no pre-seeded Al, the surface of AlN seems like a mirror. There are many random 2D nuclei, and no distinct structure can be seen in Fig. 1a. However, in Fig. 1b, the AlN layer with 5 s of pre-seeded Al shows a clear step structure surface. When the duration of pre-seeding Al is as long as 10 s, the AlN surface becomes visibly rough. In Fig. 1c, for 10 s of pre-seeding Al, a discontinued and rough surface can be seen on the sample. It has been known that the nitridation of the Si surface is one of the major impediments for nitrides grown on Si substrates. If growth was initiated by exposing the Si surface to Al, followed by exposure to NH_3 , the nitridation of Si surface can be greatly suppressed. At high temperature, NH_3 very easily reacts with Si in MOCVD. The nitridation occurs if there is no pre-seeding of Al to Si surface. In case of oxidation of Si(111) surface, only a 1-nm-thick oxide will totally demolish the step structure of Si(111) surface [10]. In growth of nitrides, the amorphous SiN_x layers are commonly 3 nm thick [11,12]. So it can be concluded that without a pre-seeded Al to Si surface, growth will lead to nitridation of Si

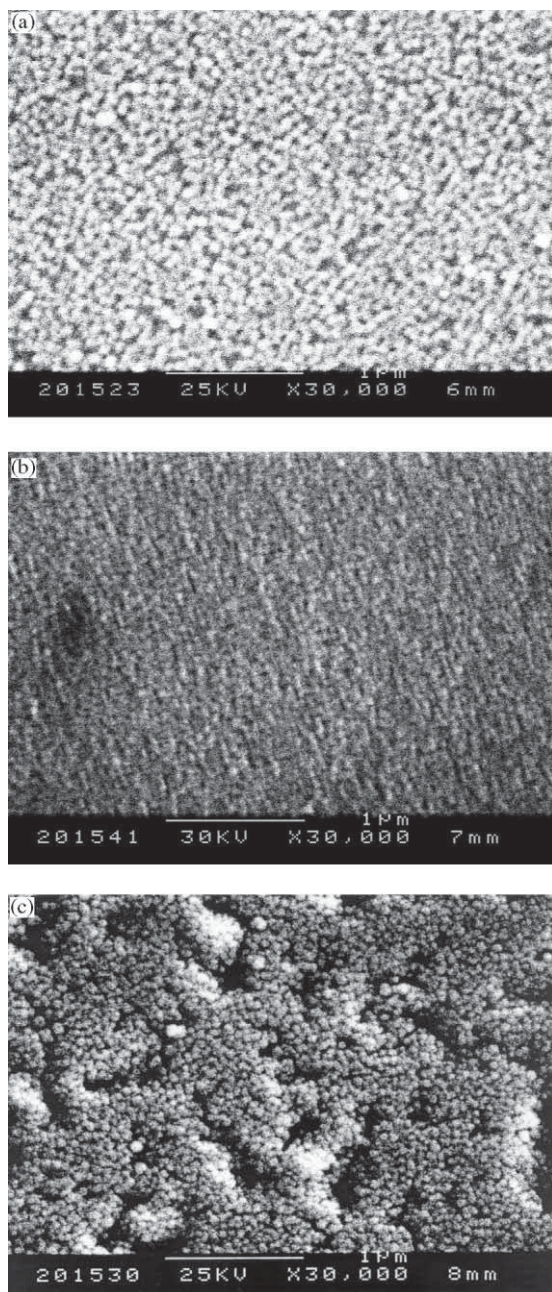


Fig. 1. The surface of AlN buffer layers on Si(111) substrate with pre-seeding Al for 0 s (a), 5 s (b) and 10 s (c), respectively.

surface as shown in Fig. 1a, and cannot achieve step-flow 2D-growth mode. The opportune duration of pre-seeding Al to Si surface will suppress nitridation. From Fig. 1b, the surface of AlN

maintained the step structure of Si substrate, which clearly shows the step-flow 2D-growth mode. If the duration of pre-seeding Al is extended, too many Al will accumulate on the substrate surface. Subsequent AlN growth will also not achieve the 2D-growth mode, and form a discontinued and rough surface, as shown in Fig. 1c.

3.2. Characteristics of GaN epilayer

A 0.8- μm -thick GaN epilayer grown on the optimized AlN buffer layer shows a smooth surface as observed by optical microscope, and there are no cracks or micro holes in the film. Fig. 2 shows a representative X-ray spectrum from the above sample. Only the GaN(0002), (0004) and AlN(0002) peaks were present, indicating good crystallinity. Due to the Si substrate miscut, the Si(111) peak was deduced. The PL spectrum of a GaN layer is shown in Fig. 3. Fig. 3 represents the PL at 77 K, which shows a sharp and strong near band emission. The free exciton emission (FX_A) and bound exciton emission (I_2) are clearly seen, and the donor–acceptor (DAP) and the phonon replicas can also be distinguished. The deep level emission (around 550 nm) is almost not seen. Raman scattering measurements were done at room temperature using 488 nm excitation from an Ar^+ laser. Fig. 4 shows a typical Raman spectrum, with the dominant GaN E_2 phonon near 563 cm^{-1} . The intensity and full width at half maximum (FWHM) are comparable to the results on sapphire. The weak and broad peaks at 625 and

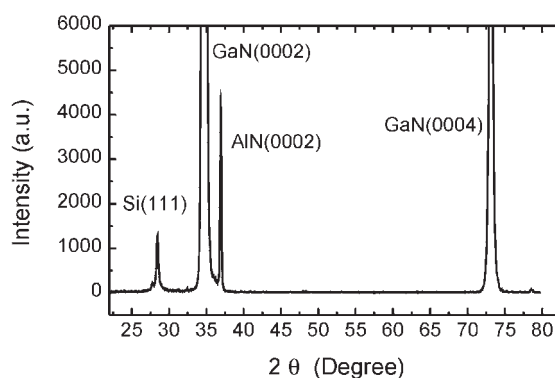


Fig. 2. The XRD data of a GaN layer on Si(111) with optimized AlN buffer layer.

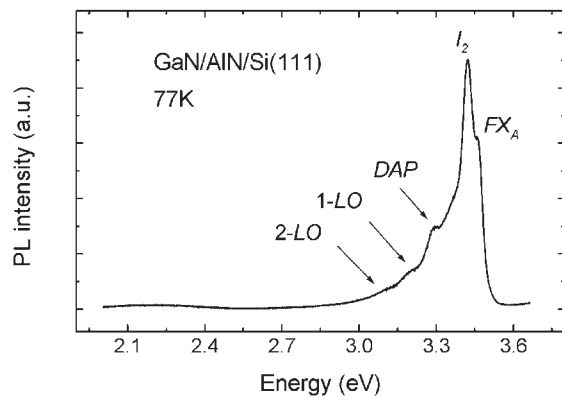


Fig. 3. The PL spectrum of GaN layer at 77 K shows FXa and I_2 emission, and the DAP and its phonon duplicates can be distinguished.

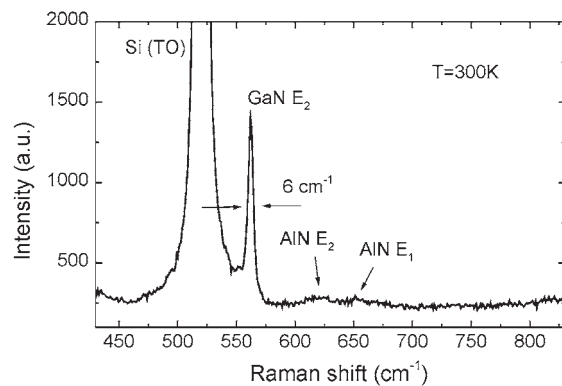


Fig. 4. Raman scattering data of the GaN layer at room temperature using 488 nm excitation from an Ar⁺ laser.

655 cm^{-1} come from AlN E_2 and E_1 phonon, respectively. The presence of a 150-nm-thick AlN between GaN and Si substrate permits us to measure the carrier concentration and mobility by the Hall effect. Van der Pauw measurements give a carrier concentration of $1.3 \times 10^{17}\text{ cm}^{-3}$ and a Hall mobility of $210\text{ cm}^2/\text{Vs}$ at room temperature, which are also comparable to the results on sapphire.

3.3. Characteristics of GaN M–S–M photodetectors

Metal–Semiconductor–Metal (M–S–M) photo-detectors have been fabricated on GaN/Si(111)

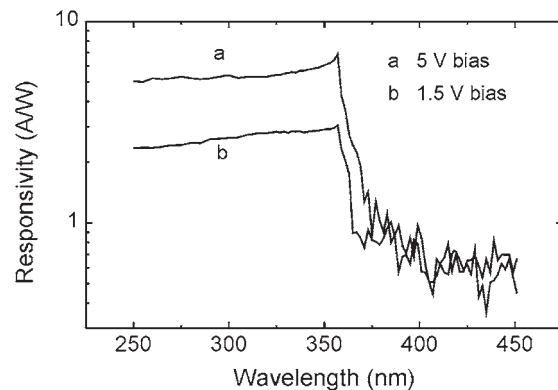


Fig. 5. The responsivity as a function of wavelength for an M–S–M GaN/Si(111) detector.

with AlN buffer layer. An interdigitated finger electrode was made on the GaN films using photolithography. The fingers are $10\text{ }\mu\text{m}$ wide and $360\text{ }\mu\text{m}$ long with $15\text{-}\mu\text{m}$ -wide spacings. Al was used as ohmic contacts. The typical resistance of the detectors is about $1\text{ K}\Omega$.

The responsivity as a function of wavelength for an M–S–M GaN/Si(111) detector is shown in Fig. 5. There is a sharp cut-off wavelength at 363 nm. A maximum responsivity of 6.9 A/W was achieved at 357 nm under a 5.0 V bias. In UV spectral region, the detector shows a very high responsivity, with only a little decrease from 360 to 250 nm. The responsivity of the detector drops by nearly an order of magnitude across the cut-off wavelength.

4. Conclusions

High quality GaN epilayers were grown on Si(111) substrates using high-temperature-grown AlN as buffer layer by RTP/LP-MOCVD. It was found that pre-seeding Al to Si surface is a critical condition for AlN growth on Si. Two-dimensional growth of AlN was achieved under optimized condition. The PL, Raman scattering and Hall measurements verify the high quality of GaN films on Si(111) with AlN buffer layer. GaN-based metal–semiconductor–metal photoconductive detectors have been fabricated on the GaN films. These detectors show a sharp cut-off wavelength at 363 nm. A maximum responsivity of 6.9 A/W was

achieved at 357 nm under a 5.0 V bias. These results indicate that high quality GaN films on Si(111) can be obtained using the AlN buffer layer, and the potential application of GaN films based on Si substrates.

Acknowledgements

This work was supported by the National Science Foundation of China and National High Technology R&D Project of China, No. 69636010, No. 69636040, No. 69987001 and No. 69806006.

References

- [1] S. Guha, N.A. Bojarczuk, Appl. Phys. Lett. 72 (1998) 415.
- [2] A. Osinsky, S. Gangopadhyay, J.W. Yang, R. Gaska, D. Kuksenkov, H. Temkin, I.K. Shmagin, Y.C. Chang, J.F. Muth, R.M. Kolbas, Appl. Phys. Lett. 72 (1998) 551.
- [3] T. Takeuchi, H. Amano, K. Hiramatsu, N. Sawaki, I. Akasaki, J. Crystal Growth 115 (1991) 634.
- [4] A. Watanabe, T. Takeuchi, K. Hirose, H. Amano, K. Hiramatsu, I. Akasaki, J. Crystal Growth 128 (1993) 391.
- [5] P. Kung, A. Saxler, X. Zhang, D. Walker, T.C. Wang, I. Ferguson, M. Razeghi, Appl. Phys. Lett. 66 (1995) 2958.
- [6] J.W. Yang, C.J. Sun, Q. Chen, M.Z. Anwar, M.S. Khan, S.A. Nikishin, G.A. Seryogin, A.V. Osinsky, L. Chernyak, H. Temkin, C. Hu, S. Mahajan, Appl. Phys. Lett. 69 (1996) 3566.
- [7] N.P. Kobayashi, J.T. Kobayashi, P.D. Dapkus, W.J. Choi, A.E. Bond, X. Zhang, D.H. Rich, Appl. Phys. Lett. 71 (1997) 3569.
- [8] Y. Nakada, I. Aksenov, Appl. Phys. Lett. 73 (1998) 827.
- [9] E.S. Hellman, D.N.E. Buchanan, C.H. Chen, MRS Internet J. Nitride Semicond. Res. 3 (1998) 43.
- [10] N. Miyata, H. Watanabe, M. Ichikawa, Appl. Phys. Lett. 73 (1998) 3923.
- [11] P. Chen, B. Shen, J.M. Zhu, Z.Z. Chen, Y.G. Zhou, S.Y. Xie, R. Zhang, P. Han, S.L. Gu, Y.D. Zheng, S.S. Jiang, D. Feng, Chin. Phys. Lett. 17 (2000) 224.
- [12] S. Tanaka, Y. Kawaguchi, N. Sawaki, M. Hibino, K. Hiramatsu, Appl. Phys. Lett. 76 (2000) 2701.
- [13] S.A. Nikishin, N.N. Faleev, V.G. Antipov, S. Francorur, L. Grave de Peralta, G.A. Seryogin, H. Temkin, T.I. Prokofyeva, M. Holtz, S.N.G. Chu, Appl. Phys. Lett. 75 (1999) 2073.