2002

# Growth of GaN films on porous SiC substrate by molecular-beam epitaxy

F. Yun
*Virginia Commonwealth University*

Michael A. Reshchikov
*Virginia Commonwealth University*, mreshchi@vcu.edu

L. He
*Virginia Commonwealth University*

***See next page for additional authors***



Yun, F., Reshchikov, M.A., He, L., et al. Growth of GaN films on porous SiC substrate by molecular-beam epitaxy. Applied Physics Letters, 81, 4142 (2002). 

**Authors**
F. Yun, Michael A. Reshchikov, L. He, Hadis Morkoç, C. K. Inoki, and T. S. Kuan

# Growth of GaN films on porous SiC substrate by molecular-beam epitaxy

F. Yun,[a)] M. A. Reshchikov, L. He, and H. Morkoç
*Virginia Commonwealth University, Department of Electrical Engineering, Richmond, Virginia 23284*

C. K. Inoki and T. S. Kuan
*University at Albany, SUNY, Dept of Physics, Albany, New York 12222*

(Received 26 July 2002; accepted 7 October 2002)

Porous SiC (PSiC) substrates were used for the growth of GaN by reactive molecular-beam epitaxy with ammonia as the nitrogen source. Improved quality of GaN films has been demonstrated for growth on PSiC substrates, as compared to that on standard 6H–SiC substrates. Cross-sectional transmission electron microscopy and electron diffraction showed a reduction in dislocation density and a higher degree of lattice and thermal relaxation in the GaN films grown on porous substrates. The submicron GaN films exhibit a rocking curve linewidth of 3.3 arcmin for (0002) diffraction and 13.7 arcmin for $(10\bar{1}2)$ diffraction. Low-temperature photoluminescence showed an excitonic transition with a full width at half maximum of 9.5 meV at 15 K, as well as high quantum efficiency, on the GaN layer grown on PSiC when the thin skin layer on porous SiC was removed before growth. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1524304]

GaN has been receiving much attention in the applications to high-temperature high power electronic devices as well as visible to UV optoelectronic devices. Therefore, intense effort has been made toward the growth of high-quality GaN films in terms of electrical, optical, and structural properties. It is well known that the biggest obstacle is the relatively high density of defects including threading dislocations associated with the growth on non-native substrates. Recently, researchers have been intrigued by the epitaxial growth on porous substrates, both porous GaN and porous SiC.[1–9] They have explored the growth of SiC on porous SiC (PSiC) substrates,[1,6] and the growth of GaN on porous GaN layer on top of SiC substrates by chemical vapor deposition.[7–9] These preliminary experiments have shown signs of improvement in the epitaxial layer.

The purpose of using a porous template for growth emanates from the belief that the nanopatterned porous structure would favor lateral growth, which would lead to a reduced extended defect density. Due to the electrical conductive nature of a 6H–SiC substrate, it is easy to convert it into porous material through electrochemical anodization. Therefore, it is of practical interest to study the growth of GaN on top of this PSiC substrate. A recent study[5] revealed a factor of 2 reduction of dislocation density in GaN film grown on PSiC by molecular-beam epitaxy (MBE), using rf plasma-assisted nitrogen source. In this work, we report the growth and defect reduction of GaN films on PSiC by reactive MBE utilizing ammonia ($NH_3$) as the nitrogen source.

The nanometer-scale pores on 6H–SiC substrate were formed by anodization in hydrofluoric acid under UV illumination.[10] Pt was used as the cathode, while the substrate served as the anode. The as-prepared substrates usually show very few pores on the surface, while most of the pores are buried under the so-called ''skin layer.'' Figure 1(a) is the cross-sectional TEM image of an as-prepared PSiC substrate, showing such a skin layer. The porous structure underneath the skin layer is clearly observed, with a porous template thickness of $\sim$2.8 $\mu$m. Two types of discernable pores are present, sizing around 10 and 100 nm each. It is interesting to note that most of these pores do not run along the *c* direction, instead, they start from the substrate surface and penetrate into the substrate like cones, the opening angle of which depends on the anodization parameters. A skin layer of at least 60 nm is present at the substrate surface. This skin layer prevents most of the pores from penetrating into the surface. It can be removed by H annealing at 1700 °C. Figure 1(b) is an atomic force microscopic (AFM) image of a PSiC surface after the removal of the skin layer. Pores can be seen exposed at the surface with much higher density, while the dimension of pores has been enlarged and modified by this method of annealing.

GaN films were grown under Ga-rich conditions by MBE using $NH_3$ as reactive nitrogen source. Four samples were used for this study, as listed in Table I. The first sample, A, is grown on a standard (0001) 6H–SiC substrate; the second sample, B, is grown on a (0001) PSiC substrate with a

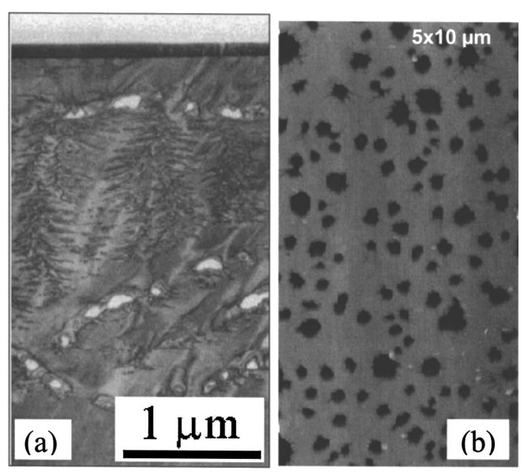


FIG. 1. (a) Cross-sectional TEM image showing the porous structure of anodized 6H–SiC substrate. The skin layer is present which blocks most pores from reaching the surface. (b) AFM surface morphology of PSiC substrate after H annealing for 1 min at 1700 °C.

[a)]Electronic mail: fyun@vcu.edu



 

TABLE I. GaN layers grown on PSiC and standard 6H–SiC substrate by MBE using $NH_3$ source.

| Sample No. | Substrate | Growth parameter | $\Delta a/\|a\|$ | Dislocation density near top GaN |
|---|---|---|---|---|
| A | Standard (0001) 6H–SiC substrate | $NH_3 = 10$ sccm, $T_s = 585\,°C$, thickness $\sim 0.15\ \mu m$ | 3.1% (90%) | $\sim 3\times10^{10}\ cm^{-2}$ |
| B | (0001) PSiC on axis, with skin layer ~60 nm | $NH_3 = 10$ sccm, $T_s = 655\,°C$, thickness $\sim 0.11\ \mu m$ | 3.3% (95%) | $\sim 2\times10^{10}\ cm^{-2}$ |
| C | (0001) PSiC off 8°, with skin layer ~60 nm | $NH_3 = 10$ sccm, $T_s = 655\,°C$, thickness $\sim 1.40\ \mu m$ | 3.6% (100%) | $\sim 5\times10^{9}\ cm^{-2}$ |
| D | (0001) PSiC, H anneal, 1700 °C/1 min. No skin layer | $NH_3 = 10$ sccm, $T_s = 650\,°C$, thickness $\sim 0.77\ \mu m$ | 3.6% (100%) | $\sim 1\times10^{9}\ cm^{-2}$ |

skin layer of ~60 nm. The thickness of the GaN in samples A and B are thin (0.11–0.15 $\mu$m), and they were grown without any buffer layers. The third and fourth samples are thicker (0.77–1.40 $\mu$m), and were grown on 4H–PSiC with a skin layer for sample C, and on 6H–PSiC with its skin layer removed for sample D, respectively. Both samples C and D are grown with a thin layer of AlN buffer (~40 nm) between GaN epilayer and the PSiC substrate. The substrate of sample C has 8° miscut toward $(11\bar{2}0)$ orientation. GaN growth temperature was about 650 °C for growth on PSiC substrate, and the $NH_3$ flow rate was fixed at 10 sccm. Nominally similar growth parameters were employed, which were optimized for GaN/6H–SiC growth. The removal of skin layer is performed by H annealing at 1700 °C for 1 min.[11]

Figure 2 shows the cross-sectional TEM images for samples A and B. For the thin GaN layer (~0.15 $\mu$m) grown on a standard 6H–SiC substrate, as shown in Fig. 2(a), a dislocation density of $\sim 3\times10^{10}\ cm^{-2}$ is observed, together with twins forming on the $c$-plane of GaN layer. The thinner GaN layer (~0.11 $\mu$m) grown on a PSiC substrate with a skin layer [Fig. 2(b)] exhibits a slightly lower density of dislocations in the order of $\sim 2\times10^{10}\ cm^{-2}$, which may be related to the smaller film thickness. Strain condition of GaN with respect to SiC can be obtained by measuring the relative lattice constant from electron diffraction pattern which includes both GaN and SiC reflections. The in-plane lattice mismatch for samples A and B are, therefore, estimated to be $\Delta a/|a| = 3.1\%$ and $\Delta a/|a| = 3.3\%$, respectively. Considering the in-plane lattice mismatch between GaN and SiC crystals (bulk material) is $\Delta a/|a| = 3.48\%$, we found the degree of strain relaxation to be 90% and 95% for samples A and B, respectively. It is clear that for the same thickness of GaN layer, it is easier to achieve lattice and/or thermal relaxation when grown on PSiC substrate, even with the presence of a skin layer.

The effect of a skin layer is significant on the dislocation distribution. First, we examine sample C, which is GaN grown on PSiC with a skin layer. The dislocation density is about $5\times10^{9}\ cm^{-2}$ for a GaN thickness up to 1.40 $\mu$m, as can be seen in Fig. 3(a). However, when the nonporous skin layer is removed from the PSiC surface, the growth quality of GaN epilayer has significantly improved. As shown for sample D in Fig. 3(b), the dislocation density near the top of

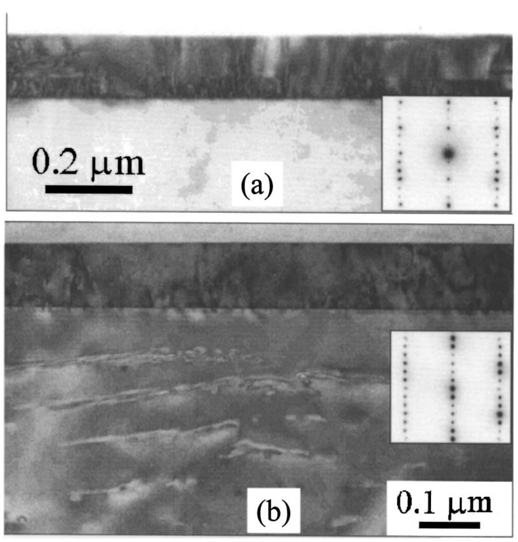


FIG. 2. Cross-sectional TEM images for (a) GaN layer (0.15 $\mu$m—sample A) grown on standard 6H–SiC substrate, and (b) GaN layer (0.11 $\mu$m—sample B) grown on PSiC substrate with skin layer. The insets show the electron diffraction patterns for GaN layer and the SiC substrates.

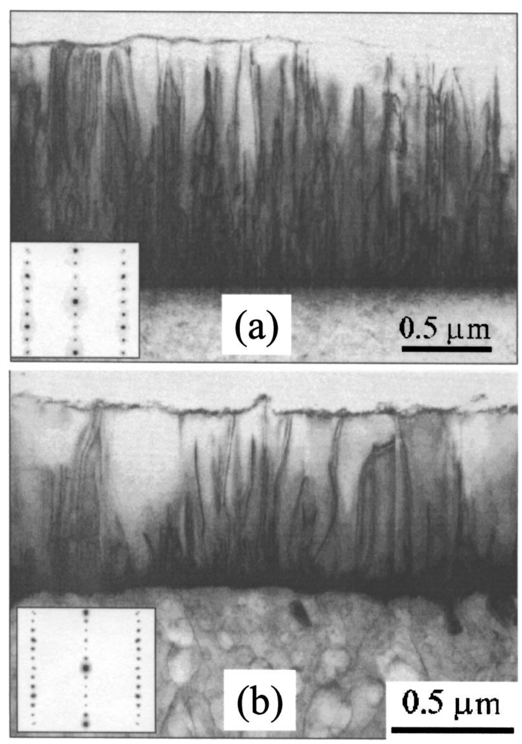


FIG. 3. Cross-sectional TEM images for (a) GaN layer (1.40 $\mu$m—sample C) grown on PSiC substrate with skin layer, and (b) GaN layer (0.77 $\mu$m—sample D) grown on PSiC substrate after the skin layer removal by high-temperature (1700 °C) anneal for 1 min. The insets show the electron diffraction patterns for GaN layer and the PSiC substrates.

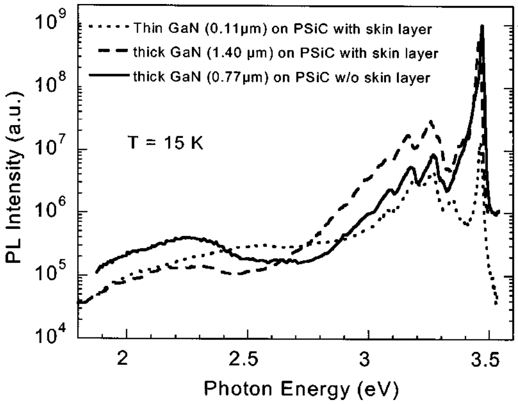


FIG. 4. Low-temperature PL spectra of GaN samples B, C, and D. Sample D shows the best PL results with the narrowest FWHM of excitonic peak (9.5 meV).

a 0.77 $\mu$m GaN grown on PSiC without a skin layer has been reduced to $\sim 1\times 10^9$ cm$^{-2}$. If the same layer were grown to a thickness of 1.40 $\mu$m, it can be predicted that the dislocation density will be further reduced. The effect of the H annealing at a high temperature can be clearly observed in Fig. 3(b). Many pores extend to the surface where the AlN buffer layer and GaN epilayer were grown, though the interface is greatly roughened due to the presence of a large quantity of pores exposed on the surface after etching. It can be also observed that some of the exposed pores are backfilled with Al and/or Ga droplets during the MBE growth (dark area inside pores). For samples C and D, the electron diffraction patterns indicate 100% relaxation based on the measured value of $\Delta a/|a|=3.6\%$ for both. As discussed in Ref. 5, when $\Delta a/|a|$ exceeds the strain-free value (3.48%), the GaN film is likely to be slightly under tensile strain. It is also possible that the lattice constant of PSiC is slightly different from SiC, as is the case with porous Si material.

A tentative growth mechanism can be suggested, though speculative at this juncture, for GaN growth on PSiC. At the beginning of growth, AlN buffer grows on the nonporous regions of SiC, followed by GaN growth on top of the AlN columns. This is supported by the observation of open tubes in the initial stages of GaN growth, especially on the tilted PSiC substrates.[5,12] As the growth progresses, lateral epitaxy is enhanced, and the open tubes are closed at the upper part of the GaN layer. These tubes may serve as a relief mechanism of strain caused by the lattice and thermal mismatch during growth. In addition, some threading dislocations start to bend, merge, and bury in the midlayer.

The crystalline quality of GaN grown on PSiC substrate was accessed by high-resolution x-ray diffraction (XRD) rocking curve ($\omega$ scan). The best full width at half maximum (FWHM) of the (0002) rocking curve diffraction obtained (sample B) was 3.3 arcmin, and that of $(10\bar{1}2)$ was 13.7 arcmin. This implies that device quality GaN film can be achieved in thin layers grown on PSC substrate.

Moreover, low-temperature photoluminescence (PL) measurements indicate a good quality of GaN films grown on PSiC substrates. Figure 4 shows the PL spectra measured at 15 K for samples B, C, and D. The spectra show the best FWHM of GaN excitonic peak to be $\sim$9.5 meV for GaN grown on PSiC with the skin layer removed (sample D), while GaN films with the skin layer exhibit FWHMs of 14–16 meV (samples B and C). The quantum efficiency of PL from thicker layers (samples C and D, both with and without skin layer) is quite high (about 1.6%), whereas that from the thin layer is low (about 0.1%), indicating a reduction of nonradiative defects (presumably dislocations) in thicker layers. The highest optical quality of sample D from PL spectra agrees with the lowest dislocation density ($\sim 1\times 10^9$ cm$^{-2}$) of this GaN layer grown on top of the porous SiC with the skin layer removed.

In conclusion, we have grown GaN epitaxial layers using PSiC substrates, both with and without the nonporous skin layer, by reactive MBE using an ammonia source. Discernable reduction in dislocation density was demonstrated in GaN grown on a PSiC template especially with the skin layer removed prior to the growth of GaN. Specifically, the dislocation density is reduced by an order of magnitude (to $\sim 1\times 10^9$ cm$^{-2}$) when compared with GaN grown on standard 6H–SiC substrates. The narrow linewidth from x-ray rocking curves, and high-quality PL spectra indicate an improved quality of GaN films grown on porous SiC substrates.

The authors would like to thank Dr. C. D. Lee and Professor R. M. Feenstra for cutting and H etching of SiC substrates. The work at both institutions (VCU and SUNY) was funded under a DoD DURINT program and monitored by C. E. C. Wood of ONR. The work at VCU also benefited from grants by AFOSR, NSF and ONR.

[1] M. Mynbaeva, S. E. Saddow, G. Melnychuk, I. Nikitina, M. Scheglov, A. Sitnikova, N. Kuznetsov, K. Mynbaev, and V. Dmitriev, Appl. Phys. Lett. **78**, 117 (2001).
[2] S. E. Saddow, M. Mynbaeva, W. J. Choyke, S. Bai, G. Melnychuk, Y. Koshka, V. Dimitriev, and C. E. C. Wood, Mater. Sci. Forum **353**, 115 (2001).
[3] X. Li, Y.-W. Kim, P. W. Bohn, and I. Adesida, Appl. Phys. Lett. **80**, 980 (2002).
[4] K. Kusakabe, A. Kikuchi, and K. Kishino, J. Cryst. Growth **237**, 988 (2002).
[5] C. K. Inoki, T. S. Kuan, C. D. Lee, A. Sagar, and R. M. Feenstra, Mater. Res. Soc. Symp. Proc. **722**, K1.3 (2002).
[6] J. E. Spanier, G. T. Dunne, L. B. Rowland, and I. P. Herman, Appl. Phys. Lett. **76**, 3879 (2000).
[7] K. Kusakabe, A. Kikuchi, and K. Kishino, Jpn. J. Appl. Phys., Part 2 **40**, L192 (2001).
[8] M. Mynbaeva, A. Titkov, A. Kryganovskii, V. Ratnikov, K. Mynbaev, H. Huhtinen, R. Laiho, and V. Dmitriev, Appl. Phys. Lett. **76**, 1113 (2000).
[9] M. Mynbaeva, A. Titkov, A. Kryzhanovski, I. Kotousova, A. S. Zubrilov, V. V. Ratnikov, V. Y. Davydov, N. I. Kuznetsov, K. Mynbaev, D. V. Tsvetkov, S. Stepanov, A. Cherenkov, and V. A. Dmitriev, MRS Internet J. Nitride Semicond. Res. **4**, 14 (1999).
[10] PSiC substrates from TDI, Inc., Silver Spring, MD 20904.
[11] A. Sagar, C. D. Lee, R. M. Feenstra, C. K. Inoki, and T. S. Kuan, J. Appl. Phys. **92**, 4070 (2002).
[12] F. Yun, M. A. Reshchikov, L. He, T. King, D. Huang, H. Morkoç, C. K. Inoki, and T. S. Kuan, Mater. Res. Soc. Symp. Proc. **719**, F1.3 (2002).