Suppressing the Initial Growth of Sidewall GaN by Modifying Micron-Sized Patterned Sapphire Substrate with H$_3$PO$_4$-Based Etchant

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Abstract: Micron-sized patterned sapphire substrates (PSS) are used to improve the performance of GaN-based light-emitting diodes (LEDs). However, the growth of GaN is initiated not only from the bottom c-plane but also from the sidewall of the micron-sized patterns. Therefore, the coalescence of these GaN crystals creates irregular voids. In this study, two kinds of nucleation layers (NL)—ex-situ AlN NL and in-situ GaN NL—were used, and the growth of sidewall GaN was successfully suppressed in both systems by modifying the micron-sized PSS surface.

Keywords: micron-sized patterned sapphire substrate; growth of GaN; sidewall GaN

1. Introduction

High-brightness GaN-based light-emitting diodes (LEDs) are used in a wide variety of applications [1,2]. However, a GaN epitaxial layer usually contains several defects due to the large lattice mismatch and the thermal expansion coefficient difference between GaN and sapphire.

An AlN (or GaN) nucleation layer (NL) is commonly introduced prior to growth of GaN epilayer to overcome this lattice mismatch problem [3,4]. Moreover, micron-sized patterned sapphire substrates (PSS) have been successfully used to reduce these defects and enhance the performance of LEDs [5–12].

When PSS are used, the growth of GaN is initiated not only from the bottom c-plane but also from the sidewall of the micron-sized patterns [13–16]. As the growth time increases, irregular voids are created during the coalescence of these GaN crystals [17].

A GaN NL is usually deposited by metal–organic chemical vapor deposition (MOCVD), and it is called in-situ GaN NL. An AlN NL can be deposited either by MOCVD or sputtered physical vapor deposition (PVD), and they are generally called in-situ AlN NL and ex-situ AlN NL, respectively. It has been found that ex-situ sputtered AlN NL has better GaN quality than in-situ GaN NL and in-situ AlN NL [15,18].

In this study, sulfuric–phosphoric acid was used to modify the micron-sized patterns in order to suppress the growth of sidewall GaN. The effect of this modification on the growth mechanism of GaN was also investigated.
2. Materials and Methods

In this study, commercial dry etching c-plane micron-sized PSS (2.8 μm width and 0.2 μm spacing) was modified. As shown in Figure 1, two kinds of PSS samples were used to investigate the effect of modification of micron-sized PSS patterns on the GaN growth mechanism: (1) RPSS (regular PSS without etching) and (2) PSSE (RPSS etched in sulfuric–phosphoric acid (ratio 3:1) at 270 °C for 30 s). As shown in Figure 1b, 3T {1105} facets were observed on the pattern of PSSE [19–23].

Two kinds of nucleation layers (NL) were used: (1) ex-situ AlN NL and (2) in-situ GaN NL. To fabricate ex-situ AlN NL, 40 nm AlN was deposited by RF-sputter system using Al target in N2 gas at 650 °C. As for the in-situ GaN NL, an in-situ 25-nm-thick low-temperature GaN layer was deposited at 550 °C by MOCVD.

As shown in Table 1, four kinds of micron-sized PSS samples were then used to investigate the effect of modification of PSS patterns on the GaN growth mechanism: (1) AlNR (RPSS with AlN NL); (2) AlNE (PSSE with AlN NL); (3) GaNR (RPSS with GaN NL); and (4) GaNE (PSSE with GaN NL).

To investigate the GaN epitaxial behavior, high-temperature undoped GaN (HTU-GaN) was grown by MOCVD at 1060 °C with chamber pressure of 200 torr (26,664 Pa) for 2 min.

3. Results

Figure 2 shows the surface morphologies of micron-sized PSS after GaN was grown. The morphologies of bottom GaN (B-GaN) and sidewall GaN (S-GaN) were different. There were two kinds of B-GaN: (1) B3-GaN (GaN grown among three micron-sized patterns) and (2) B2-GaN (GaN grown between two patterns). Two kinds of S-GaN were found: (1) S3-GaN (with AlN as NL; Figure 2a) and (2) S6-GaN (with GaN as NL; Figure 2c). To measure the thicknesses of B-GaN and S-GaN, cross-sectional SEM was carried out by focused ion beam (FIB) cutting along the dash lines as shown in Figure 2a,c. Some of the related images are shown in Figure 3, and the measured maximum thicknesses are summarized in Table 2.
As shown in Figures 2b, 3b, and Table 2, compared with AlNR, the thickness of B3-GaN was increased. Moreover, as shown in Figure 3b, irregular voids (circled with dashed lines) were observed. However, with the modification of PSS patterns (AlNE), the thickness of S3-GaN of AlNE did not diminish but decreased from 520 to 136 nm, and H was established as a constant.

As shown in Figure 3a, no void was found among GaN crystals as there was no coalescence yet. This observation suggested that instead of reducing the reaction constant of S3-GaN, the mass transport was the same for all the samples when ex-situ AlN NL was used, as shown in Figure 2a, two kinds of GaN were found on AlNR. In a reaction between A and B to give products C and D, the following applies according to the balance equation:

\[ \text{Rate} = K [A]^x [B]^y \]

where K is the rate constant; the numbers x and y are partial orders of reaction.

The measured maximum thicknesses of GaN. As GaN was grown in the same conditions.

| GaN Type | AlNR | AlNE | GaNR | GaNE |
|----------|------|------|------|------|
| Thickness (nm) | 520 | 54 | 540 | 776 |
| K | 157 | 951 |

Table 2. The measured maximum thicknesses of GaN.

Figure 2. SEM images of GaN grown on (a) AlNR, (b) AlNE, (c) GaNR, and (d) GaNE.

Figure 3. Cross-sectional SEM images from Figure 2. (a) AlNR, (b) AlNE, (c) GaNR, and (d) GaNE.
Table 2. The measured maximum thicknesses of GaN.

| Thickness (nm) | GaN Type | AlNR | AlNE | AlNOE | GaNR | GaNE | GaNOE |
|---------------|----------|------|------|-------|------|------|-------|
| H_{B3-GaN}   | 520      | 136  | 540  | 1261  | 616  | 969  |
| H_{B2-GaN}   | 520      | 54   | 540  | 776   | 157  | 951  |
| H_{S3-GaN}   | 74       | 250  | 0    | 0     | 0    | 0    |
| H_{S6-GaN}   | 0        | 0    | 0    | 371   | 641  | 0    |

4. Discussion

A simple treatment of the MOCVD thin-film growth kinetic involves mass transport and reaction [24,25]. It is reasonable to assume that the mass transport was the same for all the samples as GaN was grown in the same conditions.

In a reaction between A and B to give products C and D, the following applies according to the balance equation:

\[aA + bB \rightarrow cC + dD\] (1)

The reaction is related to the reactant concentrations in the following way:

\[\text{Rate} = K [A]^x [B]^y\] (2)

where K is the rate constant; the numbers x and y are partial orders of reaction.

In this case, there were four surface reaction constants: (1) sidewall with AlN (K_{SAlN}), (2) bottom with AlN (K_{BAlN}), (3) sidewall with GaN (K_{SGaN}), and (4) bottom with GaN (K_{BGaN}).

4.1. Ex-Situ AlN as NL

When ex-situ AlN NL was used, as shown in Figure 2a, two kinds of GaN were found on AlNR. B-GaN was initiated from the bottom c-plane as expected, while S-GaN (S_{3-GaN}) was from sidewall surfaces, which has been reported earlier [14,15,26,27]. Both B-GaN and S_{3-GaN} were Wurtzite structures. The orientation relationship between GaN (including B-GaN and S_{3-GaN}) and sapphire was established as (0001)_{GaN} // (0001) sapphire and [11\overline{2}0]_{GaN} // [1\overline{1}00]_{sapphire}.

As shown in Figure 3a, no void was found among GaN crystals as there was no coalescence yet between S-GaN and B-GaN.

Table 2 and Figure 3a show that the maximum thicknesses of B_{3-GaN} (H_{B3-GaN}) and B_{2-GaN} (H_{B2-GaN}) of AlNR were around 520 nm, which was much thicker than that of S_{3-GaN} (H_{S3-GaN}, 74 nm), indicating that K_{BAIN} was much greater than K_{S3AlN} [26].

However, with the modification of PSS patterns (AlNE), H_{S3-GaN} of AlNE did not diminish but increased. As shown in Figures 2 and 3, and Table 2, compared with AlNR, the H_{S3-GaN} of AlNE increased from 74 to 250 nm. At the same time, H_{B3-GaN} decreased from 520 to 136 nm, and H_{B2-GaN} decreased from 520 to 54 nm.

Moreover, as shown in Figure 3b, irregular voids (circled with dashed lines) were observed between S_{3-GaN} and B_{2-GaN}. These voids were created during the coalescence of GaN crystals [17].

This observation suggested that instead of reducing the reaction constant of S_{3-GaN} (K_{S3AIN}), modification of PSS patterns (AlNE) enhanced K_{SAIN} and reduced K_{BAIN}. As K_{BAIN} should be a constant, we believe this K_{BAIN} reduction should have been caused by the change in the area of the bottom c-plane.

Figure 4 is the high magnifications of (a) RPSS and (b) PSSE. In addition to sidewall facets, an extra six 6B {\{3417\}} facets were found on the bottom of patterns of PSSE [28], as shown in Figure 4b. The appearance of 6B facets reduced the bottom c-plane fraction as determined by estimating the B3 (B2) vs. total area on the SEM images.
we believe this KBAlN reduction should have been caused by the change in the area of the bottom c-plane.

Figure 4 is the high magnifications of (a) RPSS and (b) PSSE. In addition to sidewall facets, an extra six 6B \{3 4 17\} facets were found on the bottom of patterns of PSSE [28], as shown in Figure 4b. The appearance of 6B facets reduced the bottom c-plane fraction as determined by estimating the B3 (B2) vs. total area on the SEM images.

Compared with RPSS, B3 fraction of PSSE reduced from 18% to 12%, while B2 fraction reduced from 3% to 0 %. This reduction of bottom c-plane made epitaxy of GaN film on PSSE very difficult [29]. Consequently, it appeared that the KBAlN of AlNE was much less than that of AlNR.

In addition, compared with AlNR, HS$_3$-GaN of AlNE increased from 74 to 250 nm, as shown in Figures 2b and 3b and Table 2. This is because the consuming of the reactants in front of the bottom c-plane can affect reactant concentrations in front of the sidewall. As shown in Figure 4, the distance between the sidewall and the bottom c-plane was only around 1 \(\mu\)m. As the growth rate of AlNE was much smaller than that of AlNR, the formation of B-GaN of AlNE would consume only a small portion of the reactants. As a result, the reactant concentrations in front of the sidewall of AlNE were increased. Consequently, HS$_3$-GaN of AlNE was thicker than that of AlNR.

4.2. In-Situ GaN as NL

When in-situ GaN NL was used, as shown in Figure 2c, two kinds of GaN were found on AlNR: (1) B-GaN and (2) S6-GaN [13–16]. They were both Wurtzite structures, and the orientation relationship between GaN and sapphire was established as (0001)$_{\text{GaN}}$ // (0001) sapphire and [1\(\bar{1}\)00]$_{\text{GaN}}$ // [1\(\bar{1}\)0\(\bar{0}\)]$_{\text{sapphire}}$.

**Figure 4.** The high magnification SEM images of (a) RPSS, (b) PSSE, and (c) PSSO.
Table 2 and Figure 3c show that $H_{B3-GaN}$ and $H_{B2-GaN}$ of GaNR were 1261 nm and 776 nm, respectively. Their thicknesses were much greater than $H_{S6-GaN}$ (371 nm) [14,27]. In other words, $K_{BGaN}$ was much greater than $K_{S6GaN}$.

We also found that modification of PSS patterns (PSSE) did not diminish the growth of sidewall GaN (S6-GaN). Compared with GaNR, $H_{S6-GaN}$ of GaNE increased from 371 to 614 nm. At the same time, $H_{B3-GaN}$ decreased from 1261 to 616 nm, and $H_{B2-GaN}$ decreased from 776 to 157 nm, as shown in Figure 2 and Table 2. We believe that these thickness changes were also due to the reduction in the bottom c-plane of GaNE.

In both cases, beside voids between S3-GaN and B2-GaN (circled with dashed lines), voids were also found between B3-GaN and B2-GaN (squared with dashed lines). These voids were created during the coalescence of GaN crystals [17].

4.3. Bottom C-Plane Protection

To avoid the reduction of the bottom c-plane areas of micron-sized PSS, the bottom c-plane was protected by SiO$_2$ and then etched with sulfuric–phosphoric acid. This was designated as PSSO. Figure 5 shows the PSSO fabrication processes. Micron-sized RPSS was first deposited with 200-nm-thick SiO$_2$ film (Figure 5a). A photoresist (PR) layer was spun onto the surface to protect the bottom oxide (B-OX). Sidewall oxide (S-OX) and PR were then removed, as shown in Figure 5b,c. Samples were etched in sulfuric–phosphoric acid at 270 °C for 30 s. B-oxide was then removed (Figure 5e).

![Figure 5. The flow charts of PSSO fabrication processes.](image)

Figure 4c is the high magnification of the PSSO surface. Only sidewall 3T facets were found, and no 6B facets were observed. Compared with RPSS, B3 fraction and B2 fraction were the same as those of RPSS. There was no reduction in the bottom c-plane areas of micron-sized PSSO.

Two kinds of PSSO samples were then fabricated to investigate the growth mechanism of GaN: (1) AlNOE (PSSO with AlN NL) and (2) GaNOE (PSSO with GaN NL).

As shown in Table 2 and Figure 6, no S3-GaN was grown from AlNOE, and no S6-GaN was grown from GaNOE either. In both cases, no void was found among GaN crystals, as shown in Figure 7.
As a result, sidewall GaN was successfully suppressed in both NL systems.

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sidewall 3T facets were observed, and no 6B facet appeared. The bottom c-plane areas did not reduce. As a result, sidewall GaN was successfully suppressed in both NL systems.

c-plane PSS. Two kinds of nucleation layers—ex-situ AlN NL and in-situ GaN NL—were introduced prior to growth of GaN epilayer. After etching, three 3T \{1\overline{1}05\} facets were found on the pattern sidewall. At the same time, six 6B \{3\overline{4}17\} facets were observed on the bottom of the patterns. The appearance of 6B facets reduced the bottom c-plane fraction, which made epitaxy of GaN on bottom c-plane very difficult. Consequently, instead of reducing the growth of sidewall GaN, this modification appeared to enhance the growth of GaN from the sidewall of the patterns.

A 200-nm-thick SiO$_2$ film was used to protect the bottom c-plane areas. After etching, only sidewall 3T facets were observed, and no 6B facet appeared. The bottom c-plane areas did not reduce. As a result, sidewall GaN was successfully suppressed in both NL systems.

5. Conclusions

In this study, the growth of sidewall GaN was successfully suppressed by modifying the surface of micron-sized PSS. Sulfuric–phosphoric acid was used to modify the surface of dry etching c-plane PSS. Two kinds of nucleation layers—ex-situ AlN NL and in-situ GaN NL—were introduced prior to growth of GaN epilayer.

After etching, three 3T \{1\overline{1}05\} facets were found on the pattern sidewall. At the same time, six 6B \{3\overline{4}17\} facets were observed on the bottom of the patterns. The appearance of 6B facets reduced the bottom c-plane fraction, which made epitaxy of GaN on bottom c-plane very difficult. Consequently, instead of reducing the growth of sidewall GaN, this modification appeared to enhance the growth of GaN from the sidewall of the patterns.

A 200-nm-thick SiO$_2$ film was used to protect the bottom c-plane areas. After etching, only sidewall 3T facets were observed, and no 6B facet appeared. The bottom c-plane areas did not reduce. As a result, sidewall GaN was successfully suppressed in both NL systems.

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References

1. Mukai, T.; Nagahama, S.; Sano, M.; Yamamoto, T.; Morita, D.; Mitani, T.; Narukawa, Y.; Yamamoto, S.; Niki, I.; Yamada, M.; et al. Recent progress of nitride-based light emitting devices. Phys. Status Solidi A 2003, 200, 52–57. [CrossRef]

2. Mukai, T.; Yamada, M.; Nakamura, S. Characteristics of InGaN-based UV/blue/green/amber/red light-emitting diodes. Jpn. J. Appl. Phys. 1999, 38, 3976–3981. [CrossRef]

3. Amano, H.; Sawaki, N.; Akasaki, I.; Toyoda, Y. Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer. Appl. Phys. Lett. 1986, 48, 353–355. [CrossRef]

4. Nakamura, S.; Mukai, T.; Senoh, M. In situ monitoring and Hall measurements of GaN grown with GaN buffer layers. J. Appl. Phys. 1992, 71, 5543–5549. [CrossRef]

5. Wuu, D.S.; Wang, W.K.; Wen, K.S.; Huang, S.C.; Lin, S.H.; Horng, R.H.; Yu, Y.S.; Pan, M.H. Fabrication of pyramidal patterned sapphire substrates for high-efficiency InGaN-based light emitting diodes. J. Electrochem. Soc. 2006, 153, G765–G770. [CrossRef]

6. Lee, J.H.; Oh, J.T.; Kim, Y.C.; Lee, J.H. Stress reduction and enhanced extraction efficiency of GaN-based LED grown on cone-shape-patterned sapphire. IEEE Photonics Technol. Lett. 2008, 20, 1563–1565. [CrossRef]

7. Tsai, C.H.; Ma, M.H.; Yin, Y.F.; Li, H.W.; Lai, W.C.; Huang, J. Nanoscale epitaxial lateral overgrowth of GaN-based light-emitting diodes on an AlN nanorod-array template. IEEE J. Quantum Electron. 2015, 51, 2006–2009. [CrossRef]

8. Lin, H.C.; Lin, R.S.; Chyi, J.I.; Lee, C.M. Light output enhancement of InGaN light-emitting diodes grown on Masklessly etched sapphire substrates. IEEE Photonics Technol. Lett. 2008, 20, 1621–1623. [CrossRef]

9. Hsieh, C.Y.; Lin, B.-W.; Cho, H.-J.; Wang, B.-M.; Sermon Wu, Y. Investigation of GaN Films Grown on Liquid-Phase Deposited SiO2 Nanopatterned Sapphire Substrates. ECS J. Solid State Sci. Technol. 2012, 1, Q35–Q37. [CrossRef]

10. Lee, Y.J.; Hsu, T.C.; Kuo, H.C.; Wang, S.C.; Yang, Y.L.; Yen, S.N.; Chu, Y.T.; Shen, Y.J.; Hsieh, M.H.; Jou, M.J.; et al. Improvement in light-output efficiency of near-ultraviolet InGaN-GaN LEDs fabricated on stripe patterned sapphire substrate. Mater. Sci. Eng. B 2005, 122, 184–187. [CrossRef]

11. Feng, Z.H.; Lau, K.M. Enhanced luminescence from GaN-based blue LEDs grown on grooved sapphire substrates. IEEE Photonics Technol. Lett. 2005, 17, 1812–1814. [CrossRef]

12. Lee, Y.J.; Hsu, T.C.; Kuo, H.C.; Wang, S.C.; Yang, Y.L.; Yen, S.N.; Chu, Y.T.; Shen, Y.J.; Hsieh, M.H.; Jou, M.J.; et al. Enhancing the output power of GaN-based LEDs grown on wet-etched patterned sapphire substrates. IEEE Photonics Technol. Lett. 2006, 18, 1152–1154. [CrossRef]

13. Zhou, S.; Hu, H.; Liu, X.; Liu, M.; Ding, X.; Gui, C.; Liu, S.; Guo, L.J. Comparative study of GaN-based ultraviolet LEDs grown on different-sized patterned sapphire substrates with sputtered AlN nucleation layer. Jpn. J. Appl. Phys. 2017, 56, 111001. [CrossRef]

14. He, C.; Zhao, W.; Zhang, K.; He, L.; Wu, H.; Liu, N.; Zhang, S.; Liu, X.; Chen, Z. High-Quality GaN Epilayers Achieved by facet-Controlled Epitaxial Lateral Overgrowth on Sputtered AlN/PSS Templates. ACS Appl. Mater. Interfaces 2017, 9, 43386–43392. [CrossRef] [PubMed]

15. Hu, H.; Zhou, S.; Liu, X.; Gao, Y.; Gui, C.; Liu, S. Effects of GaN/AlGaN/Sputtered AlN nucleation layers on performance of GaN-based ultraviolet light-emitting diodes. Sci. Rep. 2017, 7, 1–10. [CrossRef] [PubMed]

16. Chen, S.-W.; Yang, Y.; Wen, W.-C.; Li, H.; Lu, T.-C. Significant improvement of GaN crystal quality with ex-situ sputtered AlN nucleation layers. Int. Soc. Opt. Photonics 2016, 9768, 97681D. [CrossRef]
17. Chang, L.C.; Chen, Y.A.; Kuo, C.H. Spatial correlation between efficiency and crystal structure in GaN-based light-emitting diodes prepared on high-aspect ratio patterned sapphire substrate with sputtered AlN nucleation layer. *IEEE Trans. Electron Devices* 2014, 61, 2443–2447. [CrossRef]

18. Lai, W.C.; Yen, C.H.; Yang, Y.Y.; Wang, C.K.; Chang, S.J. GaN-Based ultraviolet light emitting diodes with Ex situ sputtered AlN nucleation layer. *IEEE/OSA J. Disp. Technol.* 2013, 9, 895–899. [CrossRef]

19. Chen, Y.-C.; Hsiao, F.-C.; Lin, B.-W.; Wang, B.-M.; Sermon Wu, Y.; Hsu, W.-C. The Formation and the Plane Indices of Etched Facets of Wet Etching Patterned Sapphire Substrate. *J. Electrochem. Soc.* 2012, 159, D362. [CrossRef]

20. Shen, J.; Zhang, D.; Wang, Y.; Gan, Y. AFM and SEM Study on Crystallographic and Topographical Evolution of Wet-Etched Patterned Sapphire Substrates (PSS). *ECS J. Solid State Sci. Technol.* 2017, 6, R24–R34. [CrossRef]

21. Shen, J.; Zhang, D.; Wang, Y.; Gan, Y. AFM and SEM Study on Crystallographic and Topographical Evolution of Wet-Etched Patterned Sapphire Substrates (PSS). *ECS J. Solid State Sci. Technol.* 2017, 6, R122–R130. [CrossRef]

22. Lee, Y.J.; Chiu, C.H.; Kuo, H.C.; Lu, T.C.; Wang, S.C.; Ng, K.W.; Lau, K.M.; Yang, Z.P.; Chang, S.P.; Lin, S.Y. Simultaneously enhancing internal and extraction efficiencies of GaN-based light emitting diodes via chemical-wet-etching patterned-sapphire-substrate (CWE-PSS). *ECS Trans.* 2007, 11, 225–230. [CrossRef]

23. Plummer, J.D.; Deal, M.D.; Griffin, P.B. *Silicon VLSI Technology Fundamentals, Practice and Modeling*, 1st ed.; Prentice Hall: Upper Saddle River, NJ, USA, 2000; p. 514.

24. Ravasio, S.; Momose, T.; Fujii, K.; Shimogaki, Y.; Sugiyama, M.; Cavallotti, C. Analysis of the gas phase kinetics active during GaN deposition from NH₃ and Ga(CH₃)₃. *J. Phys. Chem. A* 2015, 119, 7858–7871. [CrossRef] [PubMed]

25. Wu, P.-Y.; Li, J.-H.; Hsu, L.-H.; Huang, C.-Y.; Cheng, Y.-J.; Kuo, H.-C.; Wu, Y.S. Effect of Sputtered AlN Location on the Growth Mechanism of GaN. *ECS J. Solid State Sci. Technol.* 2017, 6, R131–R134. [CrossRef]

26. Shang, L.; Zhai, G.; Mei, F.; Jia, W.; Yu, C.; Liu, X.; Xu, B. The effect of nucleation layer thickness on the structura evolution and crystal quality of bulk GaN grown by a two-step process on cone-patterned sapphire substrate. *J. Cryst. Growth* 2016, 442, 89–94. [CrossRef]

27. Hsueh, H.H.; Ou, S.L.; Cheng, C.Y.; Wuu, D.S.; Horng, R.H. Performance of InGaN light-emitting diodes fabricated on patterned sapphire substrates with modified top-tip cone shapes. *Int. J. Photoenergy* 2014. [CrossRef]

28. Chen, C.-C.; Hsiao, F.C.; Lin, B.-W.; Hsu, W.-C.; Wu, Y.S. Evolution of Bottom c-Plane on Wet-Etched Patterned Sapphire Substrate. *ECS J. Solid State Sci. Technol.* 2013, 2, R169–R171. [CrossRef]