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The Formation of The Hexagonal Pyramid Facets on Wet Etching Patterned Sapphire Substrate

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Currently, the wet etching patterned sapphire substrate (PSS) has attracted much attention for its high production yield. After etching in hot mixed H_2SO_4 and H_3PO_4 solution, the several etched facets were exposed on sapphire substrate. In this study, a series of etching process was used to investigate the formation. As shown in Fig. 1, when SiO_2 mask still remained, the structure of PSS comprised of six facets { $3\bar{4}17$ }. When SiO_2 mask were etched away, beside six facets, there were three extra facets { $1\bar{1}05$ } exposed on the top.

Introduction

Light-emitting diodes (LEDs) are expected to play an important role in next-generation light source. Many techniques have been developed to improve GaN-based LEDs internal quantum efficiency (IQE) and light extraction efficiency (LEE), such as epitaxial lateral overgrowth, surface roughing, metal mirror reflect layer and patterned sapphire substrate (PSS). (1-9) Currently, the PSS technique has attracted much attention for its high production yield. Besides, using the PSS technique can improve both IQE and LEE. (10-15) Two kinds of etching methods have been used to fabricate PSS:(1) dry etching and (2) wet etching. Compared to dry etching, wet etching did not have ion bombardment caused damage problem. (16,17)

In wet etching, after etching, several etched facets were exposed. These facets have been identified differently as n-like plane, (18,19) r-like plane, (13,20) and mixture of m-, r- and a-like plane. (21) It has been found beside normal wurtzite GaN, zincblende GaN has been found on these planes of PSS. (17) In this study, the formation and plane indices of these exposed etched facets were investigated by H_3PO_4 -based etching process.

Experimental

A 400-nm-thick SiO_2 was deposited on the c-plane sapphire substrate by plasma-enhanced chemical vapor deposition. The substrate with periodic dot array patterns was prepared by photolithography. The substrate with SiO_2 mask was immersed in a H_3PO_4 -based etchant at 270 for various times (12, 14 and 16 min). They were denoted as 12-, 14- and 16-PSS.

Results and Discussion

Figure 1 shows the top-view and cross-sectional SEM images of 12-, 14- and 16-PSS respectively. The structure of 12-PSS comprises of a hexagonal pyramid covered with six facets with a flat top c-plane. These six planes were designated "6-bottom" (6B) planes. The slanted angle between the intersections of 6B planes and c-plane was around 57.3°.

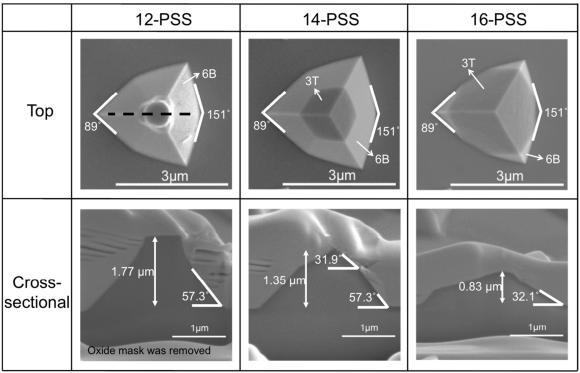


Figure 1. Top-view and cross-sectional SEM images of 12-, 14- and 16-PSS. The cross-section image indicated by dash lines along $(1\overline{2}10)$.

No top c-plane was found on 14-PSS structure. In addition to 6B facets, three facets were found on the top of 6B facets. These three facets were designated "3-top" (3T) planes and the slanted angle between the 3T planes and c-plane was around 31.9° while the angle of the 6B planes was still around 57.3°.

As the etching time increased, the areas of 3T facets increased and at the same time those of 6B decreased. When etching time reached 16 min, only few 6B facets were left. The angle of the 3T planes was around 32.1° .

The increase of 3T areas (decrease of 6B areas) might have resulted from the removing of SiO_2 hard mask during the etching process since H_3PO_4 can etch SiO_2 and sapphire simultaneously. (20,22)

The sapphire etching mechanism was schematically illustrated in Figure 2. When the SiO_2 mask still remained on the top c-plane, the 6B planes were more stable than bottom c-plane in the etching process. The size (height) of pyramid increased with the etching time. When SiO_2 mask was gone (etched away), top c-plane was also etched by H_3PO_4 -based solution. At the same time, 3T facets appeared. As the etching time increased, the height of pyramid decreased and the 3T areas increased. Besides, it is worthy to note that the slanted angles of 6B and 3T planes did not change with the etching time as shown in Figure 1.

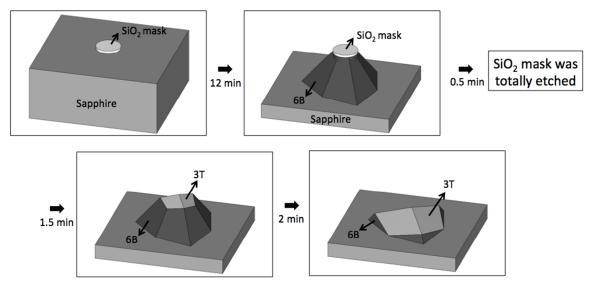


Figure 2. Schematic illustrations of etching process

The detailed analysis of the hexagonal pyramid is illustrated in Figure 3. The intercepts of the 6B plane on the a_1 , a_3 and c axes are about 3.000, 8.196 and 3.514 units. In hexagonal crystals, the Miller-Bravais indices of a plane are denoted by (*hkil*). These indices are the reciprocals of intercepts on the a_1 , a_2 , a_3 and c, respectively. The additional condition which their values must satisfy is h+k=-i. Then, take the reciprocals of these numbers in Figure 3, and multiplied with sapphire's unit length (a=4.759Å and c=12.991Å). (23) The calculated Miller-Bravais index of 6B is $\{3\overline{4}17\}$. Using the same method, the intercepts of the 3T plane on the a_1 , a_2 and c axes are about 4.914, -4.914 and 2.558 units and its index is $\{1\overline{1}05\}$.

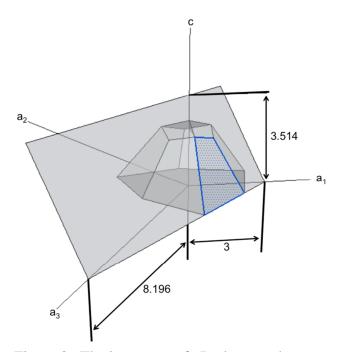


Figure 3. The intercepts of 6B plane on the axes.

Conclusion

In this study was found that when SiO_2 mask remained on the top c-plane sapphire, the PSS has a three-dimensional structure, which is composed of a hexagonal pyramid covered with six 6B facets. The plain indices of 6B were $\{3\overline{4}17\}$. When SiO_2 mask were etched away, three 3T facets were found on the top of 6B facets. The plain indices of 3T were $\{1\overline{1}05\}$.

Acknowledgments

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References

- 1. A. Sakai, H. Sunakawa and A. Usui, Appl. Phys. Lett., **71**, 2259 (1997).
- 2. K. Linthicum, T. Gehrke, D. Thomson, E. Carlson, P. Rajagopal, T. Smith, D. Batchelor and R. Davis, Appl. Phys. Lett., **75**, 196 (1999).
- 3. M. Boroditsky and E. Yablonovitch, Proc. SPIE, 3002, 119 (1997).
- 4. W. C. Peng and Y. S. Wu, Appl. Phys. Lett., 88, 18117 (2006).
- 5. C. E. Lee, Y. J. Lee, H. C. Kuo, M. R. Tsai, B. S. Cheng, T. C. Lu, S. C. Wang and C. T. Kuo, IEEE Photon. Technol. Lett., **19**, 1200 (2007).
- 6. H. W. Huang, C. H. Lin, C. C. Yu, B. D. Lee, C. H. Chiu, C. F. Lai, H. C. Kuo, K. M. Leung, T. C. Lu and S. C. Wang, Nanotechnology, **19**, 185301 (2008).
- 7. Y. S. Wu, C. Liao and W. C. Peng, Electrochem. Solid-State Lett., 10, J126 (2007).
- 8. D. S. Han, J. Y. Kim, S. I. Na, S. H. Kim, K. D. Lee, B. Kim and S. J. Park, IEEE Photon. Technol. Lett., **18**, 1406 (2006).
- S. J. Chang, C. S. Chang, Y. K. Su, R. W. Chuang, W. C. Lai, C. H. Kuo, Y. P. Hsu, Y. C. Lin, S. C. Shei, H. M. Lo, J. C. Ke and J. K. Sheu, IEEE Photon. Technol. Lett., 16, 1002 (2004).
- 10. D. S. Wuu, W. K. Wang, W. C. Shih, R. H. Horng, C. E. Lee, W. Y. Lin and J. S. Fang, IEEE Photon. Technol. Lett., **17**, 288 (2005).
- 11. Z. H. Feng and K. M. Lau, IEEE Photon. Technol. Lett., 17, 1812 (2005).
- 12. Y. J. Lee, T. C. Hsu, H. C. Kuo, S. C. Wang, Y. L. Yang, S. N. Yen, Y. T. Chu, Y. J. Shen, M. H. Hsieh, M. J. Jou and B. J. Lee, Mater. Sci. Eng. B, **122**, 184 (2005).
- 13. Y. J. Lee, J. M. Hwang, T. C. Hsu, M. H. Hsieh, M. J. Jou, B. J. Lee, T. C. Lu, H. C. Kuo and S. C. Wang, IEEE Photon. Technol. Lett., **18**, 1152 (2006).
- 14. K. Tadatomo, H. Okagawa, Y. Ohuchi, T. Tsunekawa, Y. Imada, M. Kato and T. Taguchi, J. Jpn. Appl. Phys., **40**, L583 (2001).
- 15. M. Yamada, T. Mitani, Y. Narukawa, S. Shioji, I. Niki, S. Sonobe, K. Deguchi, M. Sano and T. Mukai, J. Jpn. Appl. Phys., **41**, L1431 (2002).
- 16. M. Kappelt and D. Bimberg, J. Electrochem. Soc., 143, 3271 (1996).
- 17. J. Wang, L. W. Guo, H. Q. Jia, Z. G. Xing, Y. Wang, H. Chen and J. M. Zhou, J. Jpn. Appl. Phys., **44**, L982 (2005).

- 18. R. M. Lin, Y. C. Lu, S. F. Yu, Y. S. Wu, C. H. Chiang, W. C. Hsu and S. J. Chang, J. Electrochem. Soc., **156**, H874 (2009).
- 19. H. Gao, F. Yan, Y. Zhang, J. Li, Y. Zeng and G. Wang, J. Appl. Phys., **103**, 014314 (2008).
- 20. D. S. Wuu, W. K. Wang, K. S. Wen, S. C. Huang, S. H. Lin, R. H. Horng, Y. S. Yu and M. H. Pan, J. Electrochem. Soc., **153**, G765 (2006).
- 21. S. H. Huang, R. H. Horng, K. S. Wen, Y. F. Lin, K. W. Yen and D. S. Wuu, IEEE Photon. Technol. Lett., **18**, 24 (2006)
- 22. W. V. Gelder and V. E. Hauser, J. Electrochem. Soc., 114, 869 (1967).
- 23. W. E. Lee and K. P. D. Lagerlof, J. Electron Microsc. Tech., **2**, 247 (1985).