Journal of the Korean Ceramic Society
Vol. 41, No. 7, pp. 493~496, 2004.

Sulfuric Acid Treatment of Sapphire Substrates for Growth of High-Quality Epilayers

Ji-Won Choi,* Young-Soo No,*, Yeon-Sik Jung,* Seok-Jin Yoon,***
Tae-Whan Kim, and Won-Kook Choi*,†**

**Thin Film Materials Research Center, Korea Institute of Science and Technology, Seoul 130-650, Korea*
***Division of Electrical and Computer Engineering, Hanyang University, Seoul 133-791, Korea*

(Received March 17, 2004; Accepted June 2, 2004)

ABSTRACT

The chemical etching of sapphire substrates was performed to produce smooth surfaces on an atomic scale. The sapphire surface etched by using a H_2SO_4 solution showed a pit-free morphology and was very smooth as much as σ_{rms}=0.13 nm, that etched by using a mixture of H_2SO_4 and H_3PO_4 contained large pits with σ_{rms}=0.34 nm. The σ_{rms}'s and the number of the pits increased with increasing etching temperature. The sapphire etched by using H_2SO_4 at 320°C had the best surface. These results provide important information on the effects of etching treatment on the structural properties of sapphire for the growth of high-quality epilayers.

Key words : Chemical etching of sapphire, Pit-free morphology, H_2SO_4

1. Introduction

Potential applications of GaN or ZnO thin films in electronic and optoelectronic devices, such as light emitting diodes, laser diodes, and ultraviolet detectors, have driven extensive efforts to improve film qualities for the last two decades.[1,2] The achievement of high-quality GaN or ZnO epitaxial layers plays an important role in obtaining high efficiencies for optoelectronic devices ranging from the blue to the ultraviolet spectral region. Therefore, suitable substrates, which are lattice matched with GaN or ZnO thin films, have to be chosen and pre-treated to decrease defects and the root-mean-square standard deviation (σ_{rms}) of the average surface roughness. Initial film nucleation can take place preferentially upon the scratches and defects on these substrates. This behavior had been observed in GaN epitaxial growth on sapphire.[3] Defects from the surfaces can propagate into the deposited film and lead to degradation of the optical and electrical properties.

Sapphire has been viewed as an extremely promising substrate for GaN and ZnO epitaxial films because of its chemical compatibility, optical transparency, high-temperature stability, and relatively low price.[4] Even though chemical mechanical polishing treatment of sapphire wafers is necessary to obtain smooth, flat surfaces, this method produces scratches and residual stress on the surface, which generate defects in the thin films grown on the sapphire substrates.

Various etching techniques were introduced to remove the scratches and the residual stress on the sapphire surfaces.[5,6] In particular, an etching method utilizing a mixture of H_2SO_4 and H_3PO_4 (3 : 1) was used to obtain an atomically flat surface. Dwikusuma et al. reported that the sapphire surface etched by using a mixture of H_2SO_4 and H_3PO_4 (3 : 1) contained many pits and that the sapphire etched by using a H_2SO_4 solution at 300°C had a smooth and pit free surface.[6] Since the annealing temperatures for the etching treatment performed by Dwiksuma *et al.* were 100, 200, 300, and 400°C, the annealing intervals were too rough to determine the optimal etching temperature. For these reasons, various etching treatment, as a means of looking for optimal etching conditions for a sapphire surface, were used in this study. The surface morphology and the structural properties were characterized by using Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD) measurements.

2. Experimental Procedure

The sapphire surfaces were alternately degreased in acetone and methanol, rinsed in deionized water thoroughly, and etched in a solution of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C or in a H_2SO_4 solution at various etching temperatures for 30 min. The H_2SO_4 etching solution was heated on a PID (proportional-integral-derivative) controllable hot plate at temperatures between 300 and 350°C. The solution temperature was measured using two thermocouple probes, which were inserted into the solution and the hot plate. The solution was not stirred because some previous studies reported that stirring the solution deteriorated the surface quality.[6,7] Every etching experiment was duplicated at least three

---

[†] Corresponding author : Won-Kook Choi
E-mail : wkchoi@kist.re.kr
Tel : +82-2-958-5562 Fax : +82-2-958-6851

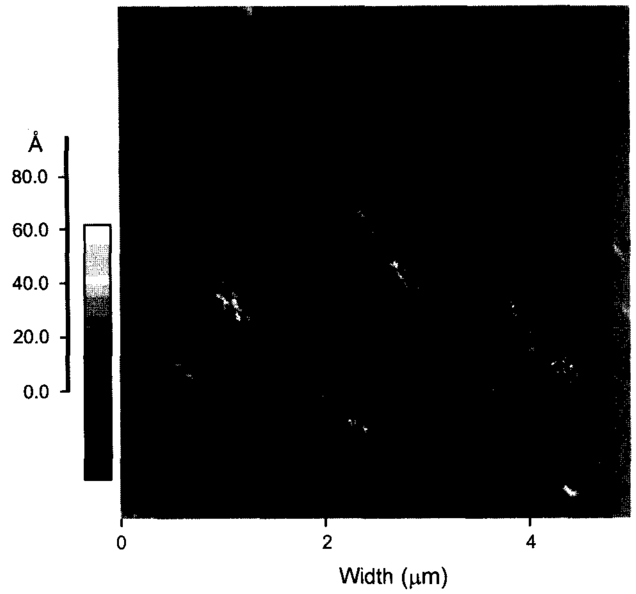

Fig. 1. AFM image of the sapphire surface etched in a mixture of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C for 10 min.

times with a fresh solution.

The surface morphology of the etched sapphire substrate was characterized by using a contact mode AFM (PSI). After the AFM data were taken for multiple locations on several specimens from each etching process, representative images were obtained. The σ_{rms} was determined from a scan over a $5 \times 5\ \mu m^2$ area. XRD measurements were performed to identify the insoluble reaction products after etching in a mixture of H_2SO_4 and H_3PO_4 (3 : 1) or in H_2SO_4.

3. Results and Discussion

Fig. 1 shows an AFM image of the sapphire surface etched in a mixture of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C for 10 min. The previous work performed by Dwikusuma *et al.* conducted etching at 100, 200, and 300°C by using a mixture of H_2SO_4 and H_3PO_4 (3 : 1). No noticeable change in the surface morphology for the sapphire surface etched at 100°C was observed. When the temperature was increased to 200°C, the scratches widened slightly, and small pits started to form along directions parallel to the scratches. The σ_{rms} of the sapphire surface etched at 200°C was 0.55 nm. When the etching temperature became 300°C, the scratches were wider and the number of pits became larger, and the σ_{rms} was about 0.45 nm. In our present works, even though a lot of pits still remained on the sapphire surface etched in a mixture of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C for 10 min, the surface was smooth and scratch free, and the σ_{rms} of the sapphire was approximately 0.34 nm.

Fig. 2 shows AFM images of the sapphire surface etched

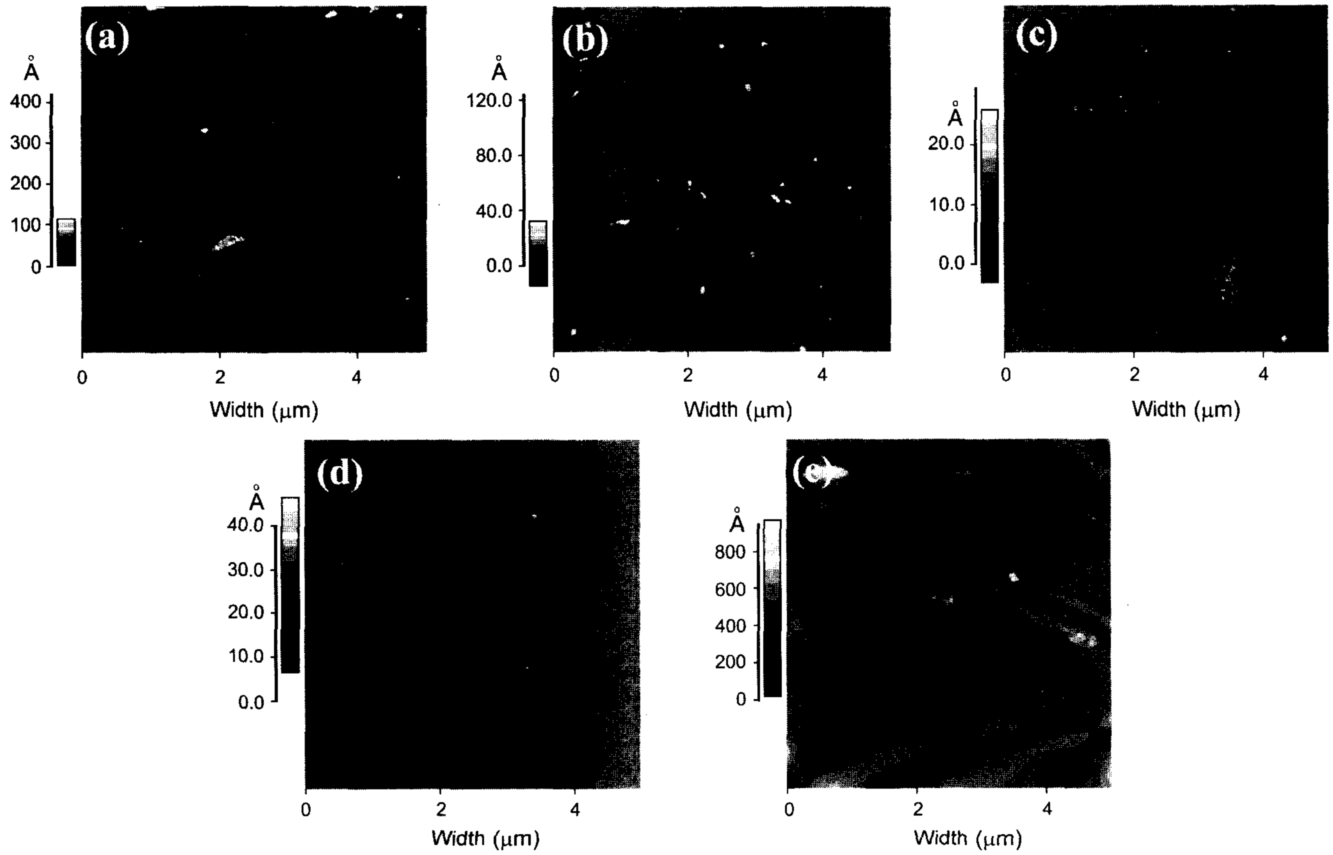

Fig. 2. AFM images of the sapphire surface etched in a H_2SO_4 solution at various temperatures for 30 min : (a) 300°C, (b) 310°C, (c) 320°C, (d) 330°C, and (e) 350°C.

in a H_2SO_4 solution at various temperatures for 30 min. The previous etching works concerning the sapphire studied by Dwikusuma *et al.* were performed at 100, 200, 300, and 400°C for 30 min by using a H_2SO_4 solution. According to them, a significant change in the surface morphology for the sapphire surface etched by H_2SO_4 at 100°C did not occur. When the temperature was increased to 200°C, the scratches still widened, and some surface pits were observed. The sapphire surface etched at 300°C contained wider scratches, but the number of the scratches was smaller, and a few surface pits were observed in a large area scan of the surface. The surface etched at 300°C became smoother with the σ_{rms} of 0.30 nm. While the scratches were completely removed at an etching temperature of 400°C, the value of the σ_{rms} was as large as 0.45 nm.

According to the ref. [7], the sulfuric acid etching mechanism was explained as follows. At low temperature, the etching is commenced by reaction between Al^{3+} and the SO_4^{2-} ions to form soluble aluminum sulfate complexes, $Al(SO_4)^+$ and $Al(SO_4)^{2-}$, from [9]

$$Al^{3+} + nSO_4^{2-} \leftrightarrow Al(SO_4)_n^{3-2n}$$

As temperature increases, Al_3^+ also reacts with SO_4^{2-} to form a mixture of different phases of hydrous aluminum sulfate, $Al_2(SO_4)_3 \cdot xH_2O$ according to [7]

$$2Al_3^+ + 3SO_4^{2-} + xH_2O \leftrightarrow Al_2(SO_4)_3 \cdot xH_2O$$

After latter reaction, $Al_2(SO_4)_3$ and $Al_2(SO_4)_3 \cdot 17H_2O$ products still remains on the sapphire substrates.

In the present work, we carefully conduct etching at 300, 310, 320, 330, and 350°C for 30 min using a H_2SO_4 solution to obtain the optimal etching condition. The sapphire surface etched at 300°C contained few scratches, and some pits. The σ_{rms} of that surface was 0.32 nm, indicative of surface smoothness, and that value was approximately the same as the value reported in other literature.[6] The number of the pits decrease with increasing etching temperature to 320°C, and the surface became smoother with a σ_{rms} of 0.13 nm, as shown in Fig. 3. The values of the σ_{rms}'s for the sapphire surfaces etched at 330 and 350°C were 0.16 and 4.0 nm, respectively, and the sapphire surface etched at 350°C contained many pits. Therefore, the optimal etching temperature for the sapphire surface is 320°C.

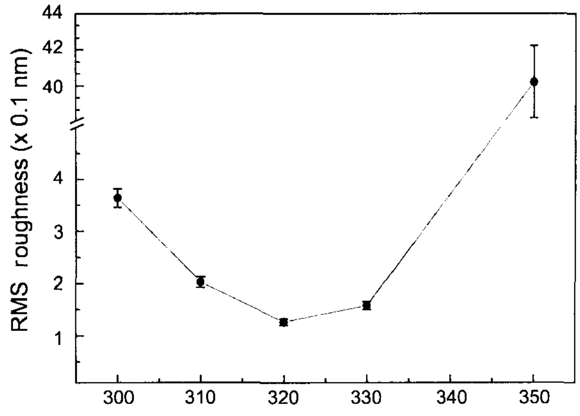

Fig. 3. The σ_{rms}'s of the surface roughnesses for the sapphire surfaces etched in H_2SO_4 at various temperatures for 30 min.

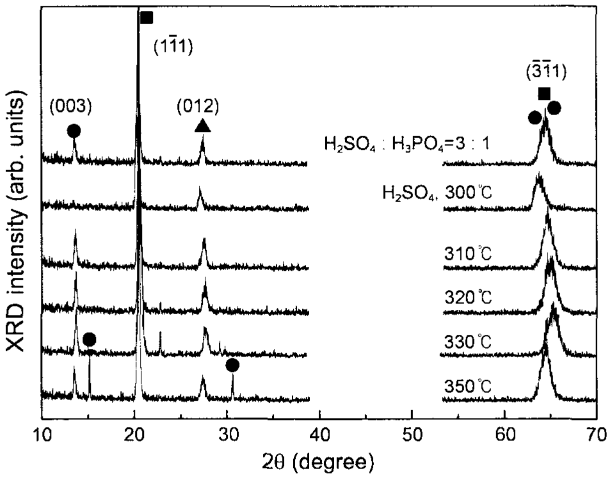

Fig. 4. XRD patterns of the sapphire surface etched in a mixture of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C for 10 min and H_2SO_4 at various temperatures for 30 min. The peaks corresponding to $Al_2(SO_4)_3$, $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 2H_2O$, and $Al_2(SO_4)_3 \cdot 17H_2O$ are represented by ●, ▲, and ■, respectively. $Al_2(SO_4)$ exhibits (003), (012), and their higher-order orientations, and $Al_2(SO_4)_3 \cdot 17H_2O$ has (1$\bar{1}$1) and ($\bar{3}\bar{1}$1) orientations.

Fig. 4 shows XRD patterns of the sapphire surface etched in a mixture of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C for 10 min and in H_2SO_4 at various temperatures for 30 min. All the surfaces etched under various conditions have a mixture of polycrystalline aluminum sulfates, $Al_2(SO_4)_3$, $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 2H_2O$, and $Al_2(SO_4)_3 \cdot 17H_2O$. The minimum number of insoluble crystals existed on the surface etched at 300. The XRD patterns of the sapphire surfaces etched in H_2SO_4 at 310 and 320°C show similar behaviors to that of the sapphire surface etched in a mixture of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C, and an extra peak corresponding to the $Al_2(SO_4)_3$ phase appears below 15° in the 2θ range. When the etching temperature was increase to 350°C, peaks related to mixtures of polycrystalline aluminum sulfates started to appear on the surface at 15° and 30° in the 2θ range.

In summary, the optimal etching conditions of sapphire substrates were investigated to obtain smooth surfaces on an atomic scale for growth of high-quality thin films. The surface etched by using a mixture of H_2SO_4 and H_3PO_4 (3 : 1) at 160°C was scratch free, but many pits were observed; the value of σ_{rms} was 0.34 nm. The surface etched by using H_2SO_4 at 320°C showed an almost pit free morphology and an ultra-smooth surface with a σ_{rms} of 0.13 nm. The σ_{rms} of the surface roughness and the number of pits increased with increasing etching temperature from 320 up to 350°C, as did the concentrations of the polycrystalline aluminum sulfates existing on the surface. The sapphire etched by using H_2SO_4 at 320°C had the best surface morphology. These present observations can help improve etched sapphire surfaces for the growth of high-quality epilayers.

Acknowledgement

This work is supported in part by the KIST Future-Resource Program (2E17733).

REFERENCES

1. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, "Room-Temperature Continuous-Wave Operation of InGaN Multi-Quantum-Well Structure Laser Diodes with a Lifetime of 27 h," *Appl. Phys. Lett.*, **70** 1417-19 (1997).
2. H. P. Maruska and J. J. Tietjen, "The Preparation and Properties of Vapor-Deposited Single-Crystal-Line GaN," *Appl. Phys. Lett.*, **15** [327] 327-29 (1969).
3. S. Gu, R. Zhang, Y. Shi, Y. Zheng, L. Zhang, F. Dwikusuma, and T. F. Kuech, "The Impact of Initial Growth and Substrate Nitridation on Thick GaN Growth on Sapphire by Hydride Vapor Phase Epitaxy," *J. Crys. Growth,* **231** 342-51 (2001).
4. J. W. Park, J. W. Park, and J. K. Lee, "Growth of Heteroepitaxial ZnO Thin Film by off-axis Magnetron Sputtering," *J. Kor. Ceram. Soc.*, **40** 262-67 (2003).
5. Y. Golan, P. Fini, S. P. Denbaars, and J. S. Speck, "Substrate Reactivity and "Controlled Contamination" in Metalorganic Chemical Vapor Deposition of GaN on Sapphire," *Jpn. J. Appl. Phys. Part 1*, **37** 4695-703 (1998).
6. C. Heilein, J. Grepstad, T. Berge, and H. Riechert, "Preconditioning of C-Plane Sapphire for GaN Epitaxy by Radio Frequency Plasma Nitridation," *Appl. Phys. Lett.*, **71** 341-43 (1997).
7. F. Dwikusuma, D. Saulys, and T. F. Kuech, "Study on Sapphire Surface Preparation for III-Nitride Heteroepitaxial Growth by Chemical Treatments," *J. Electrochem. Soc.*, **149** G603-08 (2002).
8. A. Reisman, M. Berkenblit, J. Cuomo, and S. A. Chan, "The Chemical Polishing of Sapphire and MgAl Spinel," *J. Electrochem. Soc.*, **118** 1653-57 (1971).
9. M. K. Ridley, D. J. Wesolowski, D. A. Palmer, P. Benezeth, and R. M. Kettler, "Effect of Sulfate on the Release Rate of Al^{3+} from Gibbsite in Low-Temperature Acidic Waters," *Env. Sci. Tech.*, **31** 1922-24 (1997).