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Comparison between extended microtunnels along different crystal orientations in GaN

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Triangular prism-like extended microtunnels (EMTs) can be easily formed in specially designed epitaxial lateral overgrowth GaN thick films by selective wet chemical etching in molten potassium hydroxide (KOH). In this study, extended microtunnels along the $<1\bar{1}00>$ and the $<11\bar{2}0>$ directions were fabricated and compared. If tunnels along the $<1\bar{1}00>$ direction, the $\{11\bar{2}\bar{2}\}$ planes would be the etch stop plane. While the tunnels along $<11\bar{2}0>$ direction, the etch stop plane would become to $\{10\bar{1}\bar{1}\}$ planes. The activation energies of wet chemical etch for the $\{11\bar{2}\bar{2}\}$ planes and the $\{10\bar{1}\bar{1}\}$ planes were determined to be 23.6 kcal/mol (1.02 eV) and 22.8 kcal/mol (0.99 eV) using Arrhenius plot. On the other hand, the etching depths of the tunnels along the $<1\bar{1}00>$ direction were more than twice the depths of the tunnels along the $<11\bar{2}0>$ direction during the same etching time. The highest etch rate of the tunnels along the axial direction can reach 1000 μm/hr in $<1\bar{1}00>$ direction, which is believed to be the highest etch rate of GaN ever reported. Additional crystal facet of m-plane in GaN was also observed in the sample with extended microtunnels along the $<11\bar{2}0>$ direction.

1 Introduction Gallium nitride is a focused attention upon material with wide direct band gap, high thermal stability and excellent chemical stability, which was used widely in the last decade for optoelectronic devices in the blue and ultraviolet regions. Due to its high chemical stability, normal wet chemical etch could not provide feasible etching rate in GaN. Even with the assistance of ultraviolet light, as those applied in photoelectrochemical (PEC) etching, the etching rate is still slow. Most processing of GaN devices were done by dry etching. While dry etching has many disadvantages, such as ion-induced damage, difficulty in obtaining smooth etched sidewall. Different from dry etch, wet chemical etch can provide low damage etching, low cost, smooth sidewalls which can be used in the process of fabricating high-reflectivity laser diode facets [1, 2].

However, to date, some chemical properties of crystal facets in GaN, such as $\{10\bar{1}\bar{1}\}$ planes and $\{11\bar{2}\bar{2}\}$ planes were not understood sufficiently. Stoker *et al.* reported some properties of crystal facets of GaN, including the $\{10\bar{1}2\}$ and the $\{10\bar{1}3\}$ planes were fabricated in hot phosphoric acid (H_3PO_4), the $\{10\bar{1}0\}$ and the $\{10\bar{1}\bar{1}\}$ planes were fabricated in molten potassium hydroxide (KOH) [3, 4].

In this paper, we had demonstrated extended microtunnels in GaN by a new wet chemical etching technique with high etching rate. The microtuunels are fabricated by some special crystal facets, such as {0001}, $\{10\bar{1}\bar{1}\}$, and $\{11\bar{2}\bar{2}\}$ planes in different direction of GaN. The properties of these microtunnels in different directions of GaN would be discussed in this paper. The highest etch rate of the tunnels along the $<1\bar{1}00>$ direction and along the $<11\bar{2}0>$ direction can reach 1000 and 380 μm/hr, respectively. The GaN EMTs technique can bury microtunnels under semiconductor and can offer channels for micro-fluid studies, especially in the applications of microelectromechanical system (MEMS).

2 Experimental Our samples used in this experiment consists 90 μm thick naturally doped GaN layer grown on sapphire substrates. In the growth process, a 4 μm thick GaN template was first grown on c-plane sapphire substrate by metal-organic chemical vapor deposition (MOCVD) technique on c-plane sapphire substrates. The deposition of 300 nm SiO_2 was then followed on MOCVD GaN template by plasma-enhanced chemical vapour deposition (PECVD) at 300 °C. By using standard photolithographic technique, 5 μm-wide SiO_2 strips as the mask separated by 5μm gaps were fabricated for followed epitaxial lateral overgrowth (ELOG). The SiO_2 strips of some samples were aligned along the $<1\bar{1}00>$ direction of GaN, and the others were aligned along the $<11\bar{2}0>$ direction. Then the GaN thick-film with rough 85 μm thick was performed by hydride vapor phase epitaxy (HVPE) at 1050 °C. For the HVPE growth, NH_3 gas was used as nitrogen source and GaCl, generated from liquid Ga and HCl gas, was used as gallium source.

The samples with SiO_2 strips along the $<1\bar{1}00>$ direction and the $<11\bar{2}0>$ direction were cleaved along the m-plane $(1\bar{1}00)$ and the a-plane $(11\bar{2}0)$ of GaN, respectively. Then the samples were immersed in molten KOH between the temperature range from 170 °C to 250 °C. After the etching of molten KOH, well-shaped triangular microtunnels were observed in GaN of these samples.

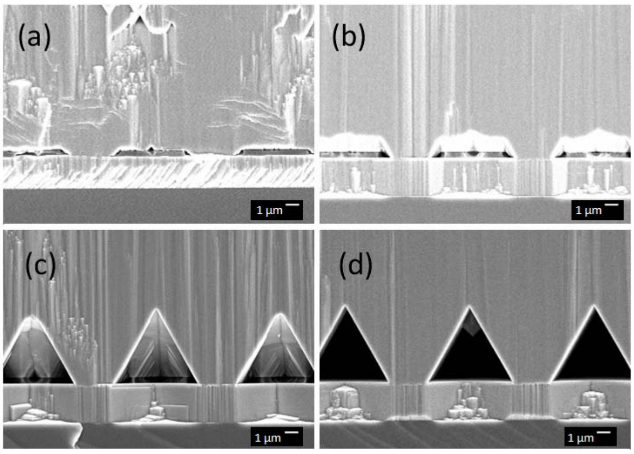

Figure 1 Cross-sectional SEM images of EMTs along the $<11\bar{2}0>$ direction produced by etching in molten KOH at (a) 170°C, (b) 190°C, (c) 210°C, and (d) 230°C for 10 minutes.

3 Results and discussion We compared the properties of GaN EMTs of different SiO_2 stripes along the $<1\bar{1}00>$ and the $<11\bar{2}0>$ directions, which were observed after the molten KOH treating. The microtunnels etched along the $<1\bar{1}00>$ direction were discussed in the previous report [5].

Figure 1 shows the cross-sectional SEM image of microtunnels along the $<11\bar{2}0>$ direction formed by wet chemical etching in molten KOH at different temperatures for 10 minutes. Figures 1(a) and 1(b) show the samples etched at 170°C and 190 °C, respectively. At both of these two etchant temperatures, the etch rate of SiO_2 and GaN are quite slow. Thus, for 10 minutes molten KOH etch, most of the SiO_2 is still residue and the GaN is barely etched. Figure 1(c) shows the sample etched at 210 °C. The triangular cross sections of tunnels were formed completely as shown in the figure. But the etch rate of SiO_2 and GaN is still restricted by the lower etchant temperature and short reacting time. Thus, EMTs have not formed long enough yet in axial direction under this etching condition. Figure 1(d) shows the cross section of triangular prism-like EMTs formed by etching in molten KOH at 230 °C. The etching depth of microtunnels in this condition was 30 μm. Figure 2 shows the cross-sectional scanning electron microscope (SEM) image of GaN EMTs. Figure 2(a) is the cross section SEM image of GaN EMTs along the $<1\bar{1}00>$ direction etched in molten KOH at 250 °C for 30 minutes. The GaN EMTs with 10 μm period could be observed clearly. Figure 2(b) is the magnified image of Fig. 2(a). The base angle in the figure is 58° which indicates that the revealed facets, i.e. the sides of the triangle, correspond to the $\{11\bar{2}\bar{2}\}$ planes in GaN. In comparison, figure 2(c) is the cross section of EMTs along the $<11\bar{2}0>$ direction etched under the same condition. The figure 2(d) is the magnified image of Fig. 2(c). The base angle is 62° which shows that the sides of GaN EMTs in different directions are formed with different family of planes, the revealed planes of GaN EMTs in $<11\bar{2}0>$ direction correspond to the $\{10\bar{1}\bar{1}\}$ planes.

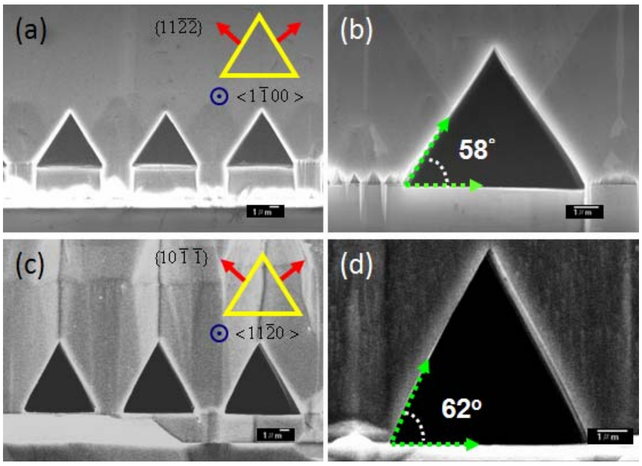

Figure 2 Cross-sectional SEM images of GaN EMTs etched by molten KOH at 250 °C for 30 minutes. (a) GaN EMTs with the SiO_2 stripes aligned along the $<1\bar{1}00>$ direction. (b) The zoom in image of (a) has a 58° of angle with respect to c-plane. (c) GaN EMTs with the SiO_2 stripes aligned along the $<11\bar{2}0>$ direction. (d) The zoom in image of (c) has a 62° angle with respect to c-plane.

By comparison of GaN EMTs formed along different directions, it is believed that the morphology of GaN EMTs and the revealed crystal facets are decided by the initial structure of ELOG stripe, i.e., the direction of the SiO_2 mask. If the ELOG stripes were along the $<1\bar{1}00>$ direction of GaN, the $\{11\bar{2}\bar{2}\}$ and $\{0001\}$ planes would be the etching stop planes of GaN EMTs. While the ELOG stripes were along the $<11\bar{2}0>$ direction of GaN, the etching stop plane of GaN EMTs would be the $\{10\bar{1}\bar{1}\}$ and $\{0001\}$ planes.

Figure 3 shows the initial stage of the formation of GaN EMTs along the $<11\bar{2}0>$ and the $<1\bar{1}00>$ directions, respectively, produced by wet chemical etching in molten KOH at 210 °C for 10 minutes. The darker region in GaN EMTs indicated by an yellow arrow as shown in figure 3 is the SiO_2 mask, and the region just above the mask is the GaN, which are both not completely etched off at this initial stage. It can show that the formation process of GaN EMTs is leading by the removing of the SiO_2 mask, as we had reported before [5]. After the removing of SiO_2, molten KOH begins to etch the $(000\bar{1})$ n-plane GaN right above the removed SiO_2 till the etch stop planes, and then triangular prism-like GaN EMTs form.

It is interesting that the m-plane GaN could be observed in GaN EMTs along the $<11\bar{2}0>$ direction. There are not additional crystal facets revealed in GaN EMTs along the $<1\bar{1}00>$ direction, except the $\{11\bar{2}\bar{2}\}$ and $\{0001\}$ planes. It is due to the selectivity of wet chemical etching between different crystal facets of GaN. $\{10\bar{1}0\}$ m-planes of GaN are more stable than $\{11\bar{2}0\}$ a-planes due to the lower surface energy [6, 7].

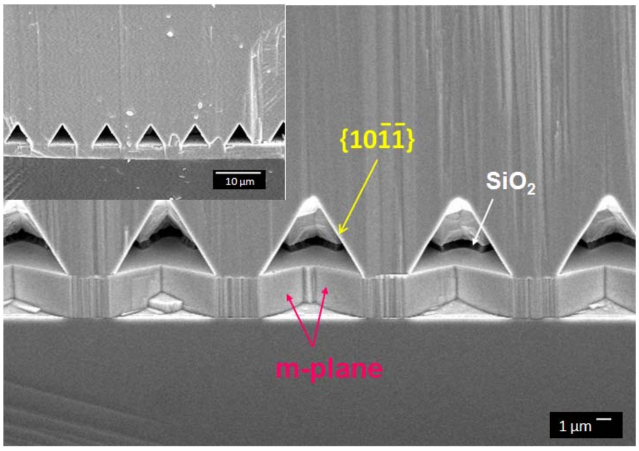

Figure 3 The bird-view cross-sectional SEM images of EMTs is along the $<11\bar{2}0>$ direction and the insert is along the $<1\bar{1}00>$ directions produced by wet chemical etching in molten KOH at 210 °C for 10 minutes.

Figure 4 shows the temperature dependence of etching depth for EMTs along the $<1\bar{1}00>$ and the $<11\bar{2}0>$ directions for the fixed etching time of 30 minutes. The depths of EMTs along the $<1\bar{1}00>$ direction are more than twice the depths of EMTs along the $<11\bar{2}0>$ direction under the same etching condition. The cause of the different etching rate between two crystal orientations can be infer that the $\{10\bar{1}\bar{1}\}$ planes are more chemically stable than the $\{11\bar{2}\bar{2}\}$ planes. It makes the cross-section size of the GaN EMTs along $<1\bar{1}00>$ direction larger than along $<11\bar{2}0>$ direction. Larger size of cross-section of the tunnels makes the etchant exchange faster than small one.

In The highest etch rate of GaN EMTs along the $<1\bar{1}00>$ direction can reach 1000 µm/hr at 250 °C. It is believed that a much higher etch rate can be achieved at higher temperatures due to its trend of exponential growth dependence. The activation energies of wet chemical etch for the $\{11\bar{2}\bar{2}\}$ family of planes and the $\{10\bar{1}\bar{1}\}$ family of planes were determined to be 23.6 kcal/mol (1.02 eV) and 22.8 kcal/mol (0.99 eV) using Arrhenius plot. The details of the results will be published later.

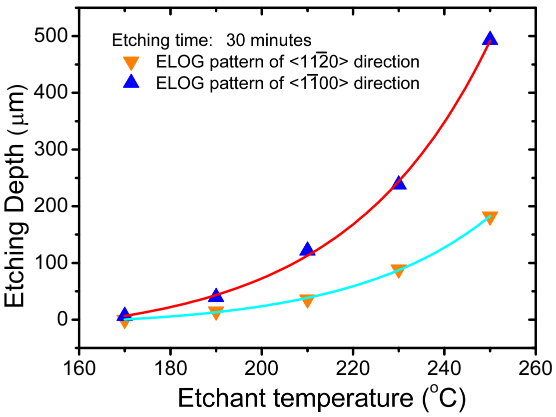

Figure 4 Temperature dependence of etch depth of EMTs along the $<1\bar{1}00>$ and $<11\bar{2}0>$ directions in molten KOH for 30 minutes.

4 Conclusion Due to selectivity of wet chemical etching of GaN in molten KOH, we demonstrated the different properties of GaN EMTs along the $<1\bar{1}00>$ direction and the $<11\bar{2}0>$ direction. The highest etch rate of EMTs of 1000 µm/hr was achieved along the $<1\bar{1}00>$ direction. The revealed crystallographic facets of triangular prism-like GaN EMTs along the $<1\bar{1}00>$ and the $<11\bar{2}0>$ directions belong to the $\{11\bar{2}\bar{2}\}$ and the $\{10\bar{1}\bar{1}\}$ planes, respectively, which are chemically stable. Additional crystal facet m-plane of GaN was observed in the samples of EMTs with SiO_2 strips along the $<11\bar{2}0>$ direction. The activation energies of wet chemical etch for the $\{11\bar{2}\bar{2}\}$ and the $\{10\bar{1}\bar{1}\}$ planes were determined to be 23.6 kcal/mol (1.02 eV) and 22.8 kcal/mol (0.99 eV), espectively.

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