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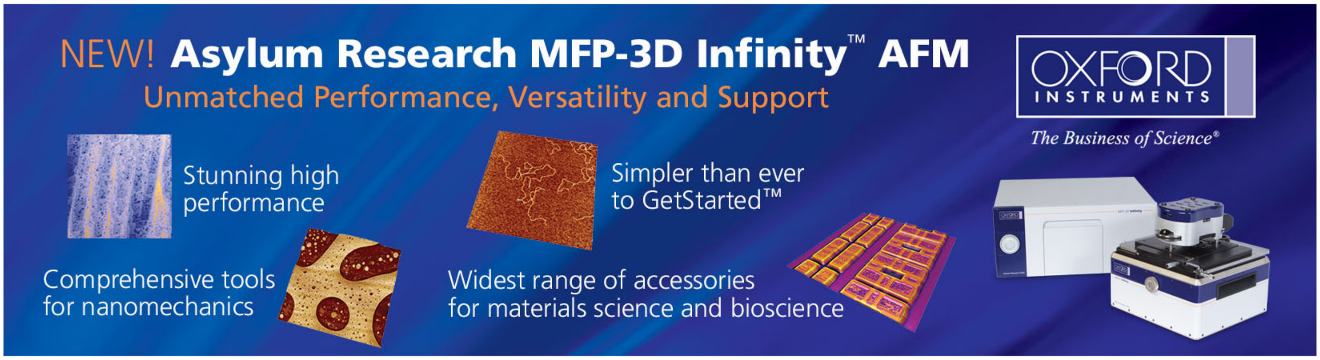

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Extended microtunnels in GaN prepared by wet chemical etch

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It is demonstrated in GaN that microtunnels extended beyond hundreds of microns can be easily achieved using wet chemical etch. To obtain this result, specially designed structures of GaN layers are first grown on sapphire substrates with metal-organic chemical vapor deposition and subsequently with hydride vapor phase epitaxy techniques. The prepared samples are then chemically etched in molten KOH. With the designed structure of GaN layers, extended microtunnels with triangular cross sections are formed. The crystallographic planes of the triangular bevels belong to the $\{11\bar{2}2\}$ family. The etch rate of the tunnel can be as high as 10 μm/min at proper etching conditions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2374841]

Gallium nitride (GaN) is a material widely used nowadays for optoelectronic devices in the blue and ultraviolet wavelength regions due to its wide direct band gap, high thermal stability, and excellent chemical stability. However, the unusual chemical stability of III nitrides has also made it difficult for wet chemical etching. A number of dry etching methods, including reactive ion etch, inductively coupled plasma etch, and chemically assisted ion beam etch, have been developed for effective etching of GaN.[1–4] But dry etching techniques usually have several disadvantages, including the generation of ion-induced damages and the difficulty in obtaining anisotropic etch and smoothly etched sidewalls.[2] It is also impossible to make tunnels buried in semiconductors by dry etching. Wet chemical etches, which can provide the advantages of low damage, low cost, and choices of selectivities in different crystal orientations, is therefore an important complement to dry etching methods.[5] However, to date, the feasible wet chemical etch rates of GaN are still slow. Even with the assistance of ultraviolet light, as those applied in the photoelectrochemical etching techniques demonstrated by many research groups,[6–17] the fastest achievable etch rate is still limited to several tens of nanometers per minute.[7,9,18] In this study, extended microtunnels (EMTs) in GaN prepared by wet chemical etches with the etch rate of more than 10 μm/min are demonstrated.

The sample used in this study consists of a roughly 90 μm thick GaN layer grown on sapphire substrates. In the growth process, a 4 μm GaN layer is first grown by standard metal-organic chemical vapor deposition (MOCVD) technique on a (0001) *c*-plane sapphire substrate followed by the deposition of a 300 nm SiO_2 layer. Photolithographic technique is then applied to fabricate stripes of 5 μm wide SiO_2 mask with 5 μm gaps between adjacent strips in the $\langle 1\bar{1}00\rangle$ direction of GaN. This MOCVD GaN layer, with patterned SiO_2 mask on its top, is used as the template for epitaxial lateral overgrowth of a roughly 85 μm thick GaN film by hydride vapor phase epitaxy (HVPE) technique at 1050 °C. For the HVPE growth, ammonia gas (NH_3) is used as the nitrogen source and GaCl, generated by reactions between hydrogen chloride (HCl) gas and liquid Ga, is used as the gallium source. Figure 1(a) illustrates the cross section of the completed structure. The completed sample is then sliced into several smaller samples of roughly 1 cm^2 in size for wet chemical etch. The chemical etchant adopted for this study is molten potassium hydroxide (KOH), whose purity is higher than 85%. Our samples are chemically etched in molten KOH from 170 to 250 °C without any photoassistance.

Figure 1(b) is the cross sectional scanning electron microscopic (SEM) picture of the EMT in a sample after being etched for more than 120 min in molten KOH at 230 °C. It is clearly observed that EMTs right above the SiO_2 masking regions have been etched into the GaN layer. Optical microscope (OM) is used to measure the depth of the tunnels. Figure 2 illustrates an OM image of the sample as viewed from the top. It is seen that the tunnels have extended beyond

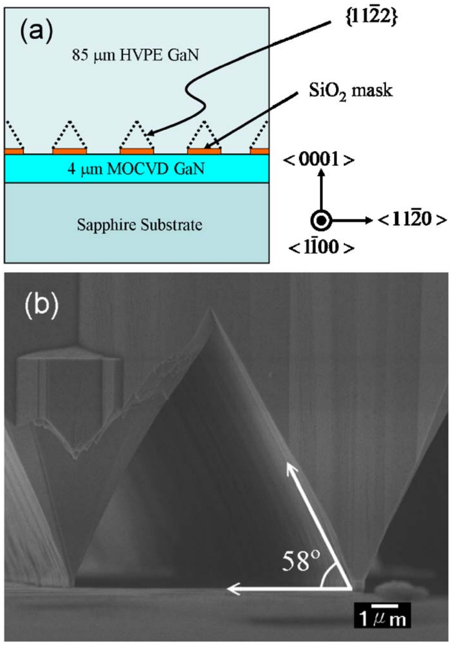

FIG. 1. (a) Cross sectional structure of the GaN sample prepared for chemical etch. The SiO_2 stripes are aligned to $\langle 1\bar{1}00\rangle$ direction. Also indicated in the figure are the $\{11\bar{2}2\}$ family planes. (b) Cross sectional SEM image of the GaN EMT after being etched for more than 120 min in molten KOH at 230 °C.

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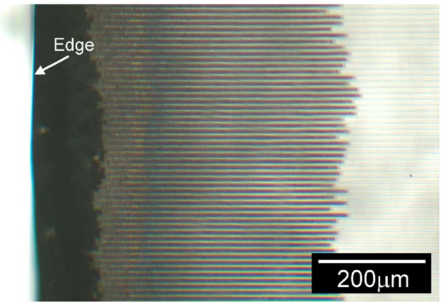

FIG. 2. Optical microscopic image of GaN EMTs after 30 min etching in molten KOH at 250 °C.

300 μm, which corresponds to an average tunnel etch rate of more than 10 μm/min. It is also observed that, even with such an extended tunnel depth, adjacent tunnels remain separated, which indicates that the etch rates along the tunnel's axial direction and on the tunnel's cross section are very different. Therefore, the etch process in the axial direction and in the cross sectional direction of the tunnels are different and should be discussed separately.

Figure 3 shows the cross sectional SEM micrographs of the EMTs with different etching conditions. Figure 3(a) is the as-grown sample before etching, while Fig. 3(b) shows the result of the sample after being etched in molten KOH at 170 °C for 30 min. Energy dispersive x-ray measurements have been applied onto the tunnel's cross section region and no traces of Si or oxygen were found, which implies that SiO_2 mask has been removed by molten KOH. A possible reaction mechanism between SiO_2 and KOH has been proposed by Blohowiak *et al.* as follows:[18]

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O.$$

Apparently, after SiO_2 is removed, molten KOH starts to etch the GaN right above the original SiO_2 masking region. Since this is the region where laterally overgrown GaN layers coalesce, the quality of GaN in this region may not be perfect and etching of GaN in this region may be easier. However, when the etchant reaches the $\{11\bar{2}2\}$ family of planes, etch rate becomes very slow. This family of planes has a 58° angle with respect to the (0001) plane, which is exactly the angle of the bevels as measured in Figs. 1(b) and 3(b)–3(d). It is believed that the etch process in the cross sectional direction can be divided into three steps, as illustrated in Fig. 3(d). The first step is the removal of the SiO_2 mask. The second step is a relatively fast etch of the less-dense GaN on the top of the SiO_2 masking region to form an equilateral triangular cross section with $\{11\bar{2}2\}$ family of planes as the etch stop planes. The final step is the slow etch in the $\langle 11\bar{2}2 \rangle$ direction.

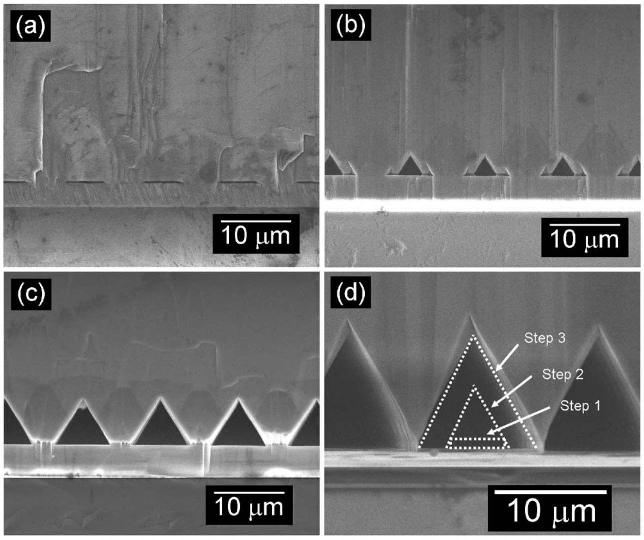

FIG. 3. Cross sectional SEM image of (a) an as-grown GaN sample before KOH etch, (b) GaN EMTs after 30 min KOH etch at 170 °C, (c) GaN EMTs after 30 min KOH etch at 230 °C, and (d) GaN EMTs after 120 min etch at 230 °C, along with an illustration of the suggested etching process in the cross section regions.

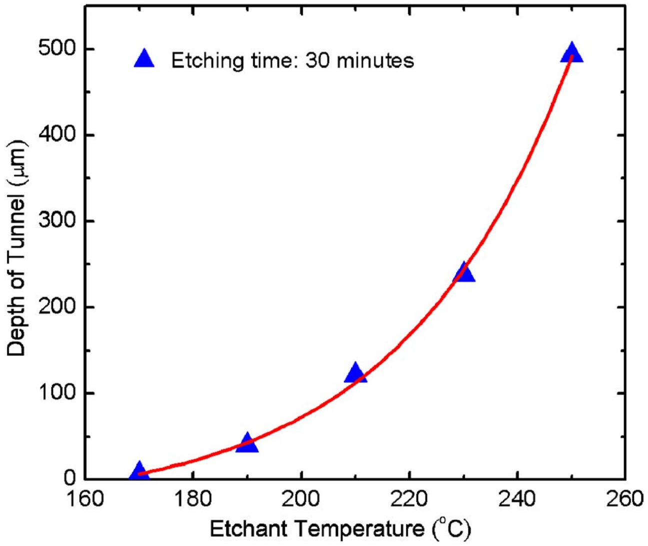

FIG. 4. Plot of the depth of GaN EMTs as a function of etchant temperature at a fixed etching time of 30 min in molten KOH.

In the axial direction of the tunnel, it is believed that the high etch rate is obtained mainly with the assistance of the fast etch rate of SiO_2 and the GaN on its top. Figure 4 plots the tunnel depths as a function of the etchant temperature with a fixed etching time of 30 min. The exponential dependence of the etch depth on etchant temperature is characteristic of either reaction-limited or diffusion-controlled etching process.[19,20] Further investigations are required to reveal the major controlling mechanism of the etch rate in the tunnel's axial direction.

In conclusion, a unique GaN wet chemical etching technique is presented. It is shown on GaN that well-shaped triangular microtunnels extended beyond hundreds of microns can be easily obtained by using wet chemical etching with molten KOH. With the designed structure of GaN layers, microtunnels with triangular cross sections are formed. The crystallographic planes of the triangular bevels belong to the $\{11\bar{2}2\}$ family. The etch rate of the tunnel can be as high as 10 μm/min.

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