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Evolution of the crystallographic planes of cone-shaped patterned sapphire substrate treated by wet etching

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ABSTRACT

A series of wet etching experiments were performed to investigate the evolution of crystallographic planes of cone-shaped patterned sapphire substrate. During the etching process, three kinds of etching zones were found. Two etching zones appeared first and vanished with increasing etching time. The other one exposed later and expanded gradually. Finally, the cone-shaped pattern with an arcuate slope transformed to a hexagonal pyramid. The calculated orientation of the crystallographic planes in the two etching zones was $\{1\,\bar{1}\,0\,3\}$ and $\{4\,\bar{3}\,\bar{1}\,27\}$, which were different from the previous reports.

1. Introduction

GaN-based light-emitting diodes (LEDs) have been intensively developed and have started to replace incandescent bulbs and fluorescent lamps in some outdoor landscape lighting and part of indoor lighting [1–3]. The patterned sapphire substrate (PSS) technique has been employed to enhance both the internal quantum efficiency and light extraction efficiency of high power LEDs [4–7]. Two main methods have been used to fabricate PSS, one is dry etching, the other is wet etching [8,9]. Dry etching technique has high etch rate of sapphire, high etch selectivity over photoresist and highly anisotropic etch profile [10]. But this method could induce damage on the sapphire surface, which might deteriorate the function of PSS [11]. Wet etching technique usually employs acidic solution to etch sapphire. The surface of etched PSS is smooth and nearly free of damage [12]. Nevertheless, a SiO_2 or SiN_x hard mask is required during the wet etching, and it has to be removed finally, which will increase the processing steps as well as the cost of the etching. Furthermore, the etch rate of acidic solution for various crystallographic planes is different, which often leads to a pyramid morphology with several specific etching planes, such as the N-, R-, M-, and A- planes [13–17]. Yu-Chung Chen et al. have reported the combination of $\{3\,\bar{4}\,17\}$ and $\{1\,\bar{1}\,05\}$ in their report [18]. Though various wet etching experiments have been carried out by many researchers, the hard masks were unavoidable in their etching processes, and the evolution process of these crystallographic planes which is of great importance for investigating the function of PSS have been rarely considered.

In this study, a cone-shaped PSS (CSPSS) was prepared by dry etching first, and then the CSPSS was etched by acidic solution. The SiO_2 or SiN_x hard mask that employed in normal wet etching was avoided, and the PSS with damage-free surface and special crystallographic planes was obtained. The evolution process of etching planes was investigated and the forming mechanism of the crystallographic planes was also discussed.

2. Experimental

The PSS was prepared on C-plane sapphire substrate. The photoresist array was formed directly on sapphire by standard

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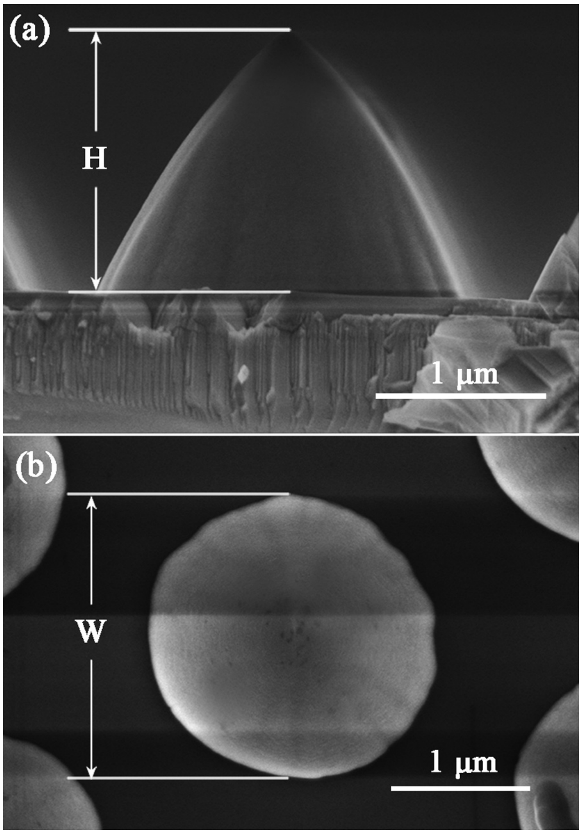

Fig. 1. SEM images of the cone-shaped pattern.

photolithography process. Then the masked sapphire substrate was etched with BCl_3/H_2 in an inductively coupled plasma (ICP) equipment to prepare the CSPSS. For investigating the evolution of the crystallographic planes, the CSPSS was immersed into a mixture solution of 98% H_2SO_4 and 85% H_3PO_4 (H_2SO_4:H_3PO_4 = 3:1) at 230 °C for 5, 10, 15, 18, 20, 25, and 30 min. Corresponding samples are named as PSS-5, PSS-10, PSS-15, PSS-18, PSS-20, PSS-25, and PSS-30. The morphologies of the samples were observed by a field emission scanning electron microscope (SEM, Hitachi S-4800).

3. Results and discussion

Fig. 1 shows the SEM images of the pattern of CSPSS. The height H is about 1.5 μm, the diameter W of the cone is about 2.2 μm, and the slope has some radian. It should be noted that there are some stripes on the arcuate slope. They extend from the top to the base-plane, making the surface of the cone not a smooth slope and the undersurface not a normal circle. As is well known, the ion bombardment during the ICP etching may induce damage on the sapphire surface, and it could be the main reason for the appearance of imperfect cone [11].

Fig. 2 provides the SEM images of the wet etched CSPSS for different etching time. Three facets are found after etching for 5 min, as shown in Fig. 2(a) and (b). For purposes of analysis, these three facets are named as “T-zones”. In addition, three new crescent-shape areas that located along the direction of the boundaries of T-zones are observed at the bottom of the cone, which are named as “A-zones”.

As etching time increased, the area of T-zones and the length of three boundaries increased gradually. The bottoms of T-zones have reached the base-plane for PSS-15, as shown in Fig. 2(e) and (f). Meanwhile, the area of A-zones continually increases, as well as the width W_A and height H_A. Due to the expansion of the area, the three parts of A-zones have almost connected with each other, making the circle-like cone into the triangle-like pattern. The undersurface-span of the pattern W_U has increased. In addition, it is noteworthy that each part of A-zones is composed of three facets. One facet locates in the middle (named as a_1), which seems like a trapezoid. The other two facets (named as a_2) look like two triangles. Moreover, although the area of arcuate slope decreases with etching time, the arcuate morphology and the stripes remain unchanged.

As we know, during the wet etching, the corrosive solution will first break the bonds between some atoms on specific crystallographic planes, making rapid etching along these planes. Consequently, the crystallographic planes with slower etching rate will be exposed earlier. Therefore, the formation of the crystallographic planes with specific orientations in wet etching can be attributed to the characteristic configuration of surface atoms and bond structure of a certain crystal [19], which leads to the diverse etching rate for various crystallographic planes. The appearance of T-zones and A-zones indicates that the etching rate of the crystallographic planes in these two zones is slower than that of the other zones. Furthermore, it is found that the diameter *W* of the cone is barely changed, and the stripes are remained on the cone surface. It is, therefore, thought that the A-zones mainly came from the etching of the base-plane along the vertical direction rather than that of the arcuate slope along the lateral direction. Comparation of the etching rate between the two zones will be discussed later.

Fig. 3 gives the SEM images of the CSPSS after etching for 18 min. It can be seen that the T-zones have already extended to the base-plane completely. The arcuate slope has been thoroughly separated, only three small parts can be observed among the T-zones. The A-zones have the same changing style with the arcuate slope, and only three small parts are left. Despite the area of A-zones decrease, the width W_A and height H_A continue to increase. Moreover, three new rhombic etching facets appear between the bottom of T-zones and the base-plane, which are named as “B-zones”. As for the size, the height *H* of the pattern decreases continually and the undersurface-span W_U increases.

When the etching time increased to 20 min, the area of T-zones increased further, as shown in Fig. 4(a) and (b). The arcuate slopes have almost vanished, the residual three parts of A-zones become even smaller, and the trapezoid facet a_1 that is shown in Fig. 2(f) transform to the triangle. Though the width W_A becomes larger, the height H_A minishes a little. As for the B-zones, the width W_B and height H_B increase obviously. In addition, it can be seen that the B-zones are composed of two kinds of crystallographic planes, and the separatrix can be observed clearly. The height *H* of the pattern decreases continually and the undersurface-span W_U has increased to about 2.75 μm. Fig. 4(c) and (d) shows the SEM images of PSS-25. It is found that the B-zones have occupied almost all the pattern. Only little T-zones remain on top of the pattern, the A-zones and arcuate slopes have disappeared completely. Concerning the size, the height *H* keeps decreasing, while the undersurface-span W_U which kept increasing in previous etching processes has decreased.

As for the PSS-30, the T-zones have disappeared completely. The cone transforms to a hexagonal pyramid that comprises of six crystallographic planes with specific orientations, as shown in Fig. 4(e) and (f). The height *H* and the undersurface-span W_U decrease to about 0.48 and 2.5 μm, respectively. When the etching time increased further, all the sizes kept decreasing, while the hexagonal pyramid shape remained unchanged (not shown here). As discussed above, the etching rate of the crystallographic planes in A-zones and T-zones was slower than that of C-plane and other planes, so they had been exposed first. As the etching process went on, the B-zones appeared later, and the three kinds of zones existed simultaneously at one stage. Considering only the B-zones are left at last, it is thought that the etching rate of the B-zones is the slowest.