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Regarding characterization techniques for investigating the topography evolution of etched PSS and determining the Miller index of exposed crystallographic planes, scanning electron microscope (SEM), focused ion beam (FIB) and atomic force microscope (AFM) have been used.9,20-22 SEM, with nanometer spatial resolution, large view-field depth, and convenient centimeter-scale survey capability, has been used for straightforward determination of in-plane dimensions of PSS (e.g., lengths and diameters) from the top view.19 However, other important profile information, say the height of patterns and slant angles of crystallographic planes, can only be obtained through SEM observation of fractured samples or sectional samples prepared by the complicated FIB method24 — sometimes an intimidatingly time-consuming task as we have experienced. AFM, a local-probe-scanning technique with nanoscale in-plane resolution and sub-angstrom vertical resolution, enables three-dimensional (3D) topography imaging.28 It is admitted that AFM imaging of complicated surface structures may be susceptible to various artifacts,29 but this problem can be solved through clever selection of appropriate AFM probes and careful validation using SEM. However, to our surprise, AFM study on crystallographic and topographical evolution of PSS was only scarcely reported.20,30 Therefore, it is promising that complementary SEM and AFM characterizations of PSS can overcome the shortcomings of two techniques and provide more reliable and accurate dimensional/profile information.

This paper is the first one of a series of three papers about wet etching behavior of PSS. Herein we carried out a systematic study on the crystallographic and topographical evolution of CPSS samples under the conventional wet etching condition (H2SO4:H3PO4 = 3:1 at volume ratio, 230°C) using complementary SEM and AFM characterizations. The second paper will systematically report the wet etching behavior of CPSS samples, including crystallographic and topographical evolutions and etching rates, under a wide range of etching conditions (H2SO4:H3PO4 from 10:1 to 0:1 at volume ratio, 200–270°C). The third paper will be devoted to wet etching behavior of the other type of PSS — cylinder-shaped PSS (CYPSS), which is though less popular than CPSS commercially whereas thanks to their steep sidewalls, can be used to successfully delineate the full spectrum of crystallographic and topographical evolution of PSS samples. The findings reported in these papers will help gain more insights into the etching behavior of PSS and fabricate optimized PSS for enhanced performance of GaN-based LEDs.

**Experimental**

**Materials.**—CPSS wafers were kindly donated by GAPSS OE Technology Co., Ltd (Xuzhou, China). The CPSS patterns were prepared using 2-inch c-plane sapphire wafers (thickness of wafers: 0.4 mm) with given crystallographic orientations of [1 1 0 0] and [1 1 2 0]. Cylinder photore sist arrays with hexagonal symmetry (pitch: 3.2 μm) were fabricated directly on c-plane sapphire by the standard photolithography process. The diameter and height of a single cylinder were 2.1 μm and 2.5 μm, respectively. Using cylinder photore sist arrays as etching masks, the sapphire substrate was subjected to inductively coupled plasma (BCl3/H2) etching to produce cone patterns with identical periodicity as the photore sist arrays. CPSS samples with the size of 10 mm × 10 mm × 0.4 mm for wet etching tests were cut from 2-inch wafers.

Because of inability of common glasswares to withstand concentrated acid attack at elevated temperature, the beaker, carrying basket, coverplates and thermocouple protection tube used for wet etching were all custom fabricated with high purity quartz sands (>99.99 wt% SiO2). The dimension of the quartz beaker is 100 mm × 100 mm, and the wall thickness is 4 mm. The quartz carrying basket, i.e., a L-shaped quartz part, consists of a quartz handling rod (Φ 6 mm × 120 mm) and a grooved plate (34 mm × 20 mm × 8 mm) for holding up to 12 samples. The schematic of the beaker reactor is shown in Fig. 1.

We used a special two coverplates design to minimize evaporation-induced loss of etchant by covering the beaker’s mouth with overlapping coverplates during the heating and etching processes, and at the same time, to facilitate convenient removal/reentry of the carrying basket (and samples) at the specific time without removing the large coverplate. The size of large coverplate is 80 mm × 80 mm × 4 mm. There are two openings in the large coverplate — the smaller round opening (Φ 6 mm) for inserting the quartz tube (Φ 6 mm) containing the thermocouple, the other rectangular opening (40 mm × 25 mm) for removal of basket. The smaller coverplate (48 mm × 40 mm × 4 mm), with only one opening for placing the handling rod of the carrying basket, was placed to cover the rectangular opening in the large coverplate during heating and etching processes.

**Wet etching.**—The CPSS samples were wet etched in a mixture of analytical grade H2SO4 (98 wt%) and H3PO4 (85 wt%) (H2SO4:H3PO4 = 3:1 at volume ratio) at 230°C for a period of 2–34 min. The etchant — a mixture of H2SO4 (90 mL) and H3PO4 (30 mL) — was poured into the quartz beaker. The beaker was heated with a commercial hotplate. The temperature of the mixture was directly measured and controlled with an immersed thermocouple (precision ±0.5°C) which was sealed in a quartz tube (see Fig. 1).

The etching process was quasi-continuous. The quartz basket loaded with up to 12 samples was placed on the inner bottom of the beaker as the mixture temperature reached 230°C and remained stable. When a specific time was reached, the smaller rectangular coverplate was uncovered, the basket loaded with samples was quickly (within 5 s) removed from the etchant. A piece of sample was removed from the groove of basket by a pair of tweezers and dropped into ultrapure water (18.2 MΩ/cm) in a clean polyfluorotr quantitative (PTFE) plasticware. Then the basket was immediately placed back inside the beaker, the smaller coverplate was placed back to recover the rectangular opening in the large coverplate. The steps above were repeated for other samples. Presumably because the volume of basket was quite small compared to the volume of etchant and the handling operation was rather swift, we did not observe significant temperature fluctuations during the sampling progress. The etching experiments were repeated more than one to check the reproducibility of the results.

**Wet cleaning.**—Before AFM and SEM characterizations, all samples were carefully cleaned using a slightly simplified version of our method13 developed for efficiently cleaning sapphire substrates. (The procedure was only briefly described below. For the details, please refer to the original paper.)13 PSS samples were sonicated in a detergent solution (detergent + EtOH + water, 1:20:79 vol%) for 30 min at room temperature, rinsed in deionized (DI) water, and blown-dried with a stream of high speed nitrogen (≥99.99%) using a nitrogen gun. Then the samples were soaked in (H2SO4 + H2O2, 3:1 vol%) solution for 20 min at 80°C, rinsed in DI water, and dried with high-pure nitrogen gas. The samples were soaked in (HCl + H2O2 + H2O, 1:1:2 vol%) solution.
solution for 20 min at 80°C, rinsed in DI water, and dried with high-pure nitrogen gas. PTFE plasticwares were used for all wet cleaning steps. Cleaned samples were stored in a sealed PTFE container prior to SEM and AFM characterizations.

Characterizations.—The morphology of PSS was characterized with a field emission SEM (Zeiss Supra 55). The acceleration voltage (AV) was set to as low as 3 kV to effectively reduce the charging effect, thus facilitating direct SEM observation without sputtering a conductive layer as required for the routine high AV observation of insulating samples. The working distance was ∼8 mm. All SEM images were recorded with the secondary electron detector.

The topography of PSS was characterized with a commercial AFM system (Bruker MultiMode 8) at ambient conditions (25°C, 35–40% RH). All images were recorded with a calibrated J scanner in the ScanAsyst mode with special Opus 4XC probes (MikroMasch) featured with sharp tips (nominal tip radius: <7 nm, force constant of cantilever: 2.5 N/m) and vertical front slant angle. Analyses of AFM results were performed with the NanoScope Analysis software. Note that for the AFM height analysis of cones or pyramids at the specific etching time, the baseline height was leveled against the c-plane.

If otherwise specified, all AFM images were only subjected to the primary first order plane fit correction to remove sample tilt so that potential artifacts induced by other image processing steps can be avoided as much as possible. We want to emphasize that all AFM images of PSS presented in this paper were carefully checked for artifacts. The AFM probes were confirmed to produce artifact-free AFM images through two methods: first, selected PSS samples were imaged in the tapping mode with special “Whisker Type” AFM probes (NSC05_10°, NT-MDT) featured with higher aspect ratio tips (nominal tip radius: 10 nm, force constant of cantilever: 11.5 N/m); second, each AFM image was compared with the corresponding SEM image for artifact detection.

Results and Discussion

Characterization of as-received CPSS.—Fig. 2a shows the top-view SEM image of cleaned as-received CPSS. Cone patterns were arranged regularly with hexagonal symmetry with the pitch (periodicity) of 3.23 ± 0.03 μm. The cone base was circular and the base diameter was 2.93 ± 0.03 μm. The SEM image (Fig. 2b) and artifact-free AFM 3D image (Fig. 2c) of a single cone confirm good circular symmetry of cones. The lateral surface of cones was named as the “S0-zone” for comparison with other zones. AFM plane-view image (Fig. 2d) confirms the shape and the pitch of cones. The corresponding AFM line profile (Fig. 2e) along the white line (Fig. 2d) shows clearly that the line segments of the cone’s lateral surface (S0-zone) were not straight: slant angles ranged from 32° (at top of cones) to 63° (around the bottom of cones). Furthermore, the mean height of cones was determined to be 1.64 ± 0.02 μm.

Etching stage I: coexistence of cone’s lateral surface with truncated zones.—At the very early stage (2 min) of wet etching in the mixture of H2SO4 and H3PO4 (H2SO4:H3PO4 = 3:1 at volume ratio, 230°C), cones began to be truncated and new zones appeared on the lateral surface. The SEM image (Fig. 3a) and AFM 3D image (Fig. 3b) show that the original lateral surface (S0-zone) shrank markedly but was still interconnected. Three new oval-shaped zones (denoted as S1-zones) with three-fold symmetry were created. Interestingly, three arc-shaped S2-zones were found at the bottom of cones. (The origin of S2-zones can be confidently attributed to the etching of c-plane underlying the original cone’s base. The experimental study on etching rates of c-plane and other zones will be reported and discussed in the following paper.) Importantly, the corresponding AFM line profile analysis (Figs. 3c and 3d) reveals that each S1-zone was convex upwards. The enlarged AFM 3D image (see the inset in Fig. 3d) confirms this finding. The height of cones, also derived from the
Figure 3. SEM images, AFM images as well as AFM line profiles of the CPSS etched for (a-d) 2 min, (e-h) 4 min, and (i-l) 6 min. S0-, S1- and S2-zones are indicated as arrows in (a), (e), (i). S0, S1 and S2 shown in (d), (h), (l) indicate the corresponding line profiles crossing the S0-, S1- and S2-zones. The enlarged AFM 3D image in (d) highlights the convex profile of the S1-zone.

line profile analysis, decreased to 1.38 ± 0.01 μm from the original 1.64 ± 0.02 μm.

At etching time of 4 min, expansion of S1-zones caused shrinkage of the S0-zone into isolated areas (Figs. 3e and 3f). Meanwhile, the area of S2-zones increased owing to the further downward etching of c-plane. The corresponding line profile analysis (Figs. 3g and 3h) shows the decreased height of cones (1.24 ± 0.02 μm). For the case of 6 min etching, S0-zones shrank whereas the area of S1-zones increased and S2-zones extended laterally (Figs. 3i and 3j). The line profile analysis (Figs. 3k and 3l) reveals that each S1-zone was still convex upwards, and the height of truncated cones decreased to 1.16 ± 0.02 μm.

Etching stage II: evolution of pyramids showing multiple crystallographic planes.—After being etched for 8 min, the truncated cones transformed to triangular pyramids, and new zones (S3-zones) appeared at the bottom of triangular pyramids. The SEM and AFM 3D images (Figs. 4a and 4b) of a single triangular pyramid show that S0-zones shrank markedly and S1-zones enlarged laterally at the same time. The AFM line profile analysis (Figs. 4c and 4d) shows that the convex S1-zone consisted of multiple planes with slant angles ranging from 32° to 42°. A close inspection of the S2-zone (Fig. 4b) reveals that it actually consisted of three facets — S21, S22 and S23, which were already reported in the literature.19 Meanwhile, three new emerging S3-zones with three-fold symmetry appeared along bottom boundaries of S1-zones due to continuously etching of c-plane underlying the pyramid’s base. Note that adjacent triangular pyramids began to merge owing to the appearance of S3-zones. Compared to the SEM image (Fig. 4a), AFM image (Fig. 4b) shows more clearly that each S1-zone consisted of two crystallographic planes. The height of cones decreased further to 931 ± 7 nm (Fig. 4d). For the case of etching time of 10 min, pre-existing zones (S0-, S1- and S2-zones) shrank whereas new emerging S3-zones extended upwards, and the area of exposed c-plane continued to decrease. The boundary between S1- and S3-zones extended laterally due to the growth of S3-zones and the etching of S1-zones (Figs. 4e and 4f). The corresponding AFM line profile analysis (Figs. 4g and 4f) reveals clearly that the upper part of S1-zone (as circled) appeared flatter than the lower curved part. The height of cones decreased further to 931 ± 7 nm.

Then, after being etched for 12 min, S0-zones were completely etched away and S1-zones shrank markedly (Figs. 5a and 5b). The area of S2-zones decreased whereas S3-zones further extended. The AFM
Figure 4. SEM images, AFM images as well as AFM line profiles of CPSS etched for (a-d) 8 min, (e-h) 10 min. The enlarged AFM 3D image in (b) highlights the morphology of S21-, S22- and S23-facets. S1 shown in (d), (h) indicates the corresponding line profiles crossing the S1-zone.

Line profile analysis (Figs. 5c and 5d) shows that the whole S1-zone was distinctly flat with a slant angle of 32.2°. Therefore, the convex S1-zone changed to the specific crystallographic planes. In addition, the height of cones decreased to 722 ± 11 nm. For the etching time of 14 min, S1-zones kept downsizing, S2-zones disappeared completely, and at the same time, S1-zones substantially extended (Figs. 5e and 5f). The AFM line profile analysis (Figs. 5g and 5h) reveals the markedly diminished S1-plane with unchanged slant angle (32.2°). The height of cones decreased to 628 ± 9 nm. Moreover, a close look at the transition area between S1-zone and S3-zone revealed significant difference in surface smoothness for two zones. AFM images (Figs. 6a and 6b) show that the surface of S1-zone was rather rugged with many bulges of 20–50 nm in size. In contrast, the surface of S2-zone was much smoother with step-terrace structures (Figs. 6c and 6d). The surface roughness of S1- and S3-zones over a 400 × 400 nm² area was Rq₁, Rmax₁ = 1.26 nm, 12.80 nm and Rq₃, Rmax₃ = 0.20 nm, 1.61 nm, respectively.

The Miller index of etched crystallographic planes was carefully determined using complementary SEM and AFM results. The CPSS etched for 12 min were chosen to determine the Miller index of S1-plane as illustrated in Fig. 7. According to the known crystallographic orientation ([1 1 0 0]) of cleaved edge of the wafer (Fig. 7a), the...
S1-plane was assigned as the \{1 \Bar{1} 0 k\} planes. The a1-, a2-, a3- and c-axes then indicate the crystallographic orientations of [2 \Bar{1} 1 0], [\Bar{1} 2 \bar{1} 0], [\Bar{1} \Bar{1} 2 0] and [0 0 0 1], respectively. A triangular pyramid (OABC) was constructed by truncating the original pyramid with the plane (ABC) formed by connecting three points (A, B, C) where each sharing edge of two S1-planes met the conjoint S2-zone. A model of triangular pyramid (OABC), together with a hexagonal coordinate system (Fig. 7b), were used to determine intercepts of the S1-plane on a1-, a2- and c-axes based on SEM and AFM analyses. The intercepts of the S1-plane on a1-, a2- and c-axes were measured to be 0.971 μm, −0.971 μm and 0.529 μm, respectively. Note that the negative value of the intercept length indicates the plane crossing the negative direction of the axes. Then, the reciprocals of values measured above were multiplied with known unit cell parameters of corundum (a = 4.759 Å and c = 12.991 Å) to straightforwardly derive the Miller index of S1-planes to be \{1 \Bar{1} 0 5\} within the experimental errors. The similar derivation procedure and the identical \{1 \Bar{1} 0 5\} crystallographic planes of sapphire were also found in the literature where a two-step wet etching process (H3PO4-based etchants without detailed information given about constituents and compositions, 270 °C) was used.

After etching for 16 min, S1-zones disappeared, and triangular pyramids with multiple families of crystallographic planes changed to hexagonal pyramids comprising a single family of crystallographic planes (S3-planes) (Figs. 8a and 8c). To derive the correct slant angle of S3-plane from AFM plane-view image (Fig. 8b), the cross-sectional...
Figure 6. Enlarged AFM images of S1- and S3-zones from Fig. 5e showing difference in surface roughness. (a) S1-zones. (b) The enlarged image of S1-zone. (c) The transition area between S1-zone and S3-zone. (d) The enlarged image of S3-zone. (AFM images were third order flattened without other image processing.)

line should be drawn vertical to the bottom edge of S3-plane. The AFM line profile analysis (Fig. 8d) gives the slant angle ($20.8^\circ$) of S3-plane. A model hexagonal pyramid (OABCDEF) was constructed by connecting bottom endpoints (ABCDEF) and the vertex (O) of original hexagonal pyramid (Fig. 8e). The intercepts of the S3-plane on a1-, a2- and c-axes were determined to be 1.827 μm, −1.461 μm and 0.525 μm, respectively (Fig. 8f). The Miller index of S3-planes was then directly derived to be \{4 ¯513 8\}. The Miller index of side planes of hexagonal pyramids is different from the literature result$^{19}$ under the same wet etching condition presumably because of some overlooked SEM characterization problems (for more discussions, see the later section). The similar hexagonal pyramid comprising \{4 ¯513 0\} crystallographic planes was reported in the literature$^{21}$ where a different continuous two-step wet etching process$^{21,22}$ with higher etching temperature (270°C) was used. The difference in Miller indexes can be attributed to different slant angles: 20.8° for our \{4 ¯5 1 3 8\} S3-planes and 25.7° for their \{4 ¯5 1 3 0\} L6B planes,$^{21}$ respectively. Furthermore, the slant angles can be underestimated through observations of not appropriately tilted FIB-sectioned samples.$^{21,22}$ This means the true slant angle could actual be larger than 25.7°.

Starting from the etching time of 20 min, hexagonal pyramids shrank markedly and began to be separated from each other. The area of exposed c-plane thus increased correspondingly (Fig. 9a). New S4-zones emerged and S3-zones shrank. Three interconnected S4-zones occupied not only the top region of the hexagonal pyramids but also narrow strip areas which extended to the baseplane along edges (Fig. 9b). At the longer etching time of 22 min, S4-zones further enlarged whereas S1-zones shrank (Figs. 9c and 9d). Note that S4-zones extended to the baseplane preferably along edges of the pyramid, but its reasons are not clear at the moment. At 24 min, S1-zones only persisted along the skirt of pyramids, S4-zones extended to the c-plane (Figs. 9e and 9f). AFM profile analyses indicate that the slant angle of S1-plane remained unchanged.

For the case of 28 min etching, S3-zones disappeared, and hexagonal pyramids changed to smaller triangular pyramids (Figs. 10a and 10c). The AFM line profile analysis (Figs. 10b and 10d) gives a low slant angle of S1-plane (14.7°). A triangular pyramid (OABC) model was constructed by connecting bottom endpoints (ABC) and the vertex (O) of the original triangular pyramid (Fig. 10e). Similarly as above, according to the relative crystallographic orientations of the triangular pyramid on c-plane sapphire substrate, the S1-plane was assigned as the \{1 1 0 k\} planes. Based on SEM and AFM results, the intercepts of the S1-plane on a1-, a2- and c-axes were determined to be 0.918 μm, −0.918 μm and 0.209 μm, respectively (Fig. 10f).
Figure 8. SEM image, AFM images, line profile analysis of the CPSS etched for 16 min, as well as a model hexagonal pyramid for Miller index determination of S3-plane. (a) SEM image. (b) AFM plane-view image. (c) AFM 3D image. (d) The line profile along the white line in (b). (e) The constructed hexagonal pyramid (OABCDEF) on the c-plane sapphire wafer with known crystallographic orientations of [1 1 2 0] and [1 1 0 0]. (f) A model hexagonal pyramid with a hexagonal coordinate system for determining intercepts of S3-plane on a1-, a2- and c-axes.

It is then straightforward to derive the Miller index of S4-planes to be \{1 1 0 1 2\}. To our best knowledge, the \{1 1 0 1 2\} crystallographic planes were reported for the first time. For similar triangular pyramids reported in the literature,\(^{21}\) the difference in the Miller indexes for our \{1 1 0 1 2\} S4-planes versus \{1 1 0 1 0\} L3T-planes\(^{21}\) can also be attributed to etching conditions and characterization methods.

For the etching time of 30–34 min, triangular pyramids kept downsizing until only apexes remained, and the gap between neighboring pyramids increased (Fig. 11). Regular ridges connecting apexes disappeared for longer etching time (images not shown here).

Merits of combined AFM and SEM characterization of PSS patterns.—It was clearly demonstrated above that combined AFM and SEM characterizations enabled accurate dimension and Miller index determinations of PSS samples. However, it is customary for researchers to exclusively use SEM (or SEM plus FIB) for this task.\(^{21,22}\) Below we (intend to) briefly discuss the merits of various techniques with the hope that AFM might be paid more attentions as a powerful tool for PSS characterization.

SEM has been extensively used to extract the dimensional information of PSS for determining the Miller index of etched crystallographic planes.\(^{19}\) The in-plane dimensions of PSS, i.e., lengths and diameters from the top view, can be straightforwardly obtained by SEM which provides nanometer spatial resolution (≈1 nm for conventional field emission SEM), large view-field depth, and convenient centimeter-scale survey capability. However, it is rather challenging and complicated to obtain accurate profile information, such as the height of patterns and the slant angle of various crystallographic planes. First, a PSS sample should be fractured to facilitate SEM observation of

Figure 9. SEM images and AFM 3D images of the CPSS etched for (a) and (b) 20 min, (c) and (d) 22 min, (e) and (f) 24 min.
patterns. Second, the fractured sample must be carefully positioned to allow accurate determination of slant angles and height of the target pattern. For example, as shown in Fig. 12a, for the hexagonal pyramid comprising six $S_3$-planes and three $S_4$-planes, in order to obtain the accurate slant angle of the $S_3$-plane, the pyramid should be extremely carefully positioned and tilted vertically against the electron beam (i.e., along the bottom edge of the $S_3$-plane). Moreover, it is not feasible to obtain all profile data for low symmetrical patterns through single SEM observation because it is impossible to rotate the tilted sample inside the SEM chamber to allow 360 degree side-view observation (other patterns obstruct the observation of the targeted pattern). Therefore, the fractured sample must be carefully positioned again for observing the $S_4$-plane and obtaining accurate slant angles (Fig. 12b). This process is intimidatingly time-consuming. For high symmetrical patterns such as cones with good circular symmetry, the positioning task is indeed not as challenging as low symmetrical patterns; however, a fractured sample must still be carefully tilted vertically against the electron beam to obtain accurate profile information.
Figure 12. Schematics illustrating proposed correct observation steps for SEM observation and FIB sample preparation of PSS samples, as well as AFM measurements for determining the profile information of PSS pyramids. SEM observation steps of fractured PSS for determining the slant angle of (a) S3-plane and (b) S4-plane. FIB preparation steps of cross-sectional PSS samples for determining the slant angle of (c) S3-plane and (d) S4-plane. (e) AFM measurement for determining the profile information of PSS. (f) Steps of AFM plane-view and 3D imaging as well as line profile analyses for determining slant angles of S3- and S4-planes.

The FIB technique has been employed to cut patterns of PSS for the following SEM cross-sectional profile characterization. Researchers have tried to derive slant angles and Miller indexes of several crystallographic planes through SEM observation of FIB-milled pyramids. However, it is challenging to obtain accurate profile of PSS patterns with SEM combined with FIB method. The following cautions should be kept in mind for this task. Again, let us take the S3-plane as the example for the illustration purpose (Fig. 12c). Firstly, the FIB cut-line should be vertical to the bottom edge of S3-plane from the top view. Secondly, during SEM observation, the FIB-milled sample should be carefully positioned and tilted vertically against the electron beam (i.e., along the bottom edge of S3-plane) so that the correct profile information of the pattern can be obtained. Otherwise, incorrect values of pattern height and slant angles may be derived. Moreover, in order to obtain the slant angle of other planes (e.g., S4-planes), more patterns need to be FIB cut from the scratch, and the SEM observation has to be carried out repeatedly (Fig. 12d).

AFM, as a local probe-scanning technique, operates by measuring the deflection of a cantilever as a sharp tip under the cantilever scans across the surface of a specimen. AFM offers nanoscale in-plane resolution and sub-angstrom vertical resolution, thus enabling quick and convenient 3D topography imaging. For the hexagonal pyramid comprising six S3-planes and three S4-planes, AFM can be used to obtain plane-view and 3D images of hexagonal pyramids (Fig. 12e). The accurate slant angles of S3- and S4-planes can then be straightforwardly derived from line profiles (Fig. 12f). Provided well-performed routine scanner calibration, AFM offers advantages over SEM (or SEM plus FIB) in sense that the comprehensive profile information of PSS can be conveniently derived in a short time. However, AFM imaging of PSS, if unskillfully used, is susceptible to various artifacts caused by the complicated tip-sample convolution effect which sometimes may hard to identify. This problem can be overcome through clever selection of appropriate AFM probes and validation using SEM as demonstrated in this study.

Conclusions

In this paper, using complementary SEM and AFM charaterizations, we systematically investigated the crystallographic and topographical evolution of CPSS under the wet etching condition (\(\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4 = 3:1, 230^\circ\text{C}\)). The following conclusions can be arrived.
At the etching stage I (2–6 min), original cones were truncated, new zones (S1- and S2-zones) appeared and then enlarged on the lateral surface of cones. Cones’ original lateral surface (S0-zone) shrank continuously whereas convex S1-zones and arc-shaped S2-zones extended.

At the etching stage II (8–34 min), truncated cones transformed into pyramids showing rich time-dependent morphological and topographical evolution behavior. At 8 min, multiple families of crystallographic planes (S1-, S2- and S3-planes) began to emerge. S2-zone shrank and eventually disappeared at 12 min. The convex S1-zone first enlarged and then shrank until 10 min, and finally at 12 min changed into the distinctly flat plane. The S2-zone transformed into three facets — S21-, S22, and S23-facets at 8 min, and shrank later. S3-zones appeared at 8 min, and further enlarged along bottom boundaries of S1-zones. When S2- and S3-zones were etched away at 16 min, hexagonal pyramids comprising only a single family of crystallographic planes (S1-planes) were found. Subsequently, S1-planes appeared and enlarged on the top of hexagonal pyramids as S3-planes shrank. The hexagonal pyramid changed to the triangular pyramid comprising S1-planes at 28 min. Finally, triangular pyramids kept downsizing and eventually disappeared for longer etching time. The surface roughness of S1- and S3-planes was quantitatively determined, with S1-planes showing much roughened surfaces than S3-planes.

The Miller indexes of three major exposed crystallographic planes (S1-, S3- and S4-planes with decreasing order of slant angles of 32.2°, 20.8° and 14.7°) were accurately determined to be \{1 1 0 5\}, \{4 5 1 38\} and \{1 1 0 12\} with the last two being reported for the first time to our best knowledge.

It was clearly demonstrated that AFM, thanks to its 3D topography imaging capability compared to SEM and FIB, can be an indispensable tool for obtaining reliable dimensional and profile information of PSS samples, as well as accurately determining Miller index of crystallographic planes.

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