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Methods of silicon surface structurization for the purpose of the deposition of III-V epitaxial layers

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This paper presents the results of the texturing of silicon substrates with various crystallographic orientations by anisotropic etching, both in a maskless process and in a process employing specially shaped mask patterns. Several etching solutions based on KOH and KOH with isopropanol, enabling a uniform texturing of silicon substrates with selected orientations in maskless process, were tested in order to find an optimal composition. We proposed a texturing process with the use of an appropriate oxide mask, which allowed the analysis of the epitaxy process in terms of orientation and inclination of sidewalls and edges of resultant structures. The structured substrate can be used for the investigation of growth of GaN epitxial layers on silicon substrates.

Keywords: textured silicon substrates, anisotropic etching, GaN epitaxy.

1. Introduction

The development of technology used for the deposition of III-V epitaxial layers on silicon substrates is one of the most challenging problems in contemporary material engineering. Its solution would enable the integration of advanced microelectronic systems made on silicon and optoelectronic systems using III-V and III-N compounds. The most important characteristics of substrates intended for epitaxial layer deposition include parameters such as crystal structure, lattice constant and the thermal expansion coefficient. Furthermore, the substrates should have appropriate smoothness, thermal and chemical stability at elevated temperatures, should be well wettable by the deposited material and not react with it. Reasonable cost and availability are also very important factors. In spite of the fact that silicon does not fulfill completely all the requirements, it has many properties which make it very promising as a prospective substrate for GaN heteroepitaxy. Firstly, silicon is much cheaper than typically applied materials and thermally stable in epitaxy temperatures (> 1000 °C). The main problems arising during the epitaxy of III-V compounds on silicon substrates are a mismatch of their lattice constants and thermal expansion coefficients. Other problems include mutual reactivity, and the poor wettability of silicon by GaN. The lattice constants mismatch of GaN and Si approach *ca*. 16%, whereas the differences in thermal mismatch coefficients reach even 80%. Discrepancies between the parameters (thermal and structural mismatch) lead to strains, which may result in cracking or peeling of the epitaxial layers.

Deposition of a GaN layer on patterned Si substrates enables one to avoid such undesired phenomena and hence significantly reduce the number of dislocations in the deposited layer. Typically, square patterns, separated by grooves or ridges directed along Si[1$\underline{1}$0] and Si[11$\underline{2}$] are used. The GaN layers with reduced number of dislocations are fabricated by lateral overgrowth. The mesas and holes with dimensions ranging from 5×5 μm^2 to 100×100 μm^2 were reported in the literature [1–4]. ZAMIR *et al*. [3] investigated maximum lateral dimension of the square mesas, patterned in Si(111), assuring crack-free GaN layer. He found it equal to 14 ± 0.3 μm. HAFFOUZ *et al*. [4] patterned Si(111) substrate in 4 μm deep holes of 1.5 μm diameter, each separated by 2.5 μm. During the epitaxy process, the GaN layer extended vertically and laterally over the holes until complete coalescence. No deposits were formed in the holes. Drastic reduction of dislocation density in the GaN layer was achieved. BIDNYK *et al*. [5] used an array of hexagonal openings, 5 μm in diameter, with 20 μm spacing to produce GaN pyramids by selective lateral overgrowth. Before the epitxy, Si(111) substrate with GaN/AlN seeding layer was covered by plasma deposited Si_3N_4 and patterned by photolitography. Contrary to the process reported in [4], the growth occurred in the openings, where the AlN seeding layer had been left.

In most cases, Si(111) plane is chosen because of its trigonal symmetry favoring epitaxial growth of the GaN(0001) plane. In Si(111), the growth occurs both in vertical as well as in three equivalent ⟨111⟩ directions, which are inclined towards the substrate at the angle of 19.6° [6].

Si substrates with crystallographic orientations different from (111) have different arrangement of (111) planes. Texturing of the substrate can expose the (111) planes. It would allow us to control the growth direction of GaN. In this paper, we present the results of texturing of silicon substrates by wet chemical etching in KOH and KOH with isopropanol solutions. The process of texturing was studied both with the use of a special oxide mask pattern and in a maskless process.

2. Maskless texturing of silicon substrates

The texturing of substrates with different crystallographic orientations, using a natural run of an etching process in solutions with appropriate compositions is the most straightforward and useful way of texturing both from technological and economic points of view. Up to now, our studies on anisotropic etching processes were mainly concerned with the roughness improvement of silicon substrates etched in KOH solutions with different concentrations and KOH solutions containing modifying additives [7]. We have, however, observed that some of the solutions yield uniformly textured surfaces, covered with miniature pyramids, whose shapes depend on the etched substrate orientation. Microscopic observations of etched substrates, arranged in [110] crystallographic zone allowed us to formulate some common principles:

– the texturing of (100) substrates is possible in low concentrated KOH and KOH + IPA solutions,

– substrates of the type (100), (133), (122) become textured in KOH solutions,

– substrates of the type (557), (335), (211), (311), (511) become covered with large, regular hillocks in KOH + IPA solutions.

Results of the observations are shown schematically in Fig. 1. Based on the results, the solutions for the texturing of silicon substrates with different orientations have been selected and etching conditions optimized.

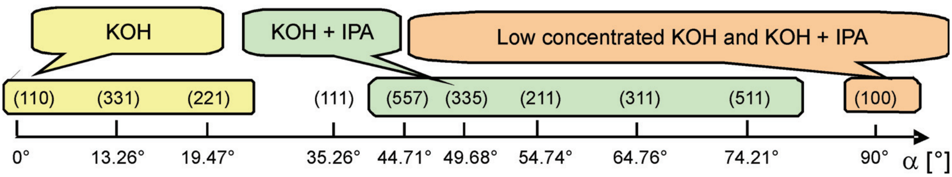
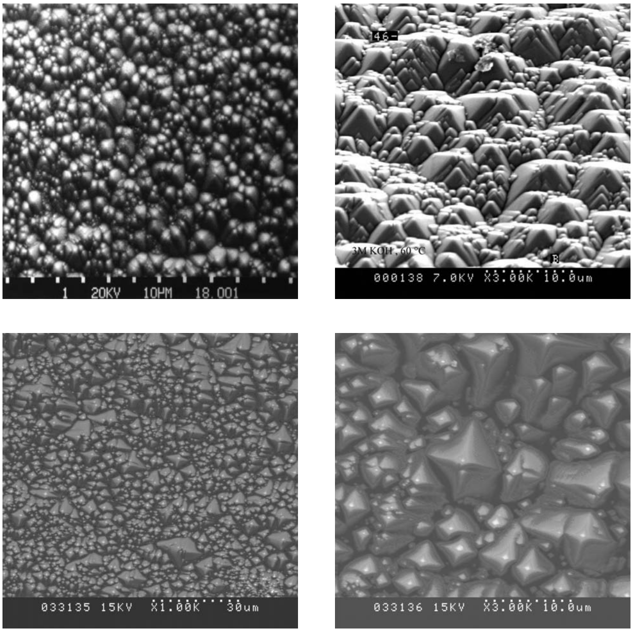


Fig. 1. Solutions for texturing Si substrates with various crystallographic orientations. The numerical values of α angle between a (*hkl*) and (110) planes are given.

Silicon substrates with (100), (110), (311) and (557) orientations were used in the experiments. The solutions were tested in the concentration range of 0.26 M to 12 M KOH. The concentration of isopropanol was varied from 0.4 M up to saturation. Prior to the etching process, the substrates were subjected to standard cleaning procedure involving organic solvents, boiling in hydrogen peroxide with sulfuric acid, immersion in dilute HF (1:100) and final rinsing in DI water. The etching was carried out in stirring conditions (ranging from 130 rpm to 210 rpm) in the temperature range of 60–80 °C. The composition of the solutions was chosen as is indicated in Fig. 1.

During the etching of (100) substrates in KOH solutions with the concentration from 1 M to 5 M it was observed that an increase in the solution concentration and stirring rate caused a more uniform and rapid covering of the surface with pyramids (which is a result of an increase in the etching rate). However, in 5 M KOH, the pyramids took on a slightly “softer” shape resembling hemisphere. The optimal texturing process took place in 3 M KOH, at 75 °C and 210 rpm. The process took 120 min. In the solutions with lower KOH concentration positive results were obtained after addition of IPA in an amount not exceeding the value which would cause solution saturation. The results are shown in Fig. 2.

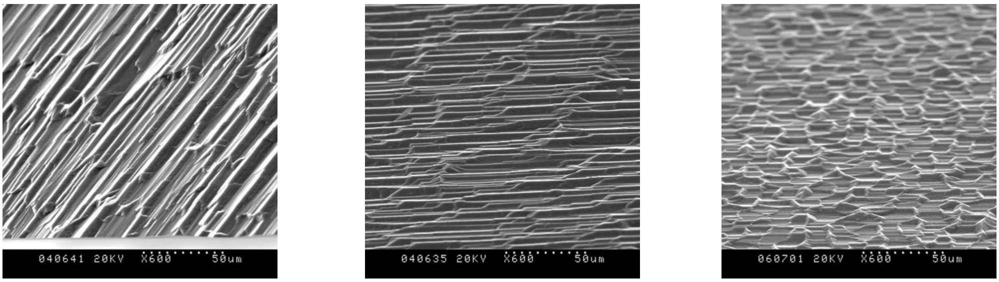
The etching of (110) substrates was carried out in the concentration range of 1 M to 12 M KOH. At low KOH concentrations the surface was uniformly covered



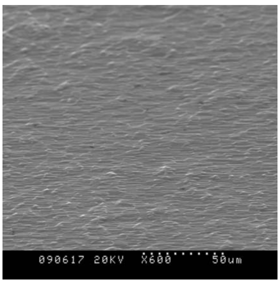
a

b

Fig. 2. Morphology of (100) surfaces etched in 3 M KOH (**a**), 1 M KOH + 1.66 M IPA (**b**); etching conditions: 75 °C, 210 rpm, 120 min.



3 M KOH 5 M KOH 7 M KOH



10 M KOH

Fig. 3. Morphology of (110) Si substrates etched in KOH solutions with different concentrations; etching conditions: 75 °C, 230 rpm, 120 min.

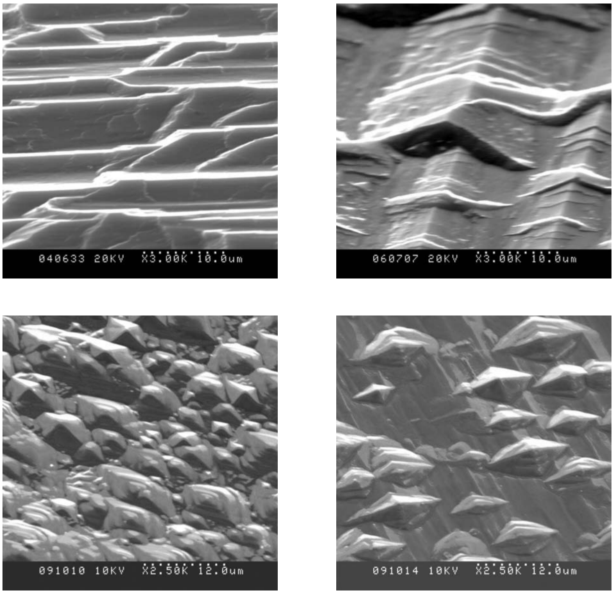


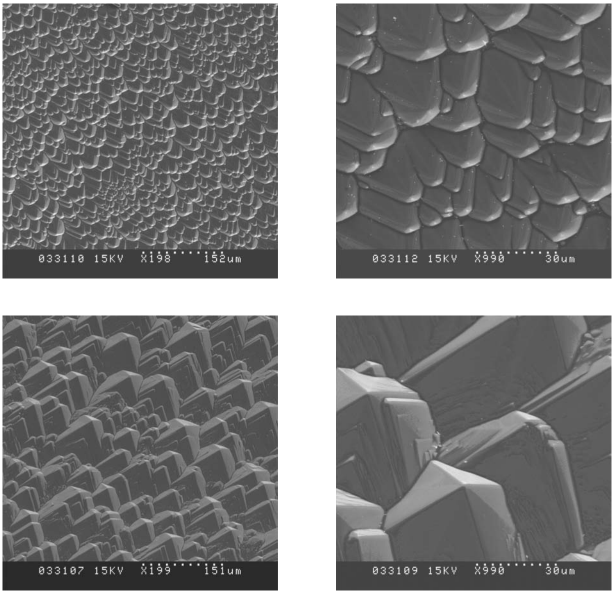
Fig. 4. Morphology of (110) substrates etched in: 3 M KOH (SEM images in two mutually perpendicular directions) – **a**, 12 M KOH – **b**.

with elongated structures, which are characteristic of orientations which undergo shortening and smoothing as the solution concentration increases. In 12 M KOH the surface started to cover with pyramids (hillocks). Therefore, both solutions with low concentration and 12 M KOH can be employed for (110) substrates texturing (Figs. 3 and 4).

A 5 M KOH solution with isopropanol was used to texture the (311) and (557) substrates. The effect of the IPA concentration (from 0.4 M to saturation) and temperature on the texturing process was examined. It was observed that an increase in temperature results in the shortening of the time necessary to complete the texturing of an etched substrate and an increase in IPA concentration causes the pyramids which develop in the process to grow in size and become sharper (Fig. 5).

3. Texturing of substrates with the use of an oxide etching mask

In GaN epitaxy on Si substrates, (111) Si wafers with triangular symmetry are usually used since the deposited layers have typically wurtzite structure. The {111} faces can easily be obtained in anisotropic etching of silicon substrates with different orientations on the sidewalls of concave and in some cases also convex structures. This is caused by the lowest etching rate of {111} planes in every type of etching solutions. Anisotropic etching of patterned substrates makes it possible to obtain {111} planes inclined at various angles, depending on the crystallographic orientation of the etched substrate. The use of such substrates in the epitaxy process enables



a

b

Fig. 5. Morphology of (311) surfaces etched in: 5 M KOH + 0.4 M IPA (**a**), 5 M KOH saturated with IPA (**b**); etching conditions: 75 °C, 230 rpm, 90 min.

an analysis of the growth of GaN layers on {111} faces inclined at various angles towards the surface.

A test mask (Fig. 6) containing circular patterns for etching holes and mesas with the diameters of 5, 10, 20, 50 μm was used to pattern the Si substrates. This mask enables the formation of 8 test structures (convex and concave) of various dimensions on a single substrate. Circular patterns do not favor any particular etching direction and {111} planes can freely develop on the etched substrate independently of its crystallographic orientation.

The texturing process was carried out with (100), (110), (111) and (557) oriented substrates in order to analyze its nature in the whole range of crystallographic planes arranged in [110] crystallographic zone (see Fig. 1). The etching was carried out in 10 M KOH and 5 M KOH IPA saturated solutions, at a temperature of 80 °C in stirring conditions at 160 rpm.

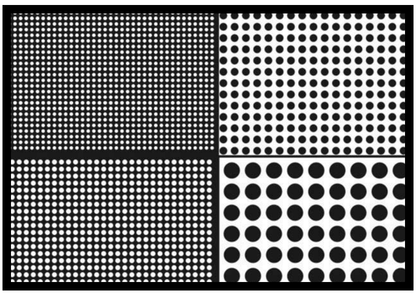
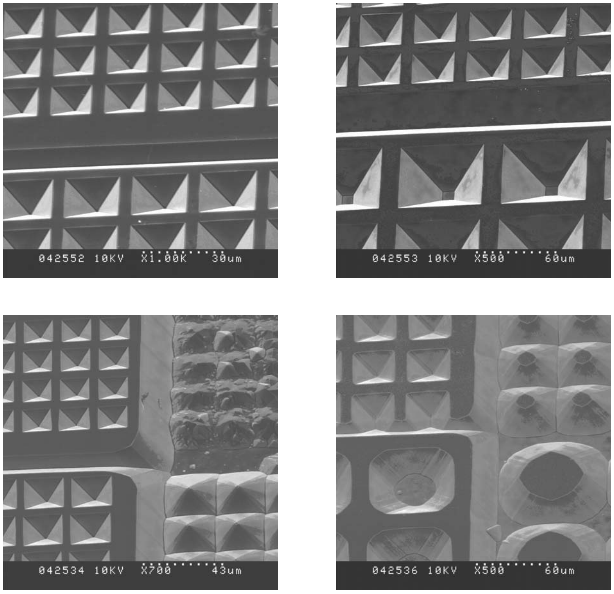


Fig. 6. A fragment of the mask pattern: on the left – mesas 5 μm and 10 μm, on the right – holes 20 μm and 50 μm.

After 40 min etching of (100) substrates in 10 M KOH, rectangular structures confined by {111} planes, inclined at the angle of 54.73° were obtained (the substrate has a four-fold symmetry) (Fig. 7**a**). All mesas were etched away because the planes, which in effect make sidewalls of the mesas, are etched in the solution at a very high rate. In order to obtain convex structures, a 5 M KOH solution with IPA was used because the etch rate of {331} planes, which evolve at the sidewalls of mesas are greatly reduced in the solution containing IPA. After 23 min etching, smaller mesas were etched away but the remaining ones took on the shape of pyramids with acute apexes, confined by {111} planes, or structures with flat apexes, confined by {331} planes (Fig. 7**b**).



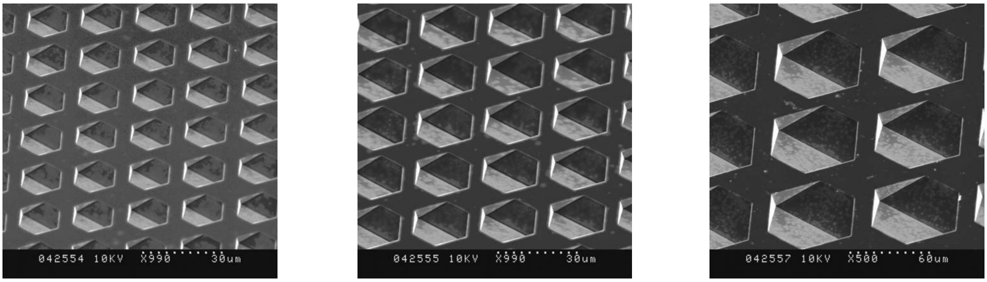
a

b

Fig. 7. Structures etched in (100) substrates in: 10 M KOH (**a**), 5 M KOH + IPA (**b**).

The texturing of (110) substrates was carried out in conditions similar to those of (100) substrates. As a result of etching in 10 M KOH, the holes closed from all sides by {111} planes and the mesas were completely etched away. In 5 M KOH with IPA, the holes and mesas whose shapes corresponded to the substrate used were obtained. Since the (110) substrates have two-fold symmetry, the {111} planes, which confine the holes are inclined towards the substrate at different angles: in A–A section at 35.27° and in B–B section at 90° (Figs. 8 and 9).

The texturing of (111) substrates is very difficult as the (111) plane is etched at a very low etching rate (several times slower than (100), independent of the composition of the etching solution). Prolonged etching time results in the underetching of convex corners, where fast etching planes Si(*hkl*) occur, and the disappearance of mesa structures (Fig. 10**a**, a substrate etched in 10 M KOH for 40 min at 80 °C).



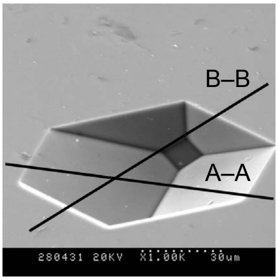
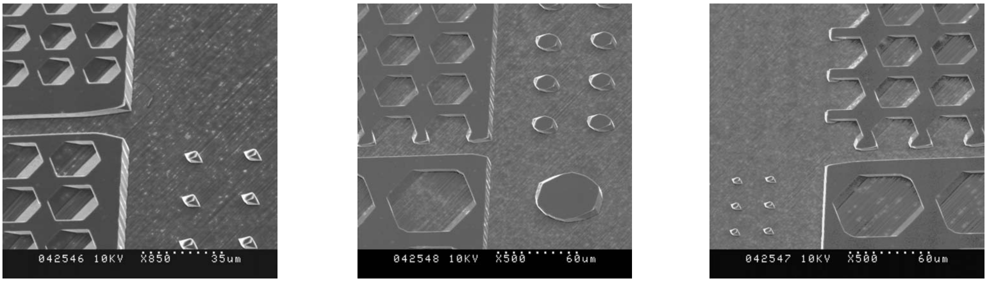


Fig. 8. Holes etched in (110) Si substrate in 10 M KOH (5 μm, 20 μm, 50 μm); below – a magnified hole with two sections perpendicular to {111} planes.



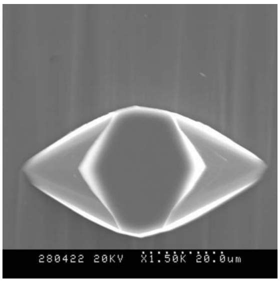
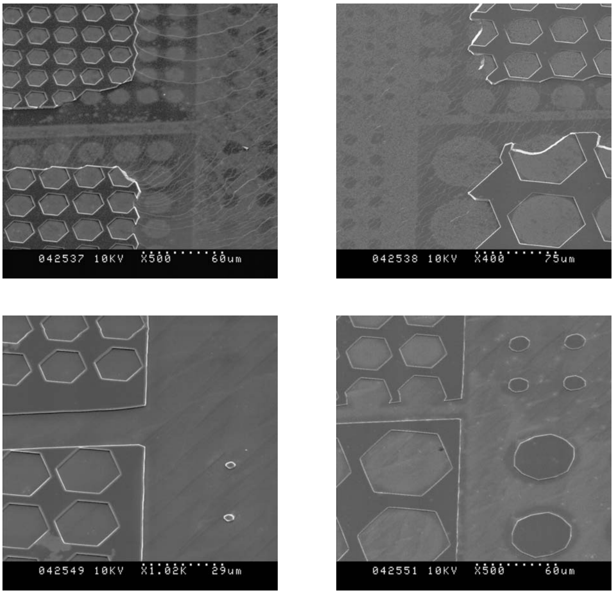


Fig. 9. Holes and mesas etched in Si(110) in 5 M KOH+IPA solution; below – a magnified mesa.

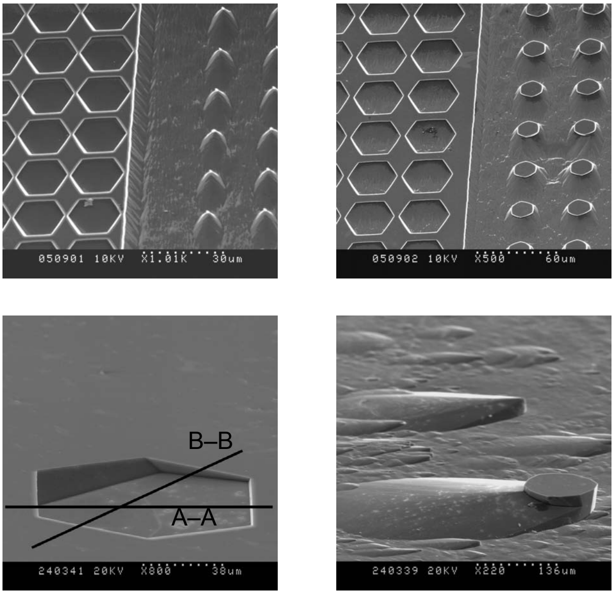
The use of 5 M KOH with IPA and a reduction of the etching time to 23 min significantly reduced the underetching of convex corners and preserved the mesa structures. The texturing was, however, very shallow and the hexagonal structures confined by {111} planes are hardly visible (Fig. 10**b**). The planes are inclined at angles of 70.53° and 109.47° towards the wafer surface in each of the three sections perpendicular to the sides of the hexagon.



a

b

Fig. 10. Holes and mesas etched in (111) substrate in: 10 M KOH (**a**), 5 M KOH + IPA (**b**).



a

b

Fig. 11. Holes and mesas etched in (557) substrate in 5 M KOH + IPA: top view of textured substrate (**a**), a magnified hole and mesa structures (**b**).

Substrates with (557) orientation were textured only in 5 M KOH with isopropanol due to the fast disappearance of the mesas in pure KOH solution. The etching time was prolonged to 50 min in order to increase the depth of the etched mesas (Fig. 11**a**). In

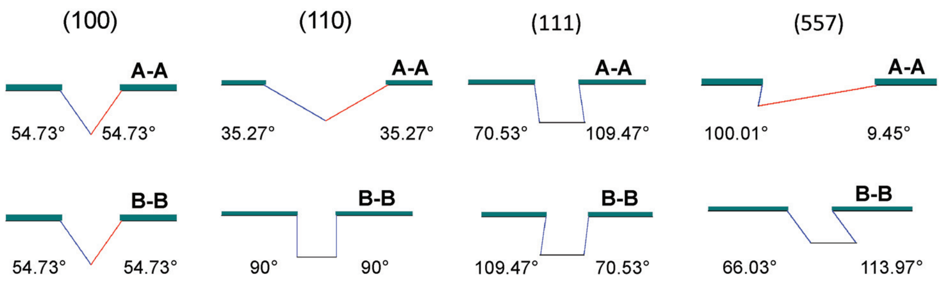


Fig. 12. Cross-sections of the holes etched in Si substrates with different crystallographic orientations.

the A–A cross-section of the etched holes, the {111} planes are inclined at a very low inclination angle of 9.45° on one side and at an obtuse angle of 100.2° on the other side. In the B–B cross-section, the angles are 66.03° and 113.97°, respectively (Fig. 11**b**).

The cross-sections of the holes obtained in the experiments are shown in Fig. 12. The use of substrates with different crystallographic orientations would enable one to obtain the {111} faces inclined at varying but strictly defined angles. The variety of the angles is practically unlimited which proves the varsatility of Si substrate texturing using this method.

4. Conclusions

In this paper, two methods of texturing silicon substrates have been presented. The most straightforward and economical one is maskless texturing during direct anisotropic etching of silicon substrates. It was shown that the substrates covered with regular structures (resembling pyramids), whose shapes depend on the substrate crystallographic orientation could be obtained by the appropriate choice of etching solution and process conditions (temperature, stirring, etching time). It should be noted that there are surfaces which undergo texturing in pure KOH solution and others which need to be treated in KOH with isopropanol. In this contribution, only some examples of etched substrates have been presented but the same idea can be used for substrates with other orientations to obtain the (111) faces inclined at various, strictly defined angles towards the etched surface.

The anisotropic etching of Si substrates of different orientations combined with the use of oxide mask patterns enabled fabrication of regularly repeating structures, both convex and concave, of different shapes. Appropriately shaped mesas can be used for GaN deposition on the apexes. It was observed that for mesa etching, KOH solution with IPA addition is more effective than pure KOH. The etching of holes enables us to obtain {111} faces inclined at arbitrary angles towards the etched surface. Determination of the relationship between the deposited epitaxial layers and inclination of {111} planes towards the substrate may well be a source of valuable information about the mechanism of deposition of epitaxial layers on textured silicon surfaces and might bring answers to the following questions:

– does epitaxy take place on faces different from {111},

– should the {111} plane be inclined at an acute, straight or obtuse angle towards the substrate to assure optimal conditions for epitaxial layer growth,

– what is the role of the type and arrangement of bonds at the intersection of {111} plane and (*hkl*) substrate,

– are there any substrates which ensure better lattice match with epitaxial layer than the commonly used (111) ones,

– is the nucleation of an epitaxial layer at the edges or apex of a mesa more likely than on a flat (*hkl*) surface,

– can maskless texturing be used in epitaxy process instead of texturing with the use of an oxide mask.

The epitaxy process carried out on the textured substrates should give an answer to the question of how to choose the crystallographic orientation of silicon substrates, the type of etching solution, the shapes and dimensions of the structures forming the texture of the surface in order to obtain optimal growth conditions for GaN layers.

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