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Silicon Wet Etch Anisotropy: Analysis of the Impact of {111}-, {110}-, {100}- Terrace Widths

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A step-based model of wet anisotropic etching of silicon is examined in conjunction with observations from wagon-wheel under-etch experiments of Si{100} and Si{110} in tetra-methyl ammonium hydroxide (TMAH) at 25 wt% at 80°C. Stepped surfaces may be composed of flat {111} terraces, and/or flat {100} or {110} terraces. Transitions (crossovers) between terrace orientations are theoretically analyzed and found to be approximately {331} and {311} planes, respectively. These crossover planes occur at several deviation angles and underetched facets. The theoretical crossovers are compared to experimental observations regarding transitions in facet configuration, roughness, and etch rate. These crossovers may significantly influence the complexity of etch rate variation and facet appearance or disappearance in an underetch experiment.

1. Introduction

In the study of wet anisotropic etching of silicon, etch models involve the movement of steps on "flat" crystallographic planes on the surface of the silicon.(1–3) The most obvious such planes are the {111}-family planes, which are also globally the slowest-etching planes in silicon. The steps are modelled as being the edges of small areas of the "flat" plane (called "terraces"). The average terrace width is a maximum (theoretically infinite, for an ideal flat surface) at {111} planes, and the average terrace width decreases for planes that deviate away from {111}.

However, under various circumstances, other planes are also observed to be either "flat" (to varying extents), locally slowest-etching, or both. Note that a local minimum in etch rate may be consistent with the presence of a "flat" plane (at the local minimum), along with step-based etching for other planes that deviate by small angles from that "flat" plane. For example, {100} and {110} planes have been observed to be flat under certain conditions,(2,4) and have been studied as the basis for step movement.(2,4,5)

Figure 1 illustrates steps and terraces for two different deviation angles away from the

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*Corresponding author, e-mail address: i_statei@sympatico.ca (unspecified) flat plane. If the flat plane is in the {111} family, the terraces are {111} facets, and the step edges are typically periodic bond chains or rows of kinks. For example, for the specific {111} plane these step edges move in <11-2> or <-1-12> directions, respectively. Figure 2 shows the general rotation angle away from a {111} plane. The angle θ_p describes rotation from {111} to {110}, while θ_k describes rotation from {111} to {100}.

Consequently, two types of planes may be identified: one, bounded by rows of kinks, features characteristic of the planes between {100} and {111} surfaces, and another, bounded by periodic zigzag bond chains (PBC-s), for the planes between {111} and {110} surfaces.(5–8) In other words, the etched planes are assumed to be built of terraces, and separated by steps, the edges of which are defined by PBC-s or rows of kinks, as depicted in Fig. 3.

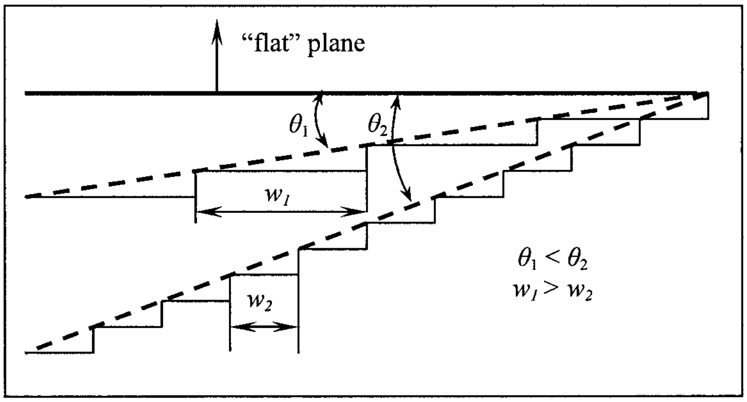

Fig. 1. Steps and terraces for two different planes deviated at angles theta ($(\theta_1 < \theta_2)$) from the "flat" plane. w_1, w_2 are the terrace widths.

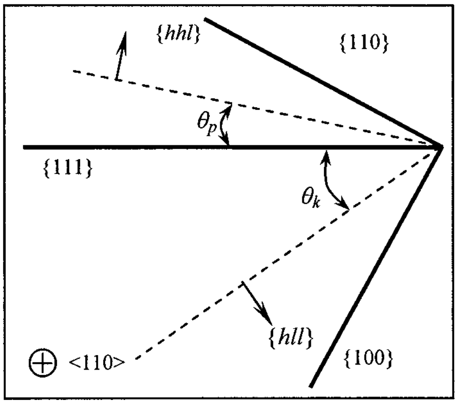

Fig. 2. Schematic view of Si surfaces viewed from the <110> direction.(6)

Figure 4 shows canonical curves(5) from experimental etches in TMAH 25 wt.%, where the silicon etch rate is plotted as a function of θ_p and θ_k. These results are based on the experimental work executed previously in the same laboratory in which oxide-covered {100} and {110} silicon samples, wagon-wheel patterned, were etched in 19 wt.% and 25 wt.% TMAH, heavily stirred at a constant temperature of 80°C.(8) This wagon-wheel experiment(9) aimed to analyze the under-etch behaviour of concave structures, specifically the profiles of the sidewalls of the etched spokes. Detailed investigation of the morphology, inclination angles, and roughness patterns of the cavity sidewall facets identified all

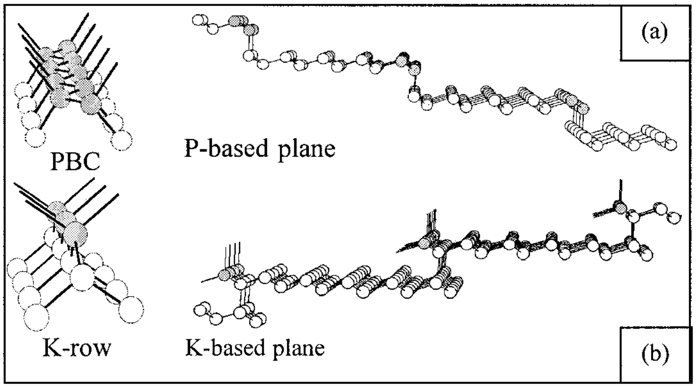

Fig. 3. Crystallographic model of (a) Periodic Bond Chain (PBC), and P-based plane, and (b) row of kinks (type 2), and K-based plane.(8)

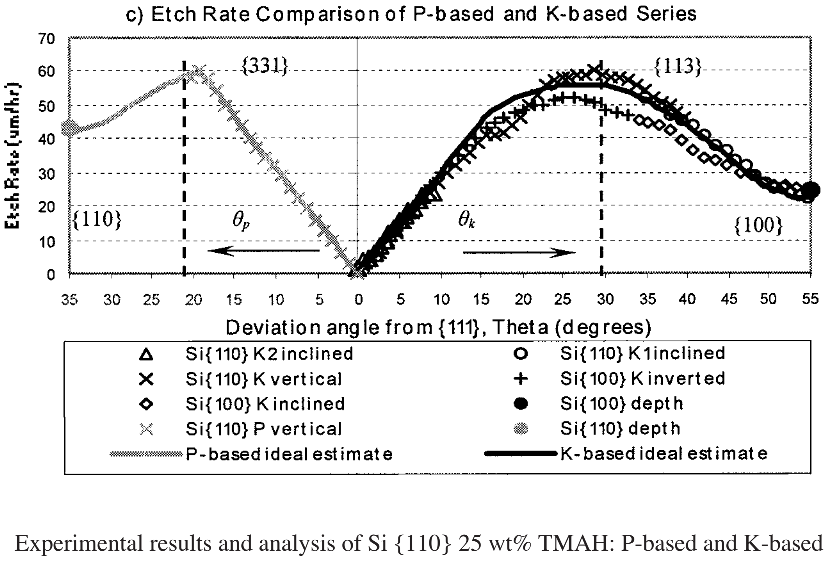

Fig. 4. Experimental results and analysis of Si {110} 25 wt% TMAH: P-based and K-based series comparison.(5)

planes appearing on the sidewalls of spokes from the wagon-wheel experiment and grouped them into two families of planes: K-based (located between the {100} and {111}surfaces in the crystal structure) and P-based (located between the {111} and {110}surfaces). Etching time and measured parameters, such as inclination angles of the exposed sidewall facets, as well as their size, allowed accurate determination of the etch rates of all exposed surfaces, a summary of which is given in Fig. 4. References 5 and 8 discuss the finding that the same crystallographic features etch at different rates (*e.g.*, for θ_k between 15° and 45°), and hypothesize that these differences are due to facet boundary effects. Obviously the {111} plane is the slowest etching, but two other local minima are present at {100} and {110}.

In this paper, the theoretical terrace widths are calculated and analyzed for planes hypothetically having {111}-, {100}-, and {110}-terraces.(7) The analyses are done as a function of deviation angle away from the {111}, {100} and {110} planes, which are treated as being hypothetically flat for the purposes of this analysis.

Step height for {111} oriented terraces: $h_{(111)} = \dfrac{5.43\sqrt{3}}{3} = 3.135$ Å, and the terrace width can be determined as: $w_{(111)} = \dfrac{h_{\{111\}}}{\tan\theta}$. Similarly, for {100} oriented terraces, $h_{(100)} = \dfrac{5.43}{2} = 2.715$ Å and $\mathrm{w}_{\{100\}} = \dfrac{h_{\{100\}}}{\tan\nu}$, and for {110} oriented terraces: $h_{(110)} = \dfrac{5.43\cdot\sqrt{2}}{4} = 1.92$ Å and $w_{\{110\}} = \dfrac{h_{\{110\}}}{\tan\xi}$.

Where θ, υ and ξ are the angles between the plane in question and the {111}, {100} or {110} oriented terrace, respectively, and 5.43 Å is the lattice constant.

From such calculations, the theoretical terrace widths can be compared at each deviation angle, as shown in Fig. 5. Note that the terrace widths would be infinite at ideally flat {110}, {111} and {100} planes, and as such these are not shown explicitly in the figure.

As Fig. 5 shows, the terrace widths decrease from the respective flat planes, leading to crossovers in the theoretical terrace widths very close to {331} for P-based planes (θ_p = 21.62°, about 14° rotated from the {110} plane, and the exact Miller Indices would be {2.913 2.913 1}), and very close to {113} for K-based planes (θ_k = 29.05°, about 26° rotated from the {100} plane, and the exact Miller Indices would be {1 1 2.940}). At the crossovers, the theoretical terrace width for K-based planes is 6.5 Å and for P-based planes is 8.57 Å.

The calculated crossovers in terrace widths occur close to the local maxima in etch rates of P-based and K-based planes seen in Fig. 4. Between {111} and {331}, the etch rate increases rapidly, as one would expect for a step-based model based on {111} terraces, increasing monotonically as a function of the deviation angle, θ_p. Between {331} and {110}, as θ_p increases the etch rate decreases, which would be consistent with the step movement being based on {110} planes instead of {111}. For K-based planes, the etch rate increases rapidly between {111} and {113}, again as one would expect for a step-based model based on {111} terraces, increasing monotonically as a function of θ_k. For θ_k greater than this, (closer to {100}), the etch rate may be consistent with a step-based model based on {100} planes, consistent with ref. 2. At the crossovers, the etched surface is expected to be rough and have both types of terraces, and the etch rates are expected to be elevated or

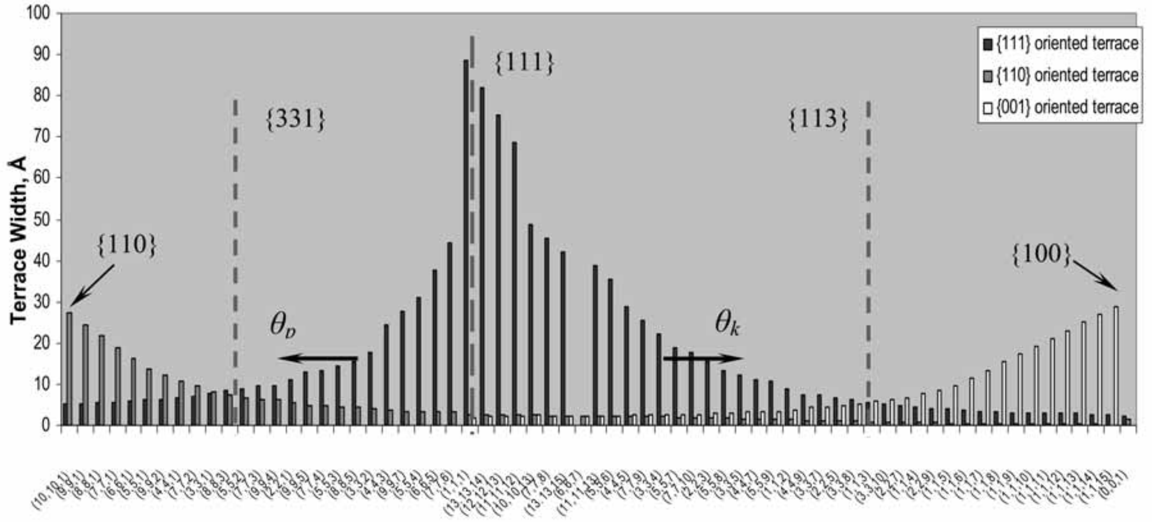

Fig. 5. Relative terrace width variation for different terrace orientations.

maximal.

2. Underetch Experiments on Si{100}

The above approach was used to analyze the step spacing of the facets on sidewalls of spokes found in wagon-wheel under-etch experiments as a function of the mask-edge deviation angle. When the crossover rotation angles (θ_p and θ_k) are transformed into the {100} coordinate system, they both fall at an approximately $\delta \approx 19°$ deviation from the intersection of the {111} plane with the {100} wafer surface (about a 26° deviation from intersections with the wafer surface of underetched {100} plane and {110} plane). Figure 6 shows these locations overlaid on the summary of facets found in underetch experiments on Si{100} in 25 wt% TMAH at 80°C. This deviation angle corresponds to a zone of 3-faceted underetched surfaces. For P-based facets this crossover is theoretically at $\delta = 18.945°$, while for K-based facets it is theoretically at $\delta = 18.784°$. It is remarkable that the crossovers in both P-based and K-based facets occur close to the same deviation angle in the {100} underetch experiment (note that this is not the case for the {110} underetch experiments — see below). At $\delta \approx 19°$, ideally, in the region very close to both crossovers, the step edges may be continuous (see Fig. 6(b)) from the upper silicon surface to the bottom of the cavity, beginning with 6.5-Å-wide terraces of both {111} and {100} on the uppermost inverted K-based plane having an inclination angle ≈108°, crossing the facet boundary to the K-based plane having an inclination angle ≈72°, and the same ideal terrace widths, and further crossing the next facet boundary to the P-based plane having an inclination angle ≈46°, w here the ideal terrace widths switch to 8.57 Å for both {111} and {110} terraces.

Figure 7 shows a SEM of an underetched sidewall at $\delta \approx 20°$, roughly corresponding to the crossovers. A very small K-inverted facet is visible at the top, and an even smaller P-

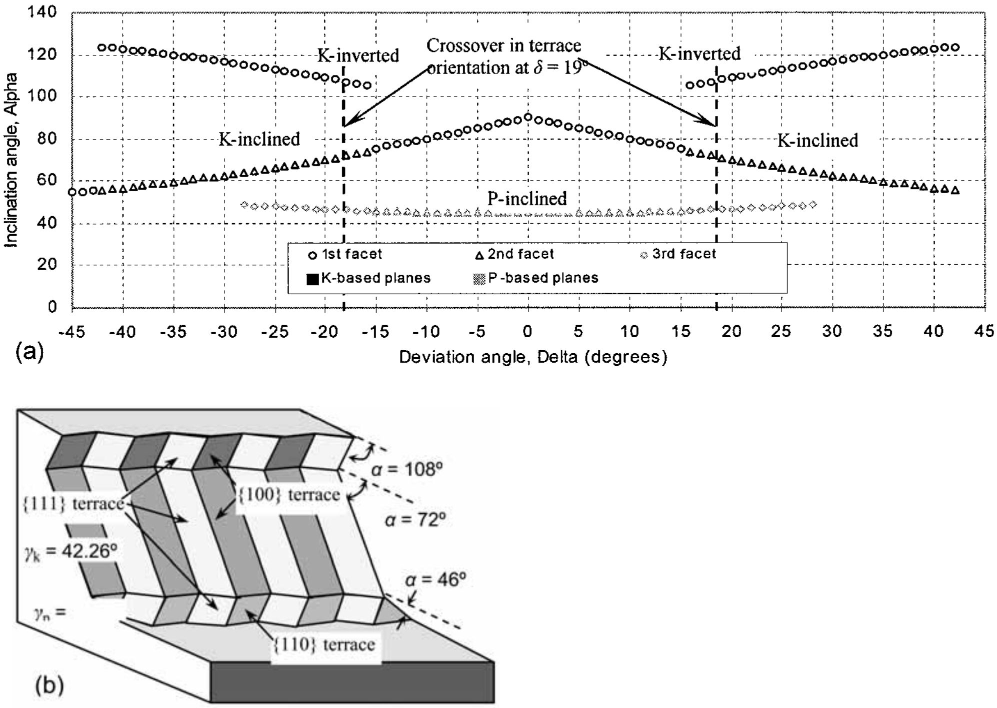

Fig. 6. (a) Summary of the experimental data representing relative position of the inclination angles of the facets on the side-walls of a spoke with respect to the deviation angle on Si {100} etched in 25% TMAH with the indication of the crossover in the terrace orientation (Figure from ref. 8). (b) schematic representation of step-based etching surfaces at deviation angle $\delta \approx 19°$ indicated in (a).

inclined facet is visible at the bottom. The large K-inclined facet in between has evident striations aligned parallel to the ideal crystallographic steps depicted in Fig. 6(b).

3. Underetch Experiments on Si{110}

The same approach was used to analyze the case of Si{110} wafers etched in 25 wt% TMAH. However, since the situation is more complex in the Si{110} system, Fig. 8 summarizes all of the theoretically available terrace-width crossovers on each of the available facets that could appear in an underetch experiment. Real underetch experiments will feature only a subset of the available facets, and therefore only a subset of the available crossovers.

Figure 9 shows the real underetch data for Si{110} etched in 25 wt% TMAH. The crossover on K-vertical is present at $\delta \approx 25°$ (to be exact, $\delta = 25.6875°$). Other crossovers on P-inclined at $\delta \approx 43°$ ($\delta = 43.522°$) and on P-vertical at $\delta \approx 76°$ ($\delta = 76.357°$) are also potentially relevant and are examined below.

Figure 10 shows schematic representations of the step-based etching surfaces showing the relative movement of steps, where appropriate. Unlike in the experiment on Si{100},

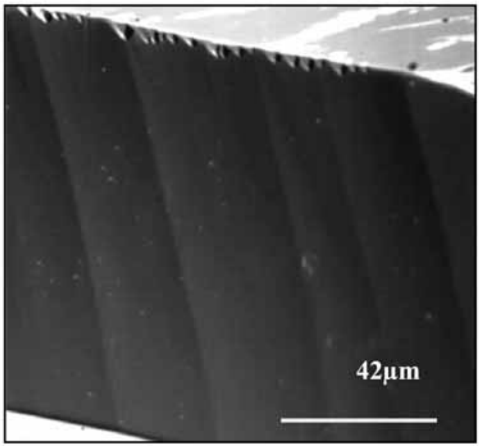

Fig. 7. SEM of sidewall of a spoke on a Si{100} wafer etched in 25% TMAH at $\delta \approx 20°$, 5 h etching time.

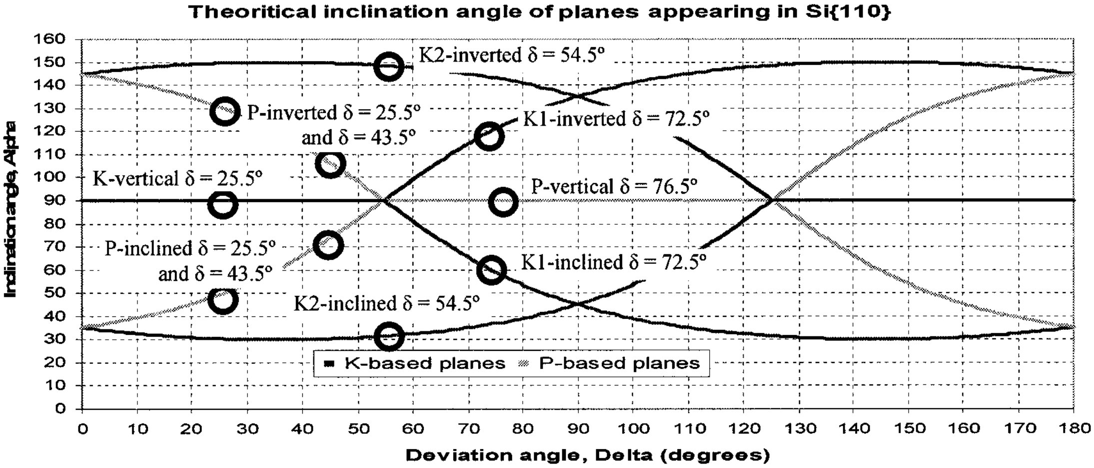

Fig. 8. Theoretical inclination angle of planes that may appear on the sidewalls of spokes in the under-etch wagon-wheel experiment.

the deviation angles at which the crossovers occur are not located at the same point. In two out of three cases the crossover planes appear as a topmost facet.

3.1 *Deviation angle* $\delta \approx 25°$ *(Fig. 10(a))*

Two facets are present on the sidewall of a spoke: a K-vertical - crossover plane, and K2-inclined - {111} oriented terrace. At $\delta \approx 25°$, the terrace edges on the lower, K-based, facet have a two-to-one correspondence with the terrace edges on the upper (crossover)

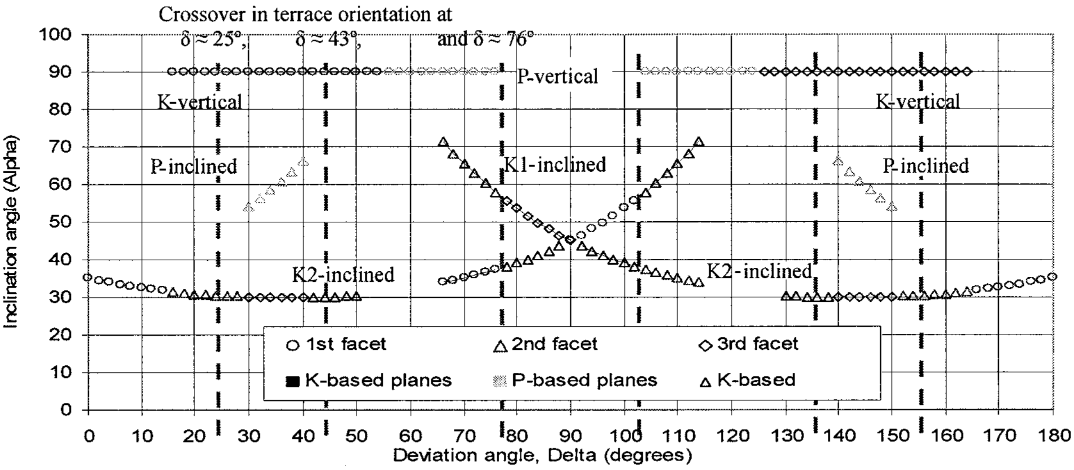

Fig. 9. Summary of the experimental data respresenting relative position of the inclination angles of the facets on the side-walls of a spoke with respect to the deviation angle on Si{100} etched in 25% TMAH with the indication of the crossover in the terrace orientation. (Figure from ref. 8)

facet. Figures 11(a) and 11(b) show the etched surfaces at $\delta \approx 43°$(near 25°). The top-most (K-vertical) facet has significant undulation (roughness).

3.2 *Deviation angle at or near* $\delta \approx 43°$

The experimental data in Fig. 9 shows a transition from three sidewall facets to two sidewall facets.

1. For $30° < \delta < 43°$ there are three facets: a K-vertical - {111} oriented terrace, a P-inclined crossover plane, and a K2-inclined {111}-oriented terrace.
2. For $\delta \geq 43°$ there are two facets: a K-vertical - {111} oriented terrace, and a K2-inclined {111}-oriented terrace (there is no crossover plane present).

The step-spacing correspondence also may be separated into two areas: (1) for $30° < \delta < 43°$, with three facets present, the step correspondence at $\delta = 42°$, for example, is 1.32:1 between P-inclined and K-vertical facets, and around 1:2.33 between P-inclined and K2-inclined facets, (see Fig. 10(c)), (2) for $\delta \geq 43°$, with only two facets present, the step correspondence at $\delta = 43°$, for example, is approximately 1:2 (1:1.94) between K-vertical and K2-inclined facets, (see Fig. 10(d)).

Figures 11(d) and 11(e), showing spokes at $\delta = 39–40°$ and $\delta = 41–42°$, respectively (the underetched surfaces on opposite sides of a spoke deviate by 1°), show the presence of the P-inclined facet, followed by its abrupt disappearance for $\delta \geq 43°$ (Fig. 11(f)). Figure 12, lower demonstrates this abrupt disappearance, between the right side of the spoke at $\delta = 41–42°$ and the left side of the spoke at $\delta = 43–44°$. This situation is also demonstrated in a panoramic view of the cross section of the Si{110} sample in the vicinity of $\delta \approx 43°$. (see Fig. 12, upper).

Note that the micrographs of the p-based inclined facet in the vicinity of the deviation angle $\delta \approx 43°$ show silicon surfaces after an etching time of 1 h 30 min. As was shown in previous works,(8) the etch rates and facets exposed in the wagon-wheel under-etch

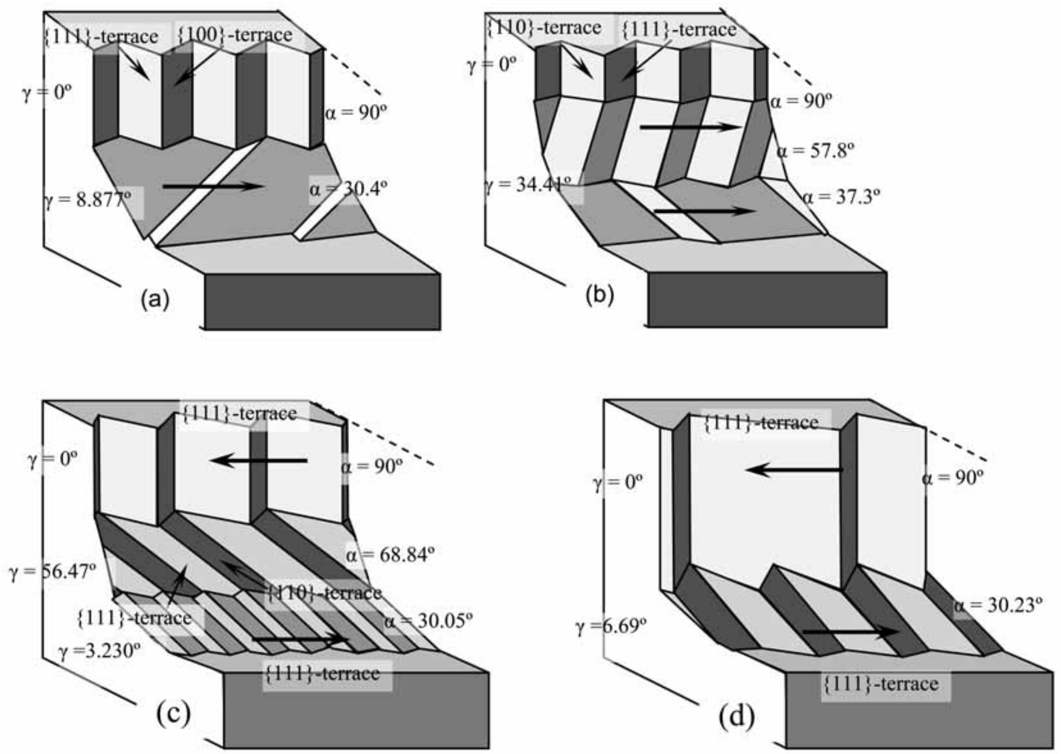

Fig. 10. Schematic representation of the step-based etching surfaces showing relative movements of steps base on the {111} oriented terrace at (a) $\delta \approx 25°$, (b) $\delta \approx 76°$, (c) $30° < \delta < 43°$ and (d) $\delta \geq 43°$(δ =4.3°)

experiment vary with time. The exact deviation angle at which the P-inclined facet disappears was found to vary slightly (±2°).

The P-inclined facet with the crossover in the terrace orientation at $\delta \approx 43°$ appears as a second facet. In the under-etch curve of Fig. 13 it can be seen that the second facet may correspond to more complex behaviour in the underetch rate. This crossover facet may influence the etch rates of adjacent facets through effects operating at the boundaries with adjacent facets.

3.3 *Deviation angle at or near* $\delta \approx 76°$

The experimental data in Fig. 9 also shows a transition from three sidewall facets to two sidewall facets.

1. For $65° < \delta < 76°$ there are three facets: a P-vertical crossover plane, a K1-inclined {100}-oriented terrace, and a K2-inclined {100}-oriented terrace.
2. For $\delta \geq 76°$ there are two facets: K1-inclined {100}-oriented terrace, and a K2-inclined {111}-oriented terrace (there is no crossover plane present).

At $\delta \approx 76°$, the P-vertical facet and the K1-inclined facet adjacent to it have a correspondence of (1 : 1.19) between the terrace edges. Figure 11(c) shows the etched surfaces at $\delta = 75.8°$ (near 76°). The top-most (P-vertical) facet is very small, as indicated

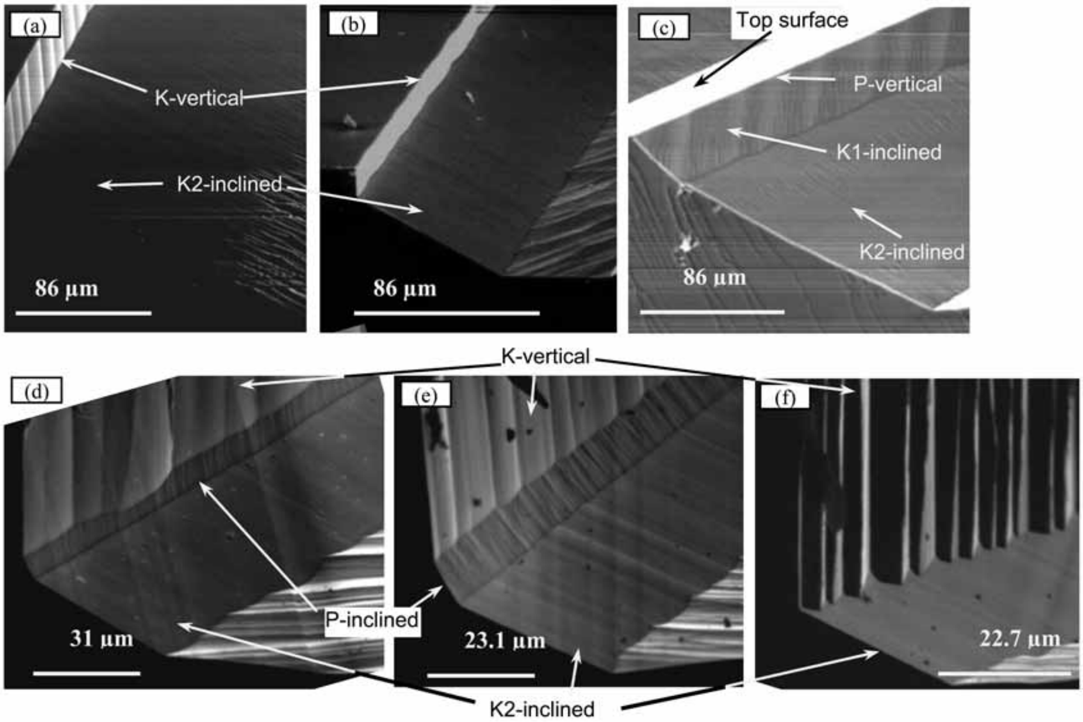

Fig. 11. SEM of sidewalls of spokes in wagon-wheel under-etch experiment etched in 25% TMAH at (a) $\delta \approx 23.5°$, etching time 1 h 30min, (b) $\delta \approx 23.8°$, etching time 3 h, (c) $\delta \approx 75.8°$, etching time 3 h, (d) $\delta \approx 38.8°$, etching time 1 h 30 min, (e) $\delta \approx 39.8°$, etching time 1 h 30 min, (f) $\delta \approx 43°$, etching time 1 h 30 min.

in the figure.

Figure 13 compares these crossover planes with the under-etch rates. The crossovers in the upper facets correspond roughly to etch rate maxima for the K-vertical facet at the $\delta \approx 25°$, plane with an etch rate ≈ 60 µm/h, and for the P-vertical facet at the $\delta \approx 76°$ plane with the etch rate ≈ 57µm/h.

Looking again at the theoretically available crossovers in Fig. 8, and comparing globally to the actual under-etch data in Fig. 9, it is possible that the crossovers significantly influence the presence or absence of certain facets. Notably:

1. the presence of the P-inclined facet only between its two crossovers at $\delta \approx 25°$ and $\delta \approx 43°$.
2. the presence of the P-vertical facet only at deviation angles below its crossover at $\delta < 76°$.

Further work is in progress to explore and analyze the correspondence of experiment with

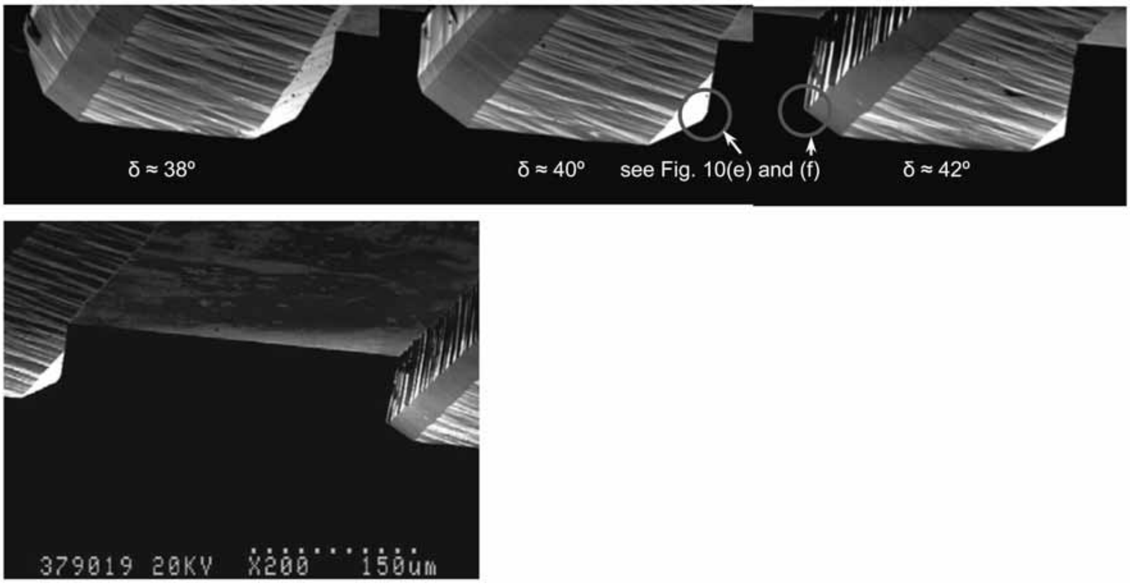

Fig. 12. (Upper) SEM of a panoramic composite view of spokes in wagon-wheel under-etching experiment etched for 1 h 30 min in 25% TMAH in vicinity of *d* ≈ 43°, (Lower) SEM of sidewalls of spokes at *d* =42°(left) and *d* =42°(right).

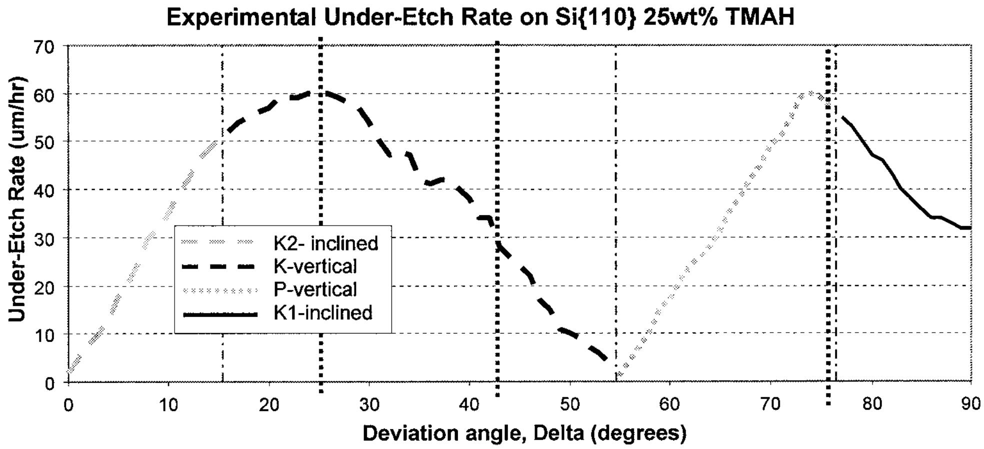

Fig. 13. Experimental under-etch datawith respect to deviation angle in the wagon-wheel under-etch experiment on Si{110} etched in 25 wt.% TMAH (Figure from ref. 8).

theory and the potential impact of such crossovers on under-etch experiments.

4. Summary

Theoretical calculation of terrace crossovers between {111}-terraces and {110}-terraces (for P-based planes), and between {111}-terraces and {100}-terraces (for K-based planes) shows that the crossovers happen close to {331} and {311} family planes, respectively.

When these planes are located in an underetch experiment on Si{100} in TMAH 25 wt%, the P-based and K-based theoretical crossovers coincide at $\delta \approx 19°$, where the underetched facets are observed to be composed of 3 facets, and there is the potential for quasi-continuous terrace edges across all three facets.

When these planes are located in an underetch experiment on Si{110} in TMAH 25 wt%, crossovers can theoretically occur at several different deviation angles. In practice, they appear at, $\delta \approx 25°$ where there are two facets, and possibly at $\delta \approx 43°$, and $\delta \approx 76°$, where there are transitions from three facets to two facets.

When the top-most facet in a wagon-wheel under-etch experiment is a crossover facet, this often corresponds to a local or global maximum in underetch rate for both Si{100} (at $\delta \approx 19°$) and Si{110} under-etch experiments (at $\delta \approx 25°$ and $\delta \approx 76°$).

Crossovers may significantly influence the complexity of etch-rate variation and facet appearance or disappearance in an under-etch experiment.

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