Evolution of hillocks during silicon etching in TMAH

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Abstract

The evolution of hillocks on (100)-silicon etched in 4 wt% tetramethyl ammonium hydroxide is studied through a detailed examination of hillock size distribution and individual hillock features using low-voltage scanning electron microscopy. Silicon samples etched for periods of 1.5, 3 and 5 min show that the population of hillocks initially comprises small, square-based pyramids with a wide distribution of aspect ratios ranging up to tall pyramids typifying \( \{111\} \)-bounded pyramids. As etching progresses, the population extends to larger pyramids, the majority of which are somewhat flatter than expected of \( \{111\} \)-bounded pyramids. Detailed examination of individual hillocks suggests that some \( \{111\} \)-bounded pyramids undergo a transformation that eventually leads to a quasi-stable bow-faced hillock configuration. Others collapse from the apex through erosion of the main faces. A number of dissolution routes are observed, and it is postulated that a hillock may undergo a series of fast transformations during its lifetime with intermediate configurations that are quasi-stable.

1. Introduction

In the anisotropic etching of silicon using alkaline solutions, hillock formation is an impediment to achieving smooth surfaces. Over the years, the nature of hillock formations on \{100\} surfaces has not only been described but has also formed the focus of etching studies. Hillocks are generally reported as being pyramidal or near-pyramidal in shape, bounded by \{111\} [1] or near-\{111\} [2] planes, giving the appearance of a bowed square perimeter. Furthermore, bevelling planes have been observed at the main edges of pyramidal hillocks [1].

In order to account for the appearance and disappearance of hillocks, Bhatnagar and Nathan [1] attempted to look for hillocks in a state of formation or annihilation but found none. Landsberger et al [3] observed that the majority of their hillocks are bow-faced, implying a stable configuration. This was explained in their model where such hillocks bounded by slow-etching \{111\} planes and intact \{101\} ledges are stable, provided some etch-retarding impurity or defect protects the apex. When the sample was removed from the etchant, and then re-etched, it was observed that the bow-faced hillocks transformed to octagonal hillocks, and were etched away rapidly by the traditional fast-etching bounding planes. In the experiments of Tan et al [2], re-etching experiments showed that the morphology of hillocks changes dramatically, and leads to the dissolution and sometimes break-up of the hillocks. As pointed out by Landsberger et al [3], the sensitivity of the hillock morphology to changes in etch conditions implies that annihilation processes observed in a re-etch experiment are unlikely to reflect the reality in a continuous etching process. Nevertheless, it shows that whatever the annihilation process, it is likely to be fast, which would then account for the poor chances of observing such an event.

To date, the nature of the point that initiates the formation of a hillock is not entirely clear. Various authors have suggested oxygen precipitates [4], and structural and impurity defects [1] in the bulk silicon that prevent etching at a point when the defect is revealed at the surface—the so-called defect theory. According to an alternative explanation, the pH theory, hydrated silicon oxide produced as a result of etching remains undissolved at the surface at low etchant pH values and acts as a mask that defines the apex of the hillock. Bhatnagar and Nathan [1] noted that a combination of both theories is required to account for observations reported so far. Yet others have suggested masking by hydrogen bubbles from the etch reaction [5–8]. Flidr et al [9] have shown that macroscopic etch hillocks form during step-flow etching of Si (111) due to site-specific kinetic factors.

Whatever the precise nature of the hillock initiation, an explanation is still required for the variety of hillocks observed.
and the annihilation of a hillock once the defect or micro-mask has been removed, if indeed such a masking mechanism is responsible for protecting the apex of a hillock. If the etch-retarding point is removed and the (100) surface lying beneath the apex merely etches down, this would give rise to flat-top hillocks which are seldom observed. Whatever mechanism is proposed would have to account for rapid dissolution of the hillock at a rate greater than the etching of the (100) surface.

This paper aims to provide some answers on the formation and growth of hillocks and the manner in which they disappear. No attempt is made to explain the relative etch rates needed to account for the annihilation phenomena observed, nor does this paper provide a detailed analysis of the etching mechanisms involved. The approach taken in this study is to analyse the hillock size and shape distribution, and to examine in detail the hillock morphologies present at various stages of etching.

2. Methodology

Tetramethyl ammonium hydroxide (TMAH) was used in this work since its desirable qualities of low toxicity and CMOS compatibility have made it an etchant of choice in MEMS work [10–12]. We have used 4% TMAH–water solutions as this coincides with the highest etching rates we obtained in earlier work [13], while providing a high density of hillocks. The primary consideration in the choice of this etchant concentration is the need to create a large number of hillocks to increase the probability of finding hillocks that are in a state of transition, i.e., formation, transformation and annihilation. At any instance in time, the latter two processes may be difficult to identify since they are likely to be rapid transitions between quasi-stable hillock configurations. As for hillocks in the state of formation, they are being formed continuously and it should be a simple matter to analyse them, provided the microscopy technique employed has sufficient resolution to resolve their features.

In steady-state etching, hillock initiation, growth, transformation and dissolution take place simultaneously over the entire wafer surface, and thus it is difficult to establish whether a particular feature observed represents a hillock in the process of growth or dissolution. The methodology adopted in this study to establish an arrow of time for a class of evolving hillocks is to examine wafers etched for different periods of time before a steady-state population of hillocks has been established. Ideally, a non-invasive in situ technique to observe the evolution of the etched surface would dispel any ambiguities, but such a technique is unknown to date—even liquid-based scanning probe microscopy techniques invariably disrupt the boundary layer at the surface.

Individual 5 × 5 mm² wafer samples from the same wafer were etched for 1.5, 3, 5, 10, 15, 30 and 45 min in 100 ml of 4 wt% TMAH at 60 °C, placed horizontally, and unstirred in a system with a reflux condenser. The wafers are n-type (100)-oriented CZ wafers of 4–8 /Ωcm resistivity, and were chemically cleaned to eliminate organic and inorganic contaminants using the standard RCA I and RCA II etches. Just prior to placement in the etch bath, the wafers were dipped in HF to eliminate any surface oxide.

The etched surfaces were inspected using a Philips XL-30 FEG scanning electron microscope (SEM) operated at low voltage (typically between 1–2 keV). The low-voltage operation enables fine surface details to be preserved in the SEM micrographs that would otherwise be lost at high electron beam voltages typically used by others in the past. Both plan and 45° tilted views of the surface are taken and stored digitally for subsequent image processing and analysis. The tilted views are used to determine the size and inclination of the bounding planes of the assumed pyramidal hillocks. It was noted that at short etching times of less than 5 min, the majority of the hillock population assumed a shape that approximates a square-based pyramid. Based on this approximation, a single inclination parameter can then be used to define the shape of the pyramid (figure 1(a)). Due to the nature of secondary electron collection from the sample, the side of the pyramid facing the electron beam appears darker (figure 1(b)), and an analysis of the aspect ratio of the triangular face yields the inclination angle θ. To provide a meaningful statistical distribution, nine regions of around 25 × 20 µm² evenly spaced over each wafer sample were analysed using image processing and analysis...
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3. Surface morphology

Unaided visual inspection of the etched samples show marked differences between samples etched for different periods of time. The samples of 1.5, 3 and 5 min are patchy and appear frosted. Low-magnification optical microscope inspection show traces left by detached gas bubbles. The 30 min samples have a uniform and lustrous surface.

At low SEM magnifications, the hillocks are generally pyramidal in shape. For the 1.5 min sample (figure 2), three major classes of hillocks are identifiable in the tilted SEM view:

(i) square-based flat-top hillocks;
(ii) sharp pyramids ($\theta > 35^\circ$); and
(iii) flattened pyramids.

In the normal SEM view, classes (i) and (iii) have roughly the same image contrast as the background, whereas sharp pyramids appear considerably brighter. In addition, there are also a number of pyramid structures that have a flattened centre but a steep-sided perimeter. In the plan view, such structures have a contrast that shows up as a bright perimeter surrounding a relatively dark core. As discussed below, these hybrid pyramids are in fact hillocks in the process of dissolution.

The high density of small, flat-top hillocks is associated with the initial immersion of the wafer into the etchant. These hillocks are not part of the population of hillocks in steady-state etching since they are never found in samples that have been etched for longer periods of time. For example, the background surface of the 3 min sample, although rough as a result of earlier formed and collapsed hillocks, shows no evidence of such flat-top hillocks. On the other hand, a sample that has been etched for 30 min, removed, rinsed, dipped in HF, and returned to the etch bath for 1.5 min, had a background surface similar to that of the 1.5 min sample. The only difference is the presence of

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1 Optimas version 6.5.
large hillocks that had resulted from the prior 30 min etch, the tips of which seem to have dissolved during the re-etch. Non-steady-state immersion effects have been observed by others [1, 2] who reported marked changes to the evolution of hillocks upon re-immersion.

4. Size and angle distribution of hillocks

The distribution of hillocks for the 1.5 min sample is shown in figure 3. The highest density of hillocks have angles around $\theta \sim 45^\circ$, and a size of less than 0.25 $\mu$m. A much larger density of sub-0.1 $\mu$m hillocks is expected than that represented in figure 3, but these could not be classified due to the limited resolution of the SEM technique. In contrast to samples that have been etched for longer periods of time, there is a substantial population of flattened pyramids ($\theta < 35^\circ$). The largest pyramids are about a micron in size and have angles between 35–55$^\circ$, while there are few, if any, large flat pyramids.

For the 3 min sample, the total number of hillocks is about the same as that of the 1.5 min sample. Note that this number only comprises those that can be classified (i.e. larger than 0.1 $\mu$m and $\theta > 5^\circ$); subjectively, the 3 min sample has a much smoother background devoid of small flat-top hillocks arising from the initial immersion. However, there is a marked change in the distribution of hillocks (figure 4); the population now stretches to a few hillocks larger than 2 $\mu$m. The hillock angle distribution is more narrowly focused in the range 35–55$^\circ$ for the larger-sized hillocks. Since the total hillock number has remained fairly constant, this suggests that many of the sharp hillocks that started small have grown in size as the $100$ base plane etches down. Since pyramids bounded by $\{111\}$ planes have an angle of $\theta = 54.73^\circ$, the median hillock population does not in fact comprise such pyramids, but hillocks that are somewhat flatter. As discussed below, these hillocks invariably have a bowed perimeter, and bounding faces that are rough.

At the same time, the population of flat hillocks follows that of the quasi-stable sharp hillocks, albeit at a lower density since they dissolve at a higher rate. As will be discussed later, the population of flat hillocks comprises those that are in the process of collapse and dissolution. Hence, flat hillocks will always be present at a size where sharp hillocks are present. The trend continues with the 5 min sample, with some reaching 4 $\mu$m in size (figure 5). For longer etch times, image processing analysis becomes increasingly inaccurate because of changes in the hillock shape that cause significant deviation from the assumed square-based pyramidal shape.

5. Hillock evolution

5.1. Quasi-stable hillocks

A high magnification examination of the hillocks revealed important features that provide a clue as to how hillocks evolve. Detailed studies were carried out on hillocks found on samples etched for 30 min, since large hillocks could be found that could be clearly resolved in the SEM. This is without loss of generality since similar hillocks in appearance, albeit smaller, can be found on samples etched for shorter periods of time.

Undoubtedly, one important quasi-stable hillock configuration is that of the pyramid bounded by $\{111\}$ planes. The smaller hillock in figure 6(a) is primarily defined by $\{111\}$ planes that are smooth and featureless, and bevelling planes along the convex edges that give the appearance of rounding at the base corners when viewed normally. The extent of these bevelling planes varies; some pyramids have almost perfectly square bases, while others show significantly chamfered corners. These bevelling planes are similar to those observed by Bhatnagar and Nathan [1]. The extent of the edge bevelling varies, giving a range of pyramids with bases that are almost perfect squares to those with noticeably chamfered corners. The angle that the basal edge of the bevelling planes makes with the nearest $\{110\}$ direction is difficult to determine accurately due to the poor resolution of the corners of the small pyramids. However, from the larger hillocks that also clearly possess similar bevelling planes (figure 6(b)), the internal angle at the base corners is approximately $128 \pm 2^\circ$. The bevelling planes are thus near $\{212\}$ planes that are reputed to be fast etching [14]. However, from the limited extent of such bevelling planes, it is clear that these planes do not ultimately convert a pyramid into an octagonal hillock.

Landsberger et al [3] observed that the hillocks in their study are bound by four faces with layered features whose
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Figure 7. Origin of bowed faces (after Landsberger et al [3]). Triangular {111} planes enclosed by ⟨101⟩ directed ledges on two sides.

direction so as to flatten this part of the pyramid (figure 11(a)). It is proposed that lines of atoms along the ⟨011⟩ direction on the ⟨111⟩ face are removed to expose ⟨100⟩ kink terraces, which then propagate down the face a layer at a time (figure 11(b)).
Figure 9. A schematic diagram showing the proposed transformation of a pyramid to a bow-faced hillock: (i) a small starting pyramid grows into (ii), a larger pyramid whose edges are bevelled; (iii) ledges initiate at the apex where the bevelling planes meet leading to (iv) the formation of more ledges and the erosion of the bevelling planes; (v) final bow-faced hillock.

Figure 10. (011) directed edges on a hillock demarcating a change in the slope of the hillock faces. Multiple edges at different levels are seen, as well as the initiation of a (101) directed ledge at a defect on the left face: (a) view at 45° sample tilt; (b) a schematic diagram highlighting salient features.

Figure 11. (a) Diagram illustrating the vertical collapse of the top portion of a pyramid. (b) Proposed etching mechanism whereby {100} terraces erode the {111} face.

in a step-flow etching process. The intercept of the bevelling planes with the eroded top is quite clearly visible, as is the change of the slope at the major hillock edges.

Figure 10(b) also shows that as a (011) directed edge moves down a pyramid on the left face, it encounters a defect which then initiates (101) directed ledges. Unlike the trace formed in the middle of a face by stacked planes enclosed by ledges, the tip of the triangular features formed here occurs at random positions on the face. It is expected that with further erosion of the main face, merged daughter hillocks will appear from these features. The micrograph (figure 10(a)) also shows that multiple edges can form giving rise to a pyramidal structure with multiple slopes at different heights.

Apparently this process of erosion can occur quite rapidly...
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Figure 12. Examples of hillock collapse via a flattening route: (a) hillock at an intermediate stage of collapse (45° sample tilt); (b) smaller hillocks, some showing a similar form of crown collapse, while others are undergoing overall transformation, and several flattened hillocks (45° sample tilt).

until the faces it exposes start to deviate considerably from the original {111} planes. Erosion occurs through terraces, sometimes indistinct, leading to the final collapse of the hillock (figure 12(a)). Among the smaller pyramids, the process is also one means by which entire pyramids can collapse (figure 12(b)). This mechanism would account for pyramids that are flatter than $\theta = 54.73^\circ$ among the population of hillocks. Incidentally, the occurrence of supporting crown structures surrounding collapsed pyramids indicates that flattened pyramids result from a collapse rather than pyramidal growth from the surface.

Figures 13 show a bow-faced hillock, with its characteristic layered structures on its rough faces, being eroded from the apex by pairs of terraces which make a rather more obtuse angle with each other than the $\langle 101 \rangle$ directed ledges, with the right-hand side face being fully uncovered. The new hillock that is being uncovered has relatively smooth faces, and a bowed perimeter. Ledges that are parallel to the main hillock edges are present on the new hillock faces, giving rise to the characteristic bow. This appears to be a case where a bow-faced hillock is being transformed into another similar but smaller hillock.

Figure 13. Bow-faced hillock transformation at intermediate stage with erosion starting from the apex: (a) plan view; (b) view at 45° sample tilt; (c) schematic diagram highlighting salient features.

The process of erosion to reveal a new quasi-stable hillock is found to occur for other different hillock shapes, ranging from well-defined tall hillocks to rather flattened and usually poorly defined hillocks. The details of the erosion vary,
Figure 14. Examples of hillocks being transformed into different configurations: (a), (b) plan and 45° sample tilt views of a rather flat hillock undergoing erosion; (c), (d) plan and 45° sample tilt views of a hillock at an advanced stage of annihilation; (e) 45° sample tilt view of a flat octagonal hillock emerging from a transformation process; (f) likely outcome of (e) after further etching.

depending on the type of hillock, but the essential process remains the same; eroding terraces first appear at the apex, and many such terraces give the appearance of a rough surface from a plan view. The new hillock that emerges is noticeably smoother than the eroding terraces and has a distinctive shape. Figure 14 shows examples of hillocks in the process of transformation. Figures 14(a) and (b) show a relatively flat hillock being eroded. In contrast to the hillock of figure 13, the oblique view shows that the height/width aspect ratio is lower, and the apex of the underlying hillock has yet to appear. Figures 14(c) and (d) show a hillock which has almost completely eroded, yet an underlying hillock shape is
still clearly present. Figure 14(e) shows a distinctly octagonal hillock emerging from a process of erosion. Once the eroding terraces have disappeared and further dissolution occurs, it is expected to yield a rather flat octagonal hillock, such as the one shown in figure 14(f).

From these observations, it is postulated that a hillock can undergo a whole series of transformations throughout its life span. Each transformation occurs through a process of erosion by terraces that emerge from the apex, to reveal a new hillock that is bounded by relatively stable crystallographic planes, which would explain the occurrence of a variety of hillock shapes. It is postulated that such quasi-stable hillocks are responsible for the large spread in distribution of hillock aspect ratio with a peak in the distribution at around \( \theta \approx 40–45^\circ \) for the whole range of hillock sizes from the smallest to the largest.

In some instances, two such erosions occurring consecutively on the same hillock can be seen. For such hillocks, the first erosion to yield a stable hillock has not fully completed before the underlying hillock apex undergoes a second erosion, thus giving rise to the two thick peaked onion skin layer appearance. The question remains as to why particular hillock configurations are apparently stable as they emerge from the erosion process. If the hillock had been protected by a micromask which was then removed during etching, it is unlikely that another such micromask would lie directly beneath to form the basis of an underlying apex. A more likely scenario is that a point site protecting the apex, once removed, will leave another point site in its wake in a continual process of erosion. It is postulated that certain hillock configurations are more stable and these become intermediate quasi-stable stages in the dissolution process.

Finally, at the end of its life span, a hillock dissolves and merges into the surface, but in the process leaves a roughened patch through which other hillocks may appear as from any other area. Such patches are easily visible when the sample is tilted.

6. Discussion and conclusion

From the angle and size distribution of hillocks at very short etching times (1.5 min), it appears that hillocks begin their life as pyramids which then grow in size as the surface etches down. The angle distribution of these small pyramids has a wide spread, ranging from very flat ones to those that typify pyramids bounded by \{111\} planes (\( \theta = 54.73^\circ \)). The peak in the angle distribution is found at \( \theta \sim 40–45^\circ \). Most of the flat ones appear to be in a state of dissolution with bowed or round-corner perimeters, whereas the sharper pyramids are defined by faces that are relatively smooth. Thus, it is likely that hillocks first emerge as \{111\}-bounded pyramids, but the majority of these will undergo transformation and dissolution even as they grow in size. With continued etching, pyramids that are relatively more stable grow in size, but eventually undergo transformation and are ultimately annihilated.

As regular \{111\}-bounded pyramids grow, their edges become bevelled, even as the \{111\} planes remain atomically smooth. Where the beveling planes meet each other, \{101\} ledges are formed and propagate down the faces to cause them to acquire a characteristic bow. Such bow-faced hillocks are quasi-stable, and can continue to grow in size.

Alternatively, kink terraces can progressively propagate down the faces from the apex to effectively flatten the hillock. This can eventually lead to the collapse of the hillock, and is responsible for pyramids with collapsed centres, especially for larger pyramids, multi-terraced square-based hillocks or simply flattened pyramids.

The bow-shaped hillocks are found to undergo further erosions and transformations. The erosion initiates at the apex, and layers of the hillock are eroded away, exposing yet another underlying hillock that appears to be quasi-stable. Emerging hillocks have been found to be flatter than the original hillocks, and can undergo further erosions to reveal further quasi-stable hillock configurations beneath. Very flat octagonal hillocks have been observed and are believed to be the end product of many such successive transformations. From the relative scarcity of such hillock transformations in transition, it is believed that the erosions take place rapidly. On the other hand, the quasi-stable hillock configurations make up the bulk of the hillock population as expected.

On a final note, since the etching was carried out in very dilute etchant (4% TMAH in water solution), the results obtained may not be characteristic of etching at higher TMAH concentrations. Nevertheless, it is hoped that the observations reported have shed some light on the multifarious hillock transformations that can take place.

References