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Collective evolution of submicron hillocks during the early stages of anisotropic alkaline wet chemical etching of Si(100) surfaces

P Sana, Luis Vázquez, Rodolfo Cuerno and Subhendu Sarkar

1 Department of Physics, Indian Institute of Technology Ropar, Nangal Road, Rupnagar, Punjab, 140001, India
2 Materials Science Factory, Instituto de Ciencia de Materiales de Madrid (CSIC), 28049 Madrid, Spain
3 Departamento de Matemáticas and Grupo Interdisciplinary de Sistemas Complejos (GISC), Universidad Carlos III de Madrid, Avenida de la Universidad 30, 28911 Leganés, Spain

E-mail: sarkar@iitrpr.ac.in

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Abstract

We address experimentally the large-scale dynamics of Si(100) surfaces during the initial stages of anisotropic wet (KOH) chemical etching, which are characterized through atomic force microscopy. These systems are known to lead to the formation of characteristic pyramids, or hillocks, of typical sizes in the nanometric/micrometer scales, thus with the potential for a large number of applications that can benefit from the nanotexturing of Si surfaces. The present pattern formation process is very strongly disordered in space. We assess the space correlations in such a type of rough surface and elucidate the existence of a complex and rich morphological evolution, featuring at least three different regimes in just 10 min of etching. Such a complex time behavior cannot be consistently explained within a single formalism for dynamic scaling. The pyramidal structure reveals itself as the basic morphological motif of the surface throughout the dynamics. A detailed analysis of the surface slope distribution with etching time reveals that the texturing process induced by the KOH etching is rather gradual and progressive, which accounts for the dynamic complexity. The various stages of the morphological evolution can be accurately reproduced by computer-generated surfaces composed by uncorrelated pyramidal structures. To reach such an agreement, the key parameters are the average pyramid size, which increases with etching time, its distribution and the surface coverage by the pyramidal structures.

Keywords: anisotropic etching, Si pyramidal structures, dynamic scaling theory, atomic force microscopy

(Some figures may appear in colour only in the online journal)
In this paper, we address the initial stages of surface etching (up to 10 min of etching under our working conditions, see below), in which the surface roughness increases with time, that is, well before roughness saturation. We study the dynamical evolution of the submicrometric hillock pattern that ensues under anisotropic KOH etching of Si(100) surfaces, focusing on the collective morphological properties of the surface, as well as their behavior with etching time. Although strongly disordered, the surface morphology is not uncorrelated. Actually, it features space correlations with scale-invariant properties akin to those found in kinetically rough systems, which in principle indicates non-trivial behavior in the spatial self-organization of the hillock pattern [31–33, 49, 50]. In particular, conspicuously large fluctuations are found to take place in the values of the surface height from point to point on the substrate. However, the time evolution is more complex than in other experimental instances in which rough interfaces occur, to such an extent that the morphological behavior is hard to reconcile with the precise expectations for kinetically rough surfaces [31, 49, 50]. This suggests the existence of very different mechanisms controlling the collective behavior of the hillock pattern at different stages during the time evolution; a fact which is also supported by the observed time evolution of the statistical distribution of the facet angles, which evidences a gradual texturization process.

Notwithstanding, systematic comparison of our experimental hillock arrangements with those synthetically obtained through open software [51] allows us to interpret the geometrical content of the space correlation functions which we measure. These findings are discussed in light of the different physical mechanisms proposed for hillock formation and dynamics under wet chemical etching of Si(100) surfaces.

2. Experiment

2.1. Sample preparation

Undoped single-side polished Si(100) surfaces were chemically etched using a KOH solution in a clean room environment. The Si wafers were procured from Vin Karola Instruments grown by the Czochralski method and having an electrical resistivity $\approx 15–20 \, \Omega \cdot \text{cm}$. Samples were prepared for different etch times. $1 \times 1 \, \text{cm}^2$ Si wafers, cut from 2 inch-diameter wafers, were ultrasonically cleaned for 15 min at room temperature with isopropyl alcohol. Each wafer was rinsed with ultrapure deionized water after sonication using a Millipore system. A 7 wt% (1.25 M) KOH solution was taken and kept on stirring at a constant temperature of 80 °C for 1.5 h. According to the literature, these can be considered as low concentration conditions. The Si wafer was dipped into KOH solution for a specific etch time at room temperature, which was kept constant for the entire process. An identical procedure was employed to etch Si wafers for etch times of 30, 90, 120, 240, 360, 480 and 600 seconds.

2.2. Sample characterization

The surface morphologies of the etched Si wafers were measured using Bruker Multimode-8 Atomic force microscopy.
(AFM) in the tapping mode. For each sample, 512 × 512 pixels images were acquired for three different image lateral sizes of 10, 25 and 50 microns. For each scan size, three different regions were scanned to account for better statistics and data reproducibility. Silicon cantilevers (Bruker) with a nominal radius of 8 nm were employed.

3. Results

3.1. Morphological characterization and scaling analysis of as-prepared samples

AFM images of KOH etched Si surfaces for different etch times are shown in figure 1. Transverse one-dimensional cuts of these images are additionally shown in figure 2. After an etching time of 30 s, mound structures appear scattered on the Si surface. These structures grow in size between 90 and 120 s, leading to a rather high density of bright spots, which is highest at 120 s, when the protruding structures become 500–700 nm wide. As can be seen in the inset, some of these structures already have a faceted pyramidal morphology, while others are more rounded. However, at 240 s, this process has led to the emergence of a few, well-defined pyramidal structures, with a bright contrast and a rather heterogeneous size distribution. These are surrounded by smaller structures; see the inset. With further etching, pyramids grow and display sharper forms. At an etch time of about 480 s, these pyramids practically form a homogeneous and compact surface. Finally, large hillocks are observed after etching the sample for 600 s, akin to the 240 s case, but with a higher pyramid coverage. Figures 1 and 2 indicate the existence of two basic lateral lengths in the morphologies, namely, the motif size, \( \xi \), and the average inter-motif distance, \( \lambda \). They are evident in the corresponding profiles for 240 s, 360 s and 600 s, where large protruding pyramidal structures are visible that are not compactly arranged. For other etching times, there is also a distribution of structures, most of which resemble a basic motif, a square pyramid. These structures are quite disordered on the substrate plane within a single AFM image, leading to a wide distribution of the inter-pyramid distances.

Overall, the AFM images show large-scale surface roughening and faceting. In order to have a deeper insight into the surface dynamics, we have analyzed the evolution of the global surface roughness, \( W(t) \) [31, 49], with etching time \( t \), provided in figure 3(a). For each time, \( W(t) \) has been computed using those images that have the largest lateral size, \( L = 50 \mu m \). Indeed, the global roughness increases with time at changing rates that last short periods of roughly 2 to 4 min. Thus, the initial stages when mound structures emerge are characterized by a relatively slow roughening, \( W(t) \sim t^\beta \) with a value of the growth exponent \( \beta_1 = 0.28 \). Moreover, the change in the growth regime at 240 s suggested by the AFM image in figure 1 is confirmed by the sharp increase in the value of the roughness: indeed, \( W(t = 240 \text{ s}) \) is more than three times larger than \( W(t = 120 \text{ s}) \). However, the roughening process slows down between 240 s and 480 s, so that \( W(t) \sim t^\beta \) with \( \beta_2 = 0.34 \). This regime corresponds to the gradual increase of the hillock density that finally reaches full coverage by pyramids at 480 s, similar to the behavior between 30 s and 120 s. Finally, at 600 s the roughness increases again substantially, becoming more than twice its value at 480 s.

Another statistical parameter that is helpful to describe the interface morphology is the skewness, \( \gamma_1(t) \), that measures the lack of up-down symmetry of the distribution of height values around its mean [49]. The experimental time evolution of \( \gamma_1 \) is plotted in figure 3(b). Thus, from 30 s to 120 s, the skewness increases from 0.4 to 1.5. At 240 s, \( \gamma_1 \) undergoes a huge increase up to a value larger than 4, which correlates with the emergence of a few, large pyramids from the background. Afterwards, between 360 s and 480 s, the skewness goes back to values which are similar to those measured within the initial time regime, with a minimum at 480 s, i.e. when the surface is fully covered by the pyramid structures. Finally, at 600 s \( \gamma_1 \) increases again, due to the fact that the surface is not fully covered by the large pyramids. Summarizing, the behavior of the skewness seems to correlate with the surface coverage...
by the emerging pyramids with respect to the homogeneous background, and to the average pyramid height relative to the surface roughness. Large $\gamma_1$ values are obtained when this coverage is low and the pyramids are relatively high, whereas the skewness is reduced for a surface with a high density of hillocks, particularly when the pyramid coverage tends towards unity, due to the enhanced symmetry of the surface morphology with respect to its average height.

Qualitatively, the behavior observed for the global roughness and the skewness suggests the following surface evolution: (1) slow roughening and an increase of $\gamma_1$ (associated with the emergence of mounds) up to 120 s. (2) A sharp increase of $W$ associated with the development of few large pyramids at 240 s, leading to a substantial increase of the skewness. (3) Slow-down of the roughening process between 300 and 480 s, due to the gradual covering of the surface by the emerging pyramids, which become more numerous with time, decreasing the value of $\gamma_1$. (4) At 600 s, $W$ increases again, due to the incomplete coverage of the surface by the existing pyramids. Similar patterns are frequently observed at long times in the present type of wet etching process [43, 47, 48].

Both, roughness and skewness are global average quantities that characterize the behavior of the surface as a whole. Further detailed information can be gained from a study of correlation functions, which are sensitive to the morphological behavior at different scales. A very useful one [32] is the surface structure factor or power spectral density (PSD) $S(k,t)$, where $k$ is the wave-vector magnitude. Figure 3(c) shows the (radially-averaged) PSD function obtained for different etching times including the pristine initial Si(100) surface. Note how the initial space correlations, encoded in the dependence of $S(k,t)$ with $k$, have disappeared at all length-scales (equivalently, all values of wave-vector $k$) already after 30 s etching time. For each time, the behavior of the PSD can be roughly seen to feature a $k$-independent ($\propto$-dependent) behavior for small (large) wave-vectors. The former implies that parts of the surface remain statistically independent, i.e. uncorrelated, at the corresponding large distances. The latter behavior is approximately consistent with power-law decay in the form $S(k) \sim 1/k^{2\alpha+2}$ for a suitable choice of the so-called roughness exponent $\alpha$. For any fixed time, there is a wave vector value $k_c$ separating small-$k$ from large-$k$ behaviors in the PSD. We estimate it (with up to 20% error bars) by measuring the crossing point between the straight line defined by the linear dependence observed at large $k$ (parallel to the dashed line in figure 3(c)) and a horizontal line describing uncorrelated, $k$-independent behavior.

The inverse of this characteristic wave-vector defines the correlation length, $\xi_c = 1/k_c$, i.e. a lateral distance within which height values are statistically correlated variables. The inset of figure 3(c) shows the thus obtained values of $\xi_c$ for different times. The correlation length increases from 700 nm at 30 s up to almost 4 $\mu$m at 240 s, then decreases down to 2.5–3 $\mu$m in the 360–480 s range, and increases back up to 5.8 $\mu$m at 600 s.

Figure 2. Typical surface profiles for the etched surfaces for times: (a) from 0 to 120 s and (b) between 240 and 600 s. Solid bars provide the vertical scales in each case and differ by a factor of 5 between the two panels.

The existence of a basic motif (the square pyramids) in our experimental topographies suggests the relevance of two associated scales, namely, the average pyramid size $\xi$ and the average inter-pyramid distance $\lambda$, which should be identifiable e.g. in the PSD data, akin to island formation in submonolayer growth [52] and to mound formation in multilayer growth [50]. Indeed, e.g. in the former context $\lambda$ can be identified from the occurrence of a well-defined maximum in the PSD at relatively small $k$. However, the $k$-dependence of our PSD curves is less clear-cut for small $k$ and requires a more detailed study, performed in section 3.2 below.

For now, we focus on the experimental large-$k$ behavior, corresponding to distances smaller than the average pyramid size. As seen in figure 3(c), the power-law behavior that is obtained is well characterized by $\alpha = 1.4 > 1$, the PSD for different times overlapping except for 120 and 240 s. This behavior is reminiscent of so-called kinetic roughening [31, 49]. A surface is said to be kinetically rough if its space and time correlations follow power laws like $W(t) \sim t^\beta$ or $S(k) \sim 1/k^{2\alpha+2}$, where $\alpha$ and $\beta$ are related in a precise way. This is encoded in a so-called dynamic scaling Ansatz for the space and time behavior of correlation functions [31, 49], which generalizes to non-equilibrium systems (hence the name kinetic) the classic scaling Ansatz describing equilibrium critical phenomena or second-order phase transitions [53]. However, power-law correlations can also occur for surfaces whose topography is dominated by a characteristic form or motif [54–56] and which are not kinetically rough, because the expected scaling Ansatz is not fulfilled. We believe this is the case in our experiments, in contrast with previous works that discuss similar wet etching processes in the kinetic roughening context [21, 35, 42, 43]. Namely, attempts to consistently analyze our data under the most comprehensive formulation of the dynamic scaling Ansatz compatible with our result that $\alpha > 1$ [45] prove unsuccessful. Hence, we believe that the exponent $\alpha$ that we measure originates in the

\[ ^4 \text{Statistically relevant length scales can be equivalently obtained from the time behavior of the surface roughness } w(l,t), \text{ as obtained over images of lateral size } l, \text{ see figure S1 in the supplemental material.} \]
well-defined geometry of the pyramids rather than in kinetic roughening.

3.2. Synthetic patterns

In order to assess the morphological relevance of the pyramidal motif along the full etching process, it is useful to analyze the slope distribution of the images. This is done in figure 4(a) (left column), which shows the AFM images of the surfaces etched after 90 and 600 s, with the corresponding slope histograms as insets. Specifically, the slope distribution shown is a 2D plot in which the independent variables are the space derivatives of the height, $m_x = \partial h/\partial x$ and $m_y = \partial h/\partial y$ along the two coordinate direction on the AFM images; the dependent variable is the fraction of points of the original AFM topograph at which the slopes happen to equal the pair of values $(m_x, m_y)$. Indeed, the two experimental surfaces display a square-symmetric pattern, as evidenced by the form of the corresponding slope histograms. This is more clear for the 600 s image, for which the signal is particularly enhanced at the vertices. In contrast, for the 90 s surface the square pattern is more blurred, although still discernible. Therefore, the slope distribution suggests that a similar basic motif is the basic component of the morphology already from the very early stages of the process, namely, the square hillocks that are so evident in the AFM topograph at 600 s.

For the shortest etching times, the slope distribution is more diffuse, indicative of an incipient surface texturing process. The fact that the basic structural motif of the evolving surface is pyramidal allows us to model the surface at the different stages by producing synthetic surfaces that readily employ such a basic morphological unit. Specifically, we make use of Gwyddion [51], an open software package for surface data analysis, in order to generate random arrangements of square pyramids. For each etching time, we have tuned the parameters controlling the synthetic surface in order to reproduce not only the measured surface roughness, but also the full experimental PSD curve, thereby reproducing the space correlations experimentally measured at that time. In this process, we have found that there are two key parameters (see the supplementary information (SI) for further details): the first and most important one is the average size of the
pyramids. Thus, in order to accurately reproduce the experimental surface correlations, we have increased the pyramid size with etching time (using motif size/image size ratios of 0.5%, 0.9%, 1.2%, 2%, 2.3%, 2.9%, and 4.5% for increasing times). Simultaneously, we have kept fixed the variance of the distribution of pyramid sizes to a relatively low value, 0.21, for all etching times. The second main parameter that controls the agreement between experimental and synthetic surfaces is the coverage of the surface by the randomly arranged pyramids. We define pyramid coverage [51] as the average number of pyramids which cover a pixel on the image. Hence, for synthetic surfaces in which the pyramids visually fill the whole surface with coverage larger than 1, there is substantial overlapping of different pyramids. Specifically, we have employed pyramid coverage equal to 4, except for 30 s (coverage = 0.8) and 240 s (coverage = 0.32).

In this way, by changing the average pyramid size and by re-scaling the lateral and vertical dimensions, we are able to reproduce the experimental images, not only qualitatively but also quantitatively. Specifically, the lateral re-scaling consists of making the image size equal to 50 microns, as the experimental images, keeping the same number of pixels in an image (512 × 512). Then, we change the pyramid size (keeping the variance at 0.21 and in most cases coverage equal to 4) in order to visually have a similar image. This is achieved by matching the relevant k-values of the experimental and the synthetic PSDs. Next, the vertical scale is changed to obtain the same roughness as in the experimental case, as well as to match the full corresponding PSDs.

Qualitative agreement can be appreciated in figure 4(a) (right column), which shows the synthetic images for 90 s (top) and 600 s (bottom), in parallel with the corresponding experimental AFM top views. The visual similarity between the experimental and synthetic images is striking, specially for 600 s. The 2D slope distributions of the synthetic morphologies are also shown as insets. The clear square-symmetric patterns confirm our previous conclusions with respect to the experimental images. The increased sharpness of the pattern in the synthetic surface for the short etching time indicates that, at the beginning of the process, the pyramidal structures are not so well developed yet. Indeed, the contrast of the 2D slope distributions is sharper and more homogeneous along the square sides in the synthetic cases, as expected due to the perfection of their pyramidal motifs. Quantitative agreement between the experimental and synthetic surfaces is confirmed in figure 4(b), where we show the PSD functions of the experimental and the synthetic 50 × 50 μm² images, for 600 s etching time. Note that the two sets of data match throughout k-space, implying virtually identical values of the global roughness. This type of quantitative agreement has been reproduced for all the etching times and scan sizes by suitably tuning the motif size, with the exceptions noted above. Small discrepancies have only been found at large k-values for the smallest images carrying a smaller number of individual hillocks, where some aliasing effects also take place.

The possibility to match the experimental images with synthetic surfaces composed by randomly arranged pyramids allows us to better interpret the PSDs of figure 3(c). As noted above, two basic length scales should occur in this system, ξ and λ. Where the former is related to the power-law regime for large k, the latter should appear as a peak in the PSD for lower k values [50, 52], which is not clearly seen in figure 3. In the SI, we further analyze our synthetic surfaces for different parameter values of the random pyramid distribution. The conclusion is that large pyramid sizes relative to the image size and large surface coverage by pyramids hamper the occurrence of the peak in the PSD which is associated with the inter-pyramid distance λ. Morphological analysis like that in [52] for submonolayer pentacene islands on flat silicon oxide surfaces can allow us to identify ξ and λ in the PSD. However, this is only possible when the surface coverage by pyramids is relatively small, which in our case occurs up to 240 s, see the SI. The high coverage and disorder of our experimental pyramidal distribution for longer times hampers application of the approach in [52]. Nevertheless, the value of λ and ξ can still be inferred from the autocorrelation (ACF) and height different correlation (HDCF) functions [50]; see the SI. Indeed, the two distances are closely correlated for t < 240 s, as expected for an arrangement of well-defined pyramids, while they are not clearly related for longer etching times, supporting a more random positioning of pyramids.

4. Discussion

The results obtained in the previous sections suggest that (i) non-trivial space correlations build up in the surface patterns, (ii) at an etching time of approximately 240 s, there is a change of behavior in the system; (iii) two basic lengths exist in the morphologies, namely, the pyramid size and the inter-pyramid distance, particularly for long etching times. The surface morphology does not display kinetic roughening properties [31], power-law behavior at distances smaller than the pyramid size being induced by the geometry of this basic motif.

The quantitative description of the experimental space correlations by our synthetic surfaces allows us to think of the morphologies in terms of a random distribution of pyramids. We can further consider this fact in light of the scenario of wet etching of silicon surfaces reviewed in the Introduction. Thus, the etching process becomes inhibited at some locations (through some of the various mechanisms proposed) that become apices where growth of pyramidal hillocks nucleates. Depending on the specific mechanism that operates, these nucleation sites can change or lose their condition dynamically, leading to a complex morphological evolution. A scenario like this corresponds in general terms to an etching process with poisoning [57]: indeed, the large surface fluctuations implied by the fact that α = 1.4 > 1 (and the time behavior of the roughness, as assessed in the SI) agree with this behaviour. This is consistent with the view that wet etching of Si(100) proceeds via etching inhibition at certain sites, already at the early stages of the process.

We can obtain further insight into the present rich morphological dynamics by considering further experimental properties of the hillock assembly. As mentioned above, one of the
main mechanisms leading to the pyramidal texturization of the Si(100) surface is based on the slower etching rate of the \{111\} planes. Hence, it is natural to study the time evolution of the facet angles with respect to the flat Si(100) plane. The corresponding data are displayed in figure 5, where we show the distribution (histogram) of facet inclination angles for different etching times. We consider the inclination to be the positive angle between the \( z \) axis, perpendicular to the \( xy \) substrate plane, and the normal direction to the facet, which is zero for horizontal facets and increases with the slope; it measures the facet orientation. Initially, up to 120 s a bimodal distribution is observed with predominant angles around 10° and 30°. This corresponds to the emergence of mounded structures. After 240 s, this distribution is even narrower and less symmetric, with a preferred maximum close to 5° (due to the smoother background) and a secondary maximum near 50° (due to the large pyramids). This correlates with the clear observation of scattered, large and well-formed pyramidal structures on the surface. At later times, a higher slope, close to 50°, develops, which becomes predominant after 600 s of etching. We should remark that the ideal angle between the \{111\} and \{100\} planes is 54.7° [24], very close to this value. Hence, the present data indicate a texturization process which evolves rapidly with time. The different dynamical stages detected in the dynamics of the roughness are related to the progressive faceting of the surface, whereby close-to-perfect pyramids eventually form. Note also that, as \{111\} planes are becoming more populated, i.e. with progressive texturization, the average etching rate decreases. Interestingly, for etching times longer than 240 s, the faceting process continues mainly via formation of smaller pyramid structures, rather than through the coarsening and growth of existing ones, see figure 2. This is consistent with the relatively low KOH concentration condition employed in our studies. Under these conditions, the etching of the background (non texturized) surface is relatively slow, which allows the formation of new pyramidal structures before the existing ones grow in height and size. This is also consistent with the fact that, at 600 s, the surface is basically composed by a distribution of pyramidal structures with a small dispersion of sizes. Recall that, in the synthetic patterns, a low variance value of the motif size was used.

We still need to address in further detail how the observed morphological behavior can be understood under the framework of the poisoning mechanisms mentioned in the Introduction. These mechanisms include the effect of bubbles [14], the adsorption of inhibiting species, like metals, from the solution [22], and the selective reactivity of specific sites on the surface [24, 58]. The effect of bubbles on the morphology is supported by the observation that, under stirring conditions which specifically prevent bubble formation, the hillock density and size are largely reduced [22]. The two remaining mechanisms are based on processes that take place at atomic scales. For instance, detailed numerical simulations are available in the literature [18, 22, 48], in which the formation and evolution of the pyramidal structures during wet etching of Si(100) surfaces is addressed. A main goal of these studies is to assess the specific microscopic mechanism that controls the onset of pyramid formation. However, it may be hard to directly infer from microscopic models the collective behavior of the surface morphology composed by an assembly of pyramids, such as is our present focus.

Under the experimental conditions that we study, masking of surface sites through the formation of hydrogen bubbles seems unlikely. First, the relatively low KOH concentration conditions should induce the formation of relatively large, or at least medium-sized, bubbles [14] that, accordingly, would lead to large pyramid sizes, which is not the case in the initial stages that we address. Moreover, except for the 240 s case, our surfaces are quite homogeneous, which suggests a uniform distribution of small bubbles over the surface. This scenario seems unlikely at these KOH concentration and short etching times. The additional mechanisms of inhibitor species [22] or selective site reactivity [24, 58] are based on a slower or null etching rate at given surface sites which thus become the pyramid apices. The latter mechanism was proposed for a H-terminated Si surface, which is likely not the case for our system, due to the KOH etching, which induces the formation of OH-terminated sites on the Si surface [14, 59]. In the former mechanism, the pyramid apices would be a consequence of the presence of species that inhibit etching. When they arrive to the surface from the solution, they should do so along random trajectories, in such a way that they would impinge the most exposed surface locations with a higher probability. In that case, they would inhibit surface sites randomly. Upon stirring, the arrival of these species should be more homogeneously distributed on the surface, which might be related with the reduced pyramidal structuring.

5. Conclusions

In summary, we have studied the early-time regime of nanopyramid hillock formation under alkaline wet chemical etching of silicon targets. Overall, the process can be understood in terms of the formation of mounds that evolve into characteristic and well-formed square pyramids, emergence of individual pyramids being essentially uncorrelated in space. Two basic length scales characterize the surface morphology, namely, the pyramid size and the average inter-pyramid
distance. The non-trivial behavior of experimental space correlation functions can be attributed to the occurrence of a well-defined pyramidal shape, coexisting with a strong heterogeneity. The behavior of correlations with etching time does not agree with kinetic roughening properties, likely due to the gradual surface texturing process that is taking place.

At any fixed time the full behavior of the observed space correlation functions can be quantitatively reproduced by that of synthetic images that have been obtained employing freely available software for surface data analysis. Actually, this agreement validates the representation of the process in terms of the uncorrelated emergence of individual, well-defined pyramids. On the way, the variation of the correlation functions of the synthetic interfaces with parameters underscores the dynamical relevance of the average pyramid size and of the surface coverage by pyramids as the main experimental features determining the morphological properties of the experimental surfaces. Finally, our findings seem to agree, at least partially, with physical mechanisms for hillock formation under wet etching which are based on some type of poisoning, more than with those advocating alternative processes, such as bubble formation.

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References

1. Space and time dependence of the surface roughness

We provide a plot of the surface roughness over windows of lateral size $l$, $w(l)$ [1], as a function of the window size for different times in Fig. S1. For each fixed time and small windows sizes $l < \ell_c$, the roughness increases as a power law $w \sim l^\alpha$ with the window size $l$. When $l$ exceeds the characteristic value $\ell_c$, the roughness saturates to an $l$-independent value. This behavior of $w(l)$ is typically found for systems displaying kinetic roughening [1, 2]. Figure S1 yields a value for the characteristic size $\ell_c$ which is close to 0.5 $\mu$m for $t < 120$ s and close to 2.5 $\mu$m at the longest time.

Figure S1. Log-log plot of the experimental surface roughness $w$ computed over windows of lateral size $l$ vs this lateral scale, for etching times as in the legend.
2. Synthetic surfaces

The possibility to generate synthetic surfaces composed of random pyramidal hillocks and to compare them with the experimental data allows us to interpret and understand the experimental PSD curves better. In general, the analysis of these correlation functions is not straightforward, since different morphological features—like the (in)existence of typical length scales, a varying degree of in-plane or/and out-of-plane disorder, etc.—can influence the value, and even the physical interpretation of the correlation length, and of the correlated and crossover regions. In this section, we analyse the effect that different characteristics of the random pyramid size distribution may have on the behaviour of the PSD for the synthetic surfaces. This allows us to clarify their role for the experimental topographies. We consider three main parameters: surface coverage by pyramids, average pyramid size, and variance of the pyramid size distribution. We have generated the corresponding synthetic surfaces by using Gwyddion [3], which allows to sequentially vary these parameters. All images have a lateral size of 2048 arbitrary units (au), although they do not necessarily have the same roughness.

2.1. Role of the pyramid size

First, we have studied how the pyramid size (with a zero variance for the distribution of pyramid sizes) affects the behaviour of the PSD for two different coverages, namely, 0.2 and 4. We first consider the case of small coverage (=0.2), see Fig. S2. In this case, a few pyramids appear scattered on top of a flat background, akin to what is found experimentally for 240 s etching time. As mentioned in the main text, two important length scales can be identified in the PSD, namely, the average pyramid size ($\xi$) and the average distance between pyramids ($\lambda$). Actually, in all cases shown in Fig. S2 the value of $1/\xi$, which is exactly known, lies well within the power-law region of the PSD. As noted in the work by Ruiz et al. [4], the average inter-pyramid distance should correspond to a peak in the PSD curve, centered at $1/\lambda$. Inspecting closely the PSDs in Fig. S2, and taking into account that they are in log-log scale, a broad peak is clear for the two smallest pyramid sizes. However, as $\xi$ increases, the power-law regime is also wider and the peak vanishes. For a fixed coverage, the absence of a peak for larger motif sizes $\xi$ is then due to the relatively small size of the window (image size) with respect to the inter-pyramid size $\lambda$, which is also larger. Figure S2 suggests that images at least 50 times larger than the motif size would be required to be able to observe the corresponding peak in the PSD curves. This has important consequences in the analysis of the experimental data.

Figure S2 also displays the height autocorrelation function (ACF) [1, 3]. Again, the two length scales $\xi$ and $\lambda$ can be identified. Thus, the pyramid size corresponds to the location of the most pronounced minimum of the curve [1], while the inter-pyramid distance $\lambda$ is observed as quasi-periodic oscillations for large $r$ values [1], as it provides their average period. As seen in Fig. S2, the period of these oscillations increases with the pyramid size, in agreement with the behaviour found in the corresponding PSDs.
Figure S2. Top panel: Synthetic 2048 × 2048 surfaces for a fixed small pyramid coverage (=0.2) and increasing values of the pyramid size, left to right, as indicated on the bottom right corner of each image, with a zero variance for the distribution of pyramid sizes. Bottom panel: (Left) PSD functions for the morphologies shown on the top panel. For each curve, the vertical arrow indicates the inverse of the lateral pyramid size. (Right) Radially averaged autocovariance functions for the indicated morphologies.

Note, small-frequency oscillations can also be noticed in the PSD curves. These can be attributed to the existence of a few well-defined shape (the pyramid) on the surface.

Figure S3. Top panel: Synthetic 2048 × 2048 surfaces for a fixed large pyramid coverage (=4) and increasing values of the pyramid size, left to right, as indicated on the bottom right corner of each image, with a zero variance for the distribution of pyramid sizes. Bottom panel: (Left) PSD functions for the morphologies shown on the top panel. For each curve, the vertical arrow indicates the inverse of lateral pyramid size. (Right) Radially averaged autocovariance functions for the indicated morphologies.
whose Fourier transform is well-known to feature such type of periodic oscillations, with an envelope that decays as a power law in $k$ \cite{5}.

Basically a similar behavior is also found for large coverage (=4), see Fig. S3): the power-law regime in the PSDs extends towards lower $k$ values as the pyramid size increases, due to the related increase of the average distance between pyramids. Again, a peak in the PSD can be only detected for the smallest pyramid sizes. In addition, the slope characterizing the power-law behavior for large $k$ is independent of the pyramid size, while the PSD curves shift downwards for increasing $\xi$. It is interesting to note that for high coverage the left endpoint $k_c$ for power-law behavior is closer to $1/\xi$. Hence, in general the correlation length, defined as $l_c = 1/k_c$ (see main text), is not necessarily equal to the motif size, $\xi$. Regarding the ACF, the behaviour is similar to the low-coverage case: the main minimum of the ACF shifts to higher values as the pyramid size $\xi$ increases and oscillations also appear for large $r$, with increasing period as the pyramid size increases. These oscillations are better defined than those observed for low coverage.

2.2. Role of the coverage

The role of the coverage is studied next in Fig. S4, where synthetic surfaces are shown with a fixed small pyramid size (=20) and different coverages. In the top panel of the figure, the coverage of the surface by pyramids increases left to right. As seen on the bottom panel, this does not change the slope of the PSD function for length scales which are smaller than the fixed pyramid size. What is important here, where the motif size
is considerably smaller than the image size, is that the main maximum in the PSD, although broad, is indeed observed for all coverages. The peak becomes noticeably broader as the coverage increases (note the logarithmic scale in both axes). That is, it is narrower when isolated pyramids are scattered on a flat substrate and their number is higher. Instead, as the surface coverage increases, surface roughness develops, blurring the neat inter-pyramid distance characteristic of the low coverage. This is confirmed in the corresponding ACF curves in which large distance oscillations are clearly more regular and periodic for low coverages. The width of the peak in the PSD should be mostly related to the disorder in the pyramid distribution over the surface. This is in contrast with the images of pentacene islands on flat silicon oxide surfaces in the submonolayer regime, where the island were quite similar and their spacing indeed more homogeneous [4]. For more on submonolayer vs multilayer behavior in this context, i.e. the role of coverage by pyramids, see Sec. 3 below.

2.3. Role of the pyramid size distribution

We have generated a last set of synthetic surfaces. Now, we have used fixed large pyramid coverage (=4) and an average pyramid size $\xi = 20$, but we have allowed for changes in the variance of the pyramid size distribution from 0 to 1, see Fig. S5; this range of values include variance =0.21, as employed for the synthetic surfaces reproducing the experimental surface correlations which are discussed in the main text.

Interestingly, for small variances (from 0 to 0.3), the PSD curves change very little, being possible to detect a broad peak at low $k$ due to the small pyramid sizes. However, with increased variance the peak becomes broader and the power-law regime of the

![Figure S5](image_url)

**Figure S5.** Top panel: Synthetic 2048 × 2048 surfaces for a fixed pyramid coverage (=4) and a fixed average pyramid size (20 au), for increasing values of the variance of the pyramid size distribution, left to right, as indicated on the bottom right corner of each image. Bottom panel: (Left) PSD functions for the morphologies shown on the top panel. For each curve, the vertical arrow indicates the inverse of the average pyramid size. (Right) Radially averaged autocovariance functions for the indicated morphologies.
PSD extends again towards low $k$. Likewise, the ACF curves present oscillations at large $r$, which become rather irregular for large variance $\geq 0.21$. Clearly, the increase in the heterogeneity of pyramid sizes leads to a decrease of the surface correlations. This conclusion is further confirmed for even larger variance $> 0.3$, for which the power-law regime of the PSD practically covers the full range of $k$ values. This is due to the development of so large inter-pyramid distances $\lambda$ that the corresponding peak of the PSD shifts to very small wave-vectors. In order to observe the peak, it would be necessary to have wider images including many more pyramids. In any case, due to the wide distribution of pyramid sizes and, therefore, of inter-pyramid distances, this peak will be quite broad.

2.4. Analysis of the synthetic surfaces

The analysis of Figs. S2 through S5 allows us to understand more precisely the behaviors observed in our experimental PSD curves. First, the space correlations observed at large wave-vector values, where power-law behavior occurs, are independent of the pyramid size, coverage, or variance of the pyramid size distribution. Actually, the power-law behavior observed for $S(k)$ in this range of $k$ coincides with that obtained for a random distribution of identical square pyramids. Hence, this behavior can be attributed to the well-defined geometrical shape of the hillocks, combined with their random positioning which damps out high-frequency oscillations in the PSD. For large coverage, the left end-point value of $k$ of the power-law-correlated region is close to the (inverse) pyramid size. In contrast, when the coverage is low and isolated pyramids occur, this value of $k$ can be much smaller than $1/\xi$. On the other hand, the peak in the PSD that originates in the inter-pyramid distance $\lambda$ is observed mainly for low coverages and small pyramid sizes. This is due to the correlation between isolated pyramids scattered on a mostly flat surface and to a statistical limitation: only when the motif size is small enough can the correlations among them lead to a well-defined peak in a very disordered system. In this sense, large variances in the motif size distribution, large coverages, and large motif sizes, all contribute to masking the inter-pyramid correlations leading to broadening, or even absence, of the corresponding peak in the PSD. To overcome this effect, larger images containing many more pyramids would be required.

All the trends observed in the study of the surface PSDs are confirmed by the corresponding ACF functions. As for the interpretation of the experimental data, two practical limitations emerge from the analysis of the synthetic images: first, the size of the pyramidal motif relative to the finite size of the image can hamper observation of the correlation peak associated to $\lambda$. As stated in the main text, we have been able to match the experimental and synthetic PSDs by using the following size ratios for the increasing etching times: 0.5%, 0.9%, 1.2%, 2%, 2.3%, 2.9%, and 4.5%. Thus, we have been able to detect such peak in the PSDs only for the shortest times, up to 240 s. Second, the non-zero variance of the pyramid size distribution (0.21 for the synthetic surfaces) also tends to broaden the peak associated with the inter-pyramid distance $\lambda$. 
Figure S6. (a) Normalized image corresponding to the experimental image for 240 s shown in Fig 1 of the main text. A threshold height value has been applied such that larger heights were set to 1 and lower ones to zero. The horizontal bar represents 10 µm. (b) Linear-log representations of the PSD of the experimental (black, left vertical axis) and the normalized (red, right vertical axis) images.

3. Analysis of the data within different coverage regimes

As noted above and in the main text, two basic length scales are relevant in the system, the pyramid size $\xi$ and the inter-pyramid distance $\lambda$. In principle, it should be possible to identify both of them in the PSD, the former being related to the power-law regime for large $k$ values, while the latter should correspond to the position of a peak in the PSD in the low-$k$ region [4, 1]. However, as we have seen with the synthetic images, the identification of $\xi$ and $\lambda$ can be more ambiguous than this, depending on parameter (experimental conditions). To reach the results and conclusions contained in the main text, we have followed different approaches as a function of the coverage of the experimental images by pyramidal hillocks, as illustrated in this section.

3.1. “Submonolayer” regime

The sample obtained after 240 s of etching is the most similar, qualitatively, to those analysed in [4], where flat pentacene islands were deposited on flat silicon oxide surfaces in a submonolayer deposition context. According to the procedure followed in [4], we produce a normalized image from the original AFM data (see Fig. 1 of the main text) in which the value 1 is given to all points with height above a threshold value, and zero to those below it, see Fig. S6a. Through this normalization process the protruding pyramids lose their proper pyramidal shapes and become cubes of unit height. Figure S6b then shows the PSD curves for both the raw data and the normalized image. The raw PSD shows a peak (see Fig. 3c in the main text) which is not very well defined. Indeed, when the normalization is performed this peak becomes clearly enhanced, particularly at very low $k$ (note the different vertical scales of the two curves in Fig. S6). This confirms that the procedure proposed by [4] can be applied to this sample, despite the difference in homogeneity and height between the pyramids in our experiment and
the pentacene islands in [4]. In particular, the peak obtained in our images corresponds to the average inter-pyramid distance $\lambda$, and analogously for our low coverage cases for $t \leq 240$ s.

3.2. “Multilayer” regime

As mentioned in the main text, for etching times longer than 240 s the surface becomes rougher and highly disordered. The resulting hillock morphology resembles, rather, that of a mounded surface in thin film deposition experiments in the multilayer regime [1], where a protruding structure can be identified as a characteristic motif in a surface which is actually quite disordered. The approach put forward in [4] cannot be successfully applied since different islands (pyramids) somehow overlap with one another. For these cases one can perform an analysis which happens to be based on the height-difference correlation function (HDCF) rather than on the PSD, see [1] for full details. Specifically, the typical length scale related to the basic motif (pyramid in our case) $\xi$ is associated with the most pronounced maximum in the HDCF curve, whereas the inter-pyramid distance $\lambda$ is related to the quasi-period of the oscillations occurring at large distances. This analysis can be performed for all etching times, see an example in Fig. S7a for the case of 600 s of etching. In particular, this identification of $\xi$ and $\lambda$ can be applied even for the shortest times, despite the fact that their corresponding PSD functions did not show any peak related with the inter-pyramid distance $\lambda$; see Fig. S7b for the full time evolution of the thus measured pyramid size and inter-pyramid distance. This fact is not surprising: indeed, different height correlation functions, either in direct or in reciprocal space, are known in practice to reflect morphological properties with different degrees of sensitivity [6]. Also, in view of the above discussion of synthetic images, we should take into account that for long etching times the motif size becomes so large, in comparison with the image size, that the statistics can be poor in order to reliably
define $\lambda$. Taking these considerations in mind, it is interesting to note that, for short etching times in the “submonolayer” regime, there is a correlation between $\xi$ and $\lambda$ that vanishes for long times in the “multilayer” time regime. Again, this agrees intuitively with the expectation for an arrangement of well-defined islands in the submonolayer case.

References