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Formation of pyramidal etch hillocks in a Kossel crystal

M.P. Suárez, D.A. Mirabella, C.M. Aldao *

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Juan B. Justo 4302, B7608FDQ Mar del Plata, Argentina

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Abstract

Surface roughening due to anisotropic etching was studied experimentally and modeled using the Monte Carlo method for a Kossel crystal. Simulations were used to explore a possible formation mechanism for the appearance of etch hillocks in two and three dimensions. Similarities with pyramidal etch hillocks that are regularly observed in anisotropic etching of Si(1 0 0) are discussed.

Keywords: Monte Carlo simulations; Scanning electron microscopy; Etching; Surface structure; Morphology; Roughness and topography; Silicon; KOH

1. Introduction

The understanding of the relationship between morphology and the processes occurring in the atomic level has been one of the goals of fundamental and applied surface science. In particular, the structural changes at the atomic level that accompany etching solutions of silicon have been the subject of long standing investigations [1–6]. The production of microstructures with nanometer precision requires a basic understanding of the surface chemistry of the etch process. In particular, there is an increasing number of devices being produced by etching of silicon single-crystals in alkaline solutions. Microdevices are fabricated using anisotropic or orientation-dependent chemical etching solutions for which KOH based solutions are one of the main etchants in practical use [1].

Wet chemical etching of Si(1 0 0) in aqueous KOH can result in the appearance of pyramidal hillocks, which are not compatible with the classical evolution of crystal shapes. The mechanisms responsible for the observed surface morphologies are not clearly understood yet. The presence of high anisotropic dissolution ratios is very well known since many years ago, with the (1 0 0) and (1 1 0) surfaces dissolving much more rapidly than

* Corresponding author.
E-mail address: cmaldao@fi.mdp.edu.ar (C.M. Aldao).

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the (1 1 1) plane [7,8]. This leads to exposing the slower etching (1 1 1) planes, which constitute the sides of pyramidal features.

However, despite anisotropic etching, protruding shapes (like pyramidal hillocks) etch fast and then one expects that they should be unstable and prone to disappear. The formation of pyramids, then, implies not only strong (1 1 1) surfaces but also that their tops etch slower than what could be anticipated in a first analysis. A satisfactory explanation for this etching rate reduction is under debate [9].

Results suggest that some kind of semipermeable or masking particles that adhere to the surface are responsible for the development of the pyramidal etch hillocks. The exact nature of these masking particles is unknown but silicate particles are a likely candidate [10]. The most marked differences in surface finishes were obtained between etching solutions saturated with either nitrogen or oxygen. It is proposed that nitrogen facilitates hydrogen formation [11]. Conversely, with oxygen, despite some inhomogeneities, hillocks-free surfaces were obtained. Thus, pyramidal hillocks formation has been proposed to be the result of surface attachment of hydrogen bubbles that cause temporary localized etch stops. Smooth surfaces are produced when bubble formation or hydrogen incorporation in the lattice is reduced or eliminated [11]. Hillocks have been observed to form and then disappear during etching and that the initial attack is at the top. This is compatible with the disappearance of the masking action. An ultrasonic bath results in the facilitated detachment of hydrogen bubbles or removal of semipermeable particles leading to the production of smooth surfaces [12–14].

In this article, we present some experimental observations and Monte Carlo results that suggest and test the basic mechanism for pyramidal hillock formation described above. We developed a model using a Kossel crystal, a crystal with a simple cubic lattice, that describes etching with a minimum of assumptions in one and two-dimensional substrates. This simple model system accounts for the observed features, indicating the general origin of the resulting surface patterns.

2. Experiments

Samples were cut from a Si wafer that was n-type, P-doped, 4.5 Ohm-cm of resistivity, oriented within 0.5° of (1 0 0). Prior to the experiments, the native oxide layer on the silicon was removed by immersion for 2 min in 2 M hydrofluoric acid at room temperature. Samples were then rinsed in bidistilled water. Studies were carried out with samples of about 1×1 cm^2 in a glass cell.

Silicon wafers were supported horizontally in a Teflon holder within a Pyrex vessel mounted on a hot plate stirrer with controlled temperature to within ±1 °C. Wafers were etched in 2 M KOH until steady state, after the etchant was allowed to reach the desired temperature, then removed from the vessel, rinsed with bidistilled water and dried by a flow of Argon. By simple visual observation, the etching reaction is accompanied with vigorous formation of hydrogen bubbles. The etched crystal surfaces were imaged with a scanning electron microscope (SEM). The specimen surfaces were not metal-coated prior to observation.

Fig. 1(a) shows an SEM image of a Si(1 0 0) surface etched in 2 M KOH for 1 h at 95 °C. The surface exhibits a rough appearance with pyramidal hillocks of different sizes, the larger ones of around 3 μm. The region between the hillocks seems to be flat, but a closer view, Fig. 1(b), shows that much smaller hillocks decorate the surface. In Fig. 2, we present similar images corresponding to a Si(1 0 0) surface etched for 2 h at room temperature, 21 °C. The surface pattern also presents pyramid like structures but there are practically no flat regions between the formed hillocks.

3. Monte Carlo simulation

The crystal surface is represented by a one- or two-dimensional matrix where each element represents the height at the surface site. Sites are visited at random and their neighborhoods are inspected in order to calculate the detachment probability of the surface particle. The detachment probability is related to the number of bonds n needed to be

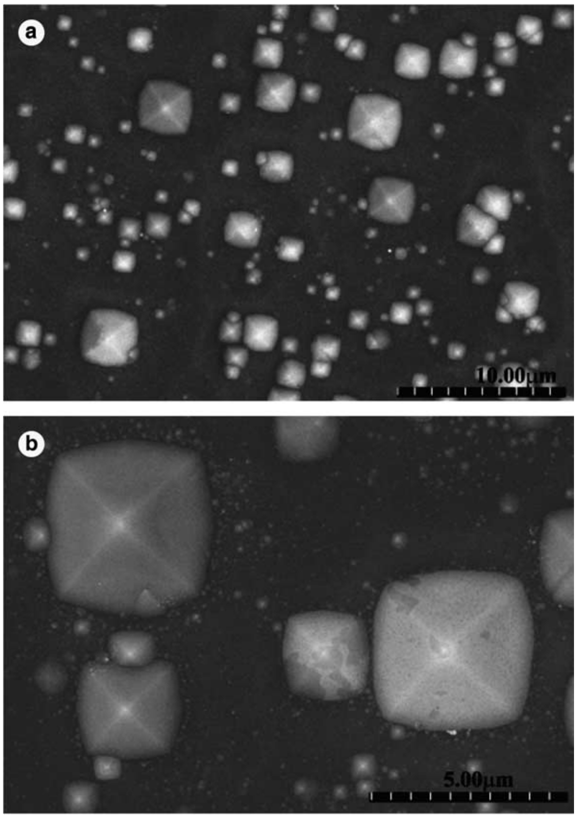

Fig. 1. Hillocks on a Si(100) surface etched in 2 M KOH during 1 h at 95 °C.

broken to remove the atom, and then their energy E: $\exp(-nE/kT)$. Our analysis is based on the so-called *solid-on-solid* (SOS) model in which overhangs are not allowed and particles arrange in columns of different heights. The substrate configuration is then completely determined by an array of integers equal to the heights of each column relative to the flat reference surface.

We are here mostly interested in the general aspect of the surface morphology. Although it is impossible to map the silicon structure on a Kossel crystal, the general trends observed in this simpler model give us insight into the basic mechanisms responsible for patterning. During the simulation, single particles are randomly removed from the surface in accordance with predefined, site-specific etch rates. Rearrangement of surface atoms is not allowed, what is expected for silicon at temperatures below 200 °C [15].

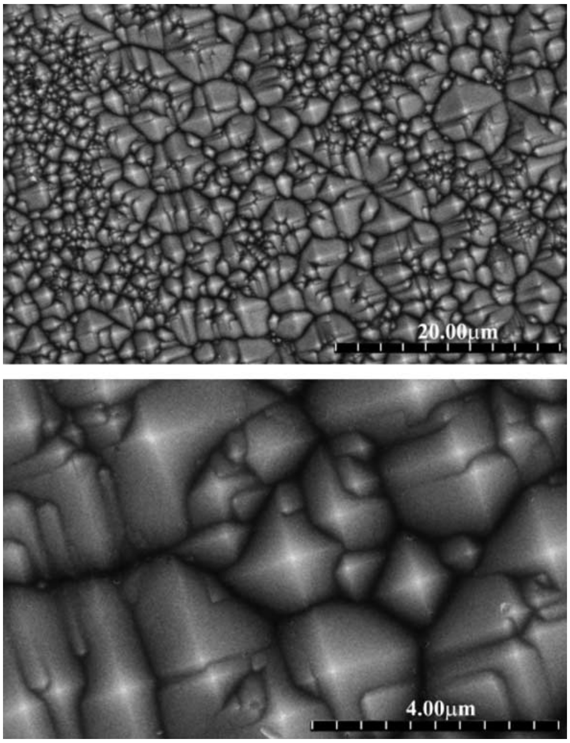

Fig. 2. Hillocks on a Si(100) surface etched in 2 M KOH during 2 h at 21 °C.

The evolving configuration for the system is found using the standard Monte Carlo method. A more effective algorithm could have been used, but our model was not very time consuming. The initial configuration was flat. The system evolved with successive annihilations of substrate particles until it approached a steady state configuration. We checked that steady state was reached by assessing the surface roughness evolution.

Etching is an irreversible process, so particles can only be eliminated. The probability for eliminating a particle was assumed to depend on the number of first neighbors. To model that (111) surfaces dissolve much more slowly than the (100) ones, we simply adopted a restricted solid-on-solid model that naturally implies no chemical attack to particles in that surface. To take into account the effect of masking an extra parameter was introduced. This parameter, P (screening factor), describes the reduction of the etch probability. Thus, under the mask the removal probability is reduced by this factor, $0 \leqslant P \leqslant 1$. Monte Carlo simulations were carried out for a square lattice of 200×200 and a 1D lattice of 1000 sites. Periodic boundary conditions were used to avoid edge effects.

It is frequently assumed that a simple bond counting model for chemical reactivity can be applied. This implies that etching occurs preferentially at steps and kinks. Bond strengths in semiconductors lead to activation energies for which kink and step etching would differ in many orders of magnitude at room temperature. However, the roughness of Si(1 0 0) monatomic steps in equilibrium, for example, indicates that effective interactions among atoms at the surface are much smaller. Indeed, experiments show that detachment events from a B-type step involving two dimers decrease by a factor of $\exp(-0.12\,\mathrm{eV}/kT)$ for every first neighbor formed by four atoms [16]. This indicates that complex mechanisms involving intermediate states must be present. Even more complex situations must arise in wet etching because of the role that the etching solution can play. Therefore, relative etching rates cannot be easily predicted based on bulk energetics.

In the simulation, a masking mechanism similar to that used by Hines and co-workers was adopted [17–19]. The masking appears whenever an apex forms, i.e. for particles without any neighbor besides the one below. This means that the formation of hillocks is controlled by the relative rates of site-specific etching that determine the appearance and disappearance of any type of surface feature. Specifically, we only introduced two parameters: the interaction energy E between neighbors and the screening factor P that reduces etching of apices.

4. Results and discussion

Before addressing the formation of pyramidal etch hillocks in three dimensions, we will discuss what can happen in two dimensions to then extend our conclusions to the more complicated pyramid formation in 3D. Hines and co-workers proposed a mechanism for step etching in Si(1 1 1). Straight step edges form when the rate of kink site etching is much higher than the rate of step site etching. However, they showed that site-specific kinetics can lead to an inherently unstable surface. It is found that $[\bar{1}\bar{1}2]$ steps sites are etched much faster than $[11\bar{2}]$ step sites. When Si(1 1 1) miscut in the $[\bar{1}\bar{1}2]$ direction is etched a characteristic morphology appears. The etched step is composed of many straight step segments oriented in the $[11\bar{2}]$ directions that constitute two-dimensional etch hillocks giving a shark's tooth shape to the whole structure [19].

To determine the origin of the hillocks we performed Monte Carlo simulations for different site-specific rate constants. In 2D, particles available to be etched away can have two (step site), one (kink), or none (point site or apex) first neighbors along the edge direction. The masking appears whenever an apex forms. To investigate the role of point sites, we tested etching with several apex etch rates as seen in Fig. 3. In order to compare our findings with those of Refs. [17–19], we adopted an etching rate for kinks equal to 1, and the etching rate for step sites equal to 0.01, which corresponds to $E/kT \approx 4.6$. For $k_{\mathrm{apex}} \geqslant 0.15$, the etched step morphology is relatively straight. As k_{apex} is decreased, etch hillocks appear. These hillocks grow larger until $k_{\mathrm{apex}} \approx 0.05$. Interestingly, a smaller apex rate increases the number of pyramids and reduces the step roughness. These results are surprisingly similar, qualitatively and quantitatively, to those found in Ref. [19] despite the simplicity of our model compared with the vicinal Si(1 1 1) surface simulated by Hines and co-workers.

For an apex to form, two opposing kinks must collide. Once formed, the small hillock can rapidly disappear if an etching event occurs for the only particle that constitutes the hillock. If the just formed apex remains stable while the surroundings are etched away, the small hillock will grow. If apex etching is too high, hillock formation is suppressed as seen in Fig. 3 for $k_{\mathrm{apex}} \geqslant 0.15$. Conversely, if apex etching is too low, hillocks grow to finally constitute the whole pattern ($k_{\mathrm{apex}} \leqslant 0.05$).

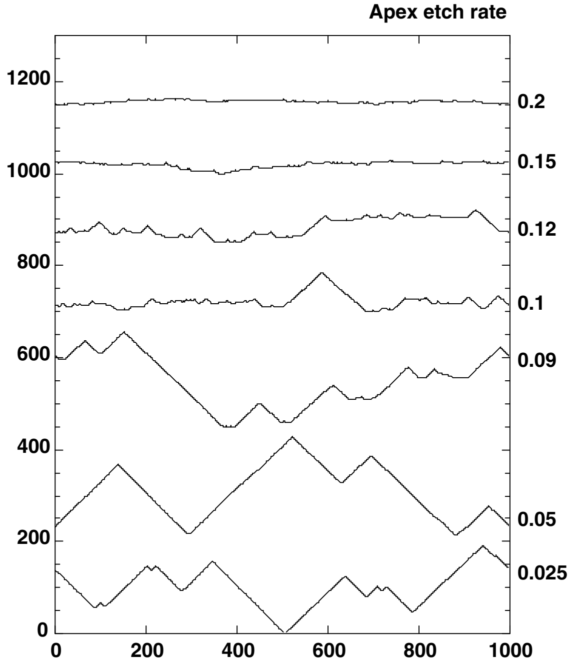

Fig. 3. Simulated etch morphologies Monte Carlo modeling outcome of a two-dimensional crystal for different etch rate for apex sites. Etching rate for kinks is always equal to 1 and the etching rate for step sites is always equal to 0.01.

A hillock-and-valley pattern is only stable for a reduced range of the apex etching rate. (We refer as a valley an almost flat region between hillocks.) In fact, the step morphology is very sensitive to k_{apex}. (Note the pattern differences for $k_{\mathrm{apex}} = 0.1$, 0.09, and 0.12 in Fig. 3.) In steady state, valleys must etch away, in average, at the same rate than hillocks. Since step etching is much slower than kink etching, the formation of kinks will be a limiting factor in the etching of valleys. Thus, etching rate of valleys increases with their size. Then, the larger the valley the larger formation rate of kinks and the faster the valleys etch. As a consequence, in this etching mode, we expect the number of hillocks to increase with k_{apex} while their sizes decrease.

The relative number of kink and step sites as a function of apex etching rate is shown in Fig. 4. As expected, the number of step sites increases with k_{apex} while the number of kink sites decreases. Since the interaction between neighbors is quite strong, $E/kT = 4.6$, the surface becomes flat when

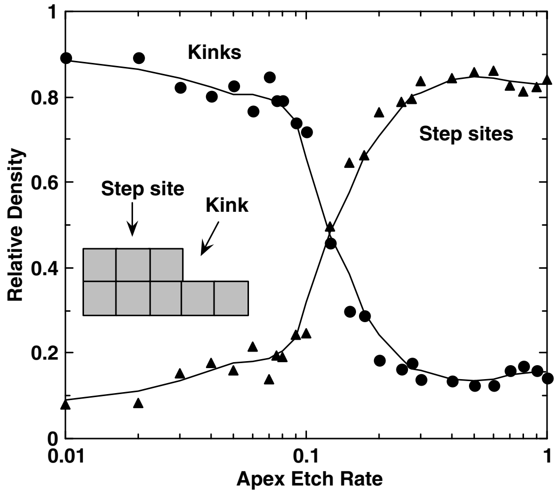

Fig. 4. Kink and step sites density as a function of apex etch rate for a two-dimensional crystal. Etching rates for kinks and step sites are 1 and 0.01, respectively. The inset shows what is understood by a step site and a kink.

masking is not relevant. A reduction of k_{apex} implies the formation of apices, the reduction of the number of step sites, and the increasing of kink sites (most of them constitutes hillock sides). Interestingly, the transition from a straight surface to a hillocked one takes place in a small range of the apex etch rate. In Fig. 5, we see that, indeed, the number of apices increases as k_{apex} decreases but only for values of $k_{\mathrm{apex}} > 0.15$.

In the range $0.05 < k_{\mathrm{apex}} < 0.15$, as discussed above, the number of hillocks increase with k_{apex}. In this regime, a larger k_{apex} implies larger valleys and then a higher kink and hillock formation. Finally, for $k_{\mathrm{apex}} < 0.05$, the number of hillocks decreases with the apex etch rate. This is a consequence of the great stability of formed hillocks of any size. Once formed, in this regime, most hillocks remain stable and then the surface presents more hillocks of smaller size as k_{apex} becomes smaller.

The above findings are confirmed from the statistical analysis of the resulting morphologies. In Fig. 5 we also show the interface width, that characterizes the surface roughness, defined as

$$w = \sqrt{\frac{1}{L}\sum_{i=1}^{L}[h(i) - \bar{h}]^2},$$

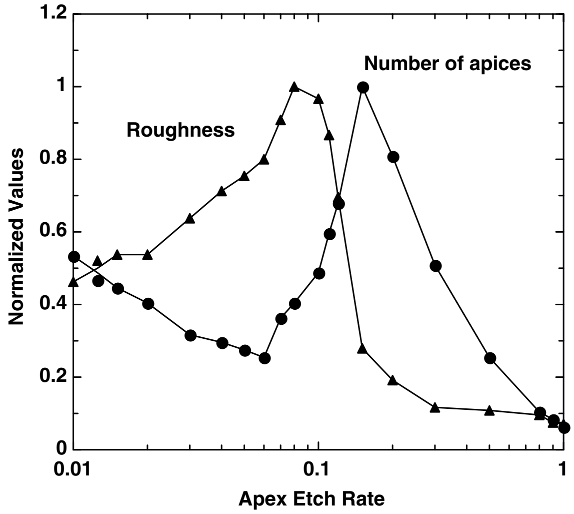

Fig. 5. Normalized number of apices and roughness as a function of apex etch rate for a two-dimensional crystal. Etching rates for kinks and step sites are 1 and 0.01, respectively.

where L is the number of sites, $h(i)$ the height of the column in site i, and $\bar{h}$ is the mean height of the surface. For $k_{\text{apex}} > 0.15$, the surface roughness is low and almost independent of k_{apex} despite the increasing number of apices. Then, a reduction of k_{apex} induces a rapid roughness increasing, the reduction of the apex number, and the rapid increasing of the number of kinks. These results are consistent with the beginning of hillock formation. This trend is observed in the range $0.08 < k_{\text{apex}} < 0.15$ indicating the appearance of larger hillocks as k_{apex} is reduced (see Fig. 3) in a hillock-and-valley morphology.

For $k_{\text{apex}} = 0.08$, valleys do not exist any longer and the roughness reaches a maximum indicating that a few number of large hillocks dominate the landscape. A further reduction of k_{apex} beyond 0.08 reduces the roughness, which is consistent with an increasing number of hillocks (see Fig. 3).

The above discussions can be extended to explain the 3D pyramid formation. Fig. 6 shows Monte Carlo simulations carried out for a square lattice of 200×200 sites. As previously stated, we considered that particles are etched away with a probability proportional to $\exp(-nE/kT)$, where n is the number of first coplanar neighbors and E the interaction energy. The second parameter is the screening factor P that reduces etching of apices. If $P = 1$, then particles would be etched at the rates dictated only by the number of first neighbors and thus the larger E the smoother the resulting surface. As P is reduced, the probability for apices increases and hillocks become stable.

In Fig. 6(b) we show the resulting surface for $E/kT = 2.3$ (corresponding to a reducing factor in the etch probability of 0.1 per neighbor) and a screening factor P of 10^{-3}. While the morphology details are emphasized in the 3D landscape, the top view on the left provides an easier way to evaluate the general aspect of the resulting pattern. The surface morphology resembles that found in the experiments (see Fig. 1(a)). For the used values of P and E, the surface presents hillock-and-valley morphology. For a one-dimensional substrate, valleys do not have the same height because they are not connected. Conversely, for a two-dimensional substrate, valleys are interconnected and then hillocks lie on a limited rough surface. We chose a value 10^{-3} for P because it is the masking corresponding to k_{apex} of 0.1 that generates hillocks in two dimensions in the work of Hines and in the present work.

In Fig. 6 we stress the influence of the parameter E for a constant value of P. As seen, the surface morphology is very sensitive to the interaction among substrate particles. Fig. 6(a) was obtained with $E/kT = 2.41$ and Fig. 6(c) with $E/kT = 2.21$. In this small range of the substrate strength, the surface morphology can present very small and unstable hillocks to big hillocks, with an almost pyramidal shape, that cover most of the surface.

A similar trend to that seen in Fig. 6 is observed if we keep E constant and vary P. For $E/kT = 2.3$, changes of about 40% in P produces similar effects that changes of 10% in $\exp(-E/kT)$. This is expected because a particle at the surface can have four neighbors. A larger value of E or a smaller value for P make hillock apices more stable and reduces the area cover by the valleys. This is observed in Figs. 6(c) and 7(a) that resemble experimental results of Fig. 2.

By reducing P, hillocks become more stable but this does not mean that they always become larger. Similarly to what was observed in 2D, hillocks

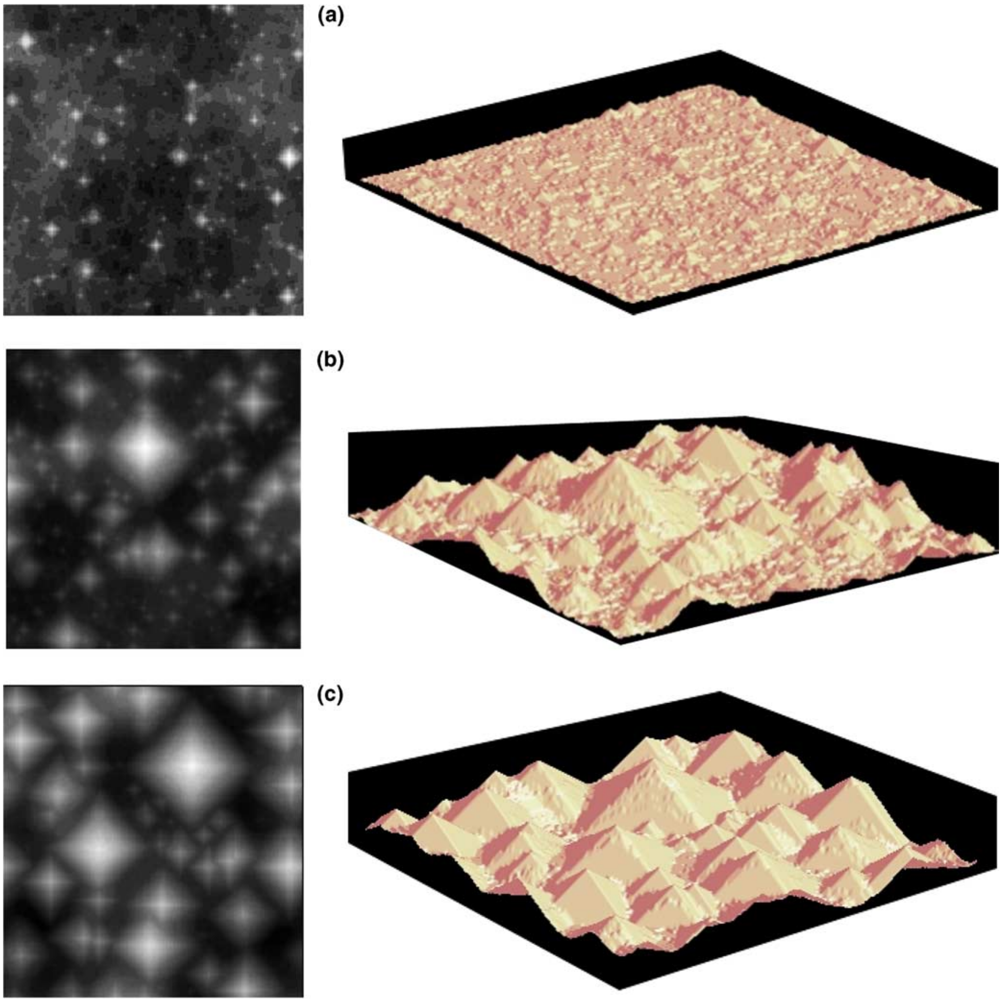

Fig. 6. Simulated etch morphologies for the surface (1 0 0) of a 3D Kossel crystal as a function of the substrate stiffness. Interaction energies among substrate particles, E/kT, are 2.41 (a), 2.3 (b), and 2.21 (c). The screening factor $P = 0.001$.

become smaller for very low values of P. Once formed, most hillocks remain stable and then large hillocks do not grow at the expense of the smaller ones. This is observed in Fig. 7(b) where a surface with a large number of small hillocks forms for $P = 2 \times 10^{-4}$.

To study in more detail the hillock morphology, we only allowed one masked site at the center of a square lattice of 500×500 sites. In particular, we were interested in testing the appearance of steps at the sides of the pyramid and their curvature. In Fig. 8 the surface obtained in this type simulation with $P = 0.01$ and $E/kT = 0$ is presented. Note the steps at the sides of the hillock, indicating that they are in fact vicinal $\{1\,1\,1\}$ surfaces. We found that the numbers of steps increases with P as they are created when the hillock top is etched away. The steps do not progress homogeneously but they are etched faster close to the ridges. Thus, steps are not straight but they present a distinctive curvature. This takes place because particles at ridges can always be etched while this is not the case for particles at any other position. Indeed, due to the restricted solid-on-solid constrain,

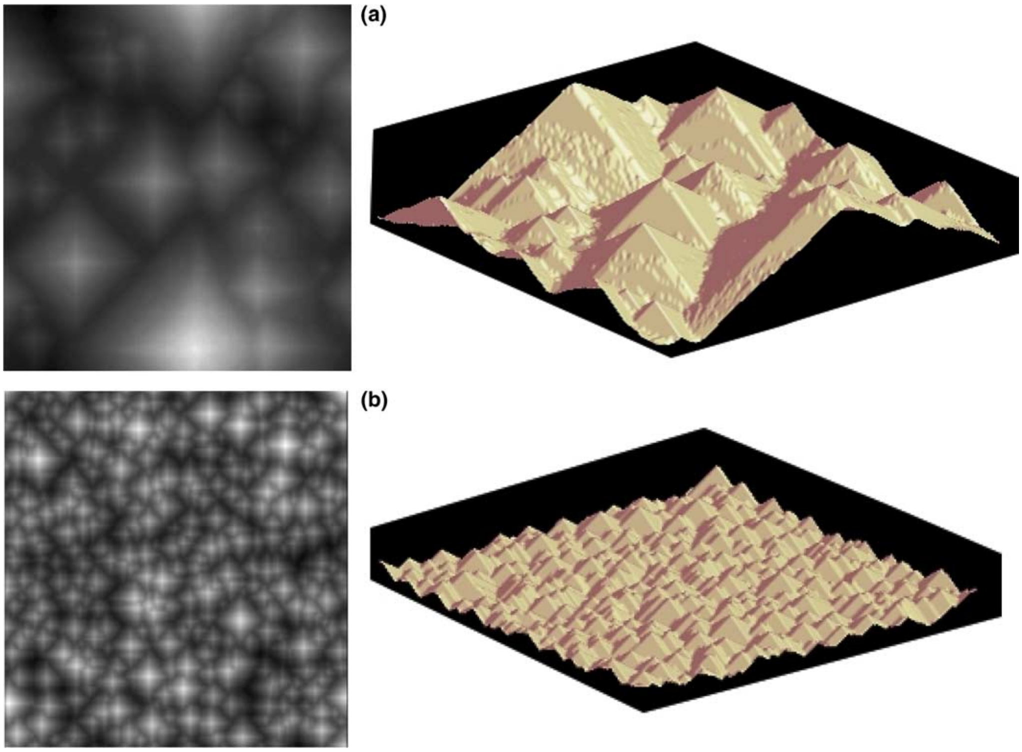

Fig. 7. Simulated etch morphologies for the surface (100) of a 3D Kossel crystal for (a) $E/kT = 2.3$ and $P = 5 \times 10^{-4}$ and (b) $E/kT = 2.3$ and $P = 2 \times 10^{-4}$. This shows that more stable apices do not always imply larger hillocks.

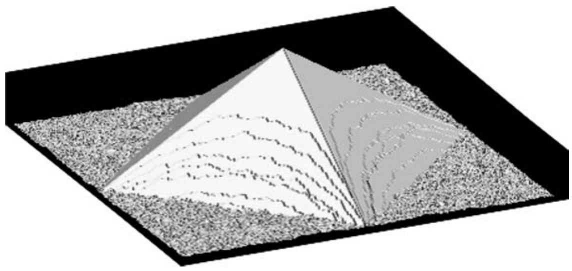

Fig. 8. Simulation of a hillock formed when there is only one masked site at the center of a square lattice of 500×500 sites. The result corresponding to $P = 0.01$ and $E/kT = 0$ is presented. Note the steps and their shapes at the sides of the pyramid.

particles at the hillock sides cannot be etched if this originates a difference of more than a particle between neighbor sites. Consequently, the hillock base does not show an exact square shape but looks more circular.

5. Conclusions

A simple, site-specific etching model shows the appearance of etch hillocks in two- and three-dimensional Kossel crystals. A systematic study of the hillock formation in 2D indicates a rich behavior dictated by the relevant parameters, the substrate strength and the screening factor for apex etching. The observed features clearly resemble those found in Si(100) wet etching. We found that changes in the substrate strength, E/kT, alter the surface morphology in the way expected due to a reduction in temperature. Also, we found that this trend could be related to a reduction in the screening factor. An interesting feature in the present model is that apex formation is dictated by the structure itself, i.e. the structure is self-generated. Other mechanisms, with an independent apex formation, should be investigated.

Acknowledgments

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