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Basic mechanisms for hillock formation during etching

D.A. Mirabella, M.P. Suárez, 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

The formation of etch hillocks was explored in the framework of a site-dependent detachment probabilities model. Monte Carlo simulations were carried out for a one-dimensional substrate within a restricted solid-on-solid model in which only first neighbour interactions are considered. We specifically focus on describing the dynamics that lead to hillock-and-valley patterns. The mechanisms responsible for the steady state morphologies were related to apex creation and annihilation, together with valley and hillock etching, but pattern formation reflects two feedback loops that interrelate these mechanisms.
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1. Introduction

Nonequilibrium processes at surfaces associated with epitaxial growth and etching have been and continue to be of great interest [1–3]. Both processes are of technological relevance because of their role in the fabrication of microelectronic devices. While theoretical models and atomistic simulations that mimic thin film growth and surface patterning are quite mature [1,2,4,5], much less attention has been paid to the study of surface morphology during material removal.

Experimental studies show that some surfaces are smooth after etching while others are covered with pits and hillocks. For Si(100), the atomic-level changes that accompany etching solutions present distinct pyramidal hillocks [6–10]. For Si surfaces, the highly anisotropic dissolution ratios are well known, with (100) and (110) dissolving much more rapidly than (111) [6]. This leads to exposing the slower etching (111) planes, which constitute the sides of pyramidal features. However, it is intriguing that, while protruding shapes like pyramidal hillocks are expected to etch rapidly, their persistence indicates that they are stabilized by some mechanism that locally reduces etching. The formation of pyramids with (111) sides implies that tops (apices) must etch slowly. It has been suggested that some type of masking effect at the top of the pyramids makes them stable but, to date, there is no consensus regarding the exact mechanism responsible for this stabilization.

* Corresponding author. Tel.: +54 223 4816600; fax: +54 223 4810046.
E-mail address: cmaldao@mdp.edu.ar (C.M. Aldao).

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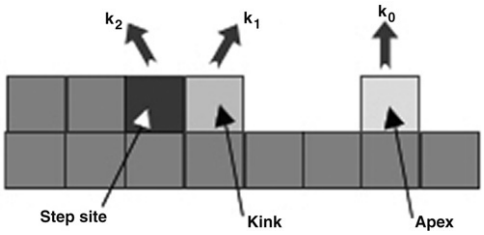

Fig. 1. Scheme depicting different particle sites and etching rates. Three configurations and then three rates for detachment are possible when considering first-neighbour interactions. Since we are dealing with a restricted solid-on-solid model, all particles have one first neighbour where they rest and neighbouring columns can differ at most by one particle. In addition, a surface particle can have two (step site), one (kink), or no (point site or apex) first neighbours along the step edge.

In modelling Si(111) etch profiles, Hines and co-workers recently took into account factors such as steric hindrance and lattice strain that can play a role in relative site reactivities [11]. Surface sites were then classified according to their structure with the topmost site of a 2D pyramid being unhindered, unstrained and relatively resistant to etching. Following their work [11–13], we reproduced the pyramidal hillock formation for a Kossel crystal with a model involving site-specific reaction rates [14].

There have been important contributions related to modelling the resulting silicon surface morphology after wet etching. For instance, Nijdam and co-workers studied the formation and stabilization of pyramids in Si(100) in great detail but they restrict the analysis to a single pyramid [9]. On the other hand, Gosálvez and coworkers reproduced a complete surface texturization [10,15]. However, none of the proposed models in these works replicates the hillock-and-valley patterns regularly observed in the experiments. This is one of the main features of our model.

On the other hand, other works deal with the appearance of large structures during epitaxial growth and erosion on crystal surfaces [16–18]. The origin of this instability has been understood to be the existence of diffusion bias and has often been associated with step-edge barriers to downward transport. This bias generates an uphill current that increases the probability for rough growth giving rise to mound formation. We stress that in the present work diffusion is not allowed and the resulting patterns are the only consequence of material removal.

Here, we focus on the underlying dynamics that lead to nontrivial hillock-and-valley patterns using a restricted solid-on-solid one-dimensional substrate model for Monte Carlo simulations. We pay special attention to the mechanisms involved in the formation and steady state size distribution of the hillocks. We specifically address the influence of the site-specific etching rates on surface phenomena, the underlying pattern dynamics and the interrelations that give rise to a hillock-and-valley morphology. The results show how coupled processes with feedback loops account for changes in what was thought to be a relatively simple system.

2. Monte Carlo simulation

Material removal (etching) from Si(111) occurs at steps, and the morphology is dominated by the resulting step flow patterns. In such a case, simulations of step retreat can be done with a one-dimensional model that focuses on the number of neighbours at a given step site. As depicted in Fig. 1, a one-dimensional step can be represented by a vector where each element represents the height at the surface site. In the simulations, particles can be removed (etched) from the step according to its site-specific etch rate. To accomplish this, sites were visited at random and their neighbourhoods were inspected to determine the detachment probability of the surface particle. In our model, only first-neighbour interactions were considered; particle rearrangement was not allowed (there was no diffusion). The parameters that determined the step morphology were the removal rates of three distinct sites related to the particle coordination number. Particles available to be removed could have two (step site), one (kink), or zero (point site or apex) first neighbours along the step with etching rates written as k_i, where i is the coordination number. Since we are interested in the steady-state morphology, only the ratios of these parameters are relevant.

Our analysis was based on the *restricted solid-on-solid* (RSOS) model in which there were no overhangs and a maximum height difference of one between neighbouring columns was allowed. Thus, the substrate configuration was completely determined by an array of integers equal to the heights of each column relative to the flat reference surface. The evolving configuration for the system was found using the standard Monte Carlo method in a 1D lattice of 1000 sites. Periodic boundary conditions were used to avoid edge effects. The system evolved with successive

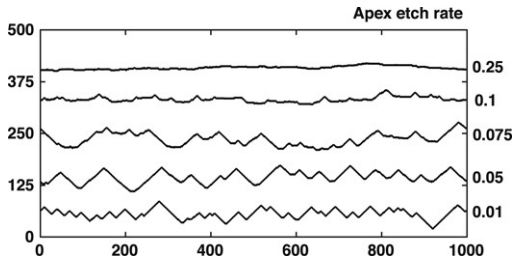

Fig. 2. Monte Carlo modelling outcome of a one-dimensional substrate for different apex-etching rates. Etching rate for kinks is always equal to 1 and the etching rate for step sites is always equal to 0.005. The surface is quite flat for high values of the apex-etching rates but hillocks develop as k_0 is decreased. A hillock-and-valley pattern is only stable for a limited range of k_0.

annihilations of substrate particles until it approached a steady-state configuration. We checked that steady state was reached by assessing the surface roughness evolution.

3. Results and discussion

We performed Monte Carlo simulations for a variety of site-specific rate constants. Slow-etching step sites and relatively stable hillock apices were needed for hillocks to form [11–14]. Thus, kinks must be the fastest etching sites, and a value of 1 was adopted for their detachment probability. Step sites must be robust, and we explored different values for the detachment probability from them; the results presented here correspond to a probability of 0.005.

To investigate the role of point sites, we tested etching with several apex-etching rates k_0 as shown in Fig. 2. Interestingly, the transition from a flat surface to a hillocked one takes place in a small range of the apex-etching rate. The probability of atom removal from a flat step, k_2, is relatively small and the surface is quite flat for high values of k_0, e.g. $k_0 = 0.25$ in Fig. 2, but etch hillock developed as k_0 was decreased. A reduction of k_0 implies stable apices that can develop into hillocks. Fig. 2 also shows that a hillock-and-valley pattern is only stable for a limited range of apex-etching rates (a valley is a flat region between hillocks). The sensitivity of the step morphology is evident by comparing the results for $k_0 = 0.1$ and 0.075.

Fig. 3 shows that the number of apices increases as k_0 decreases but this behaviour is far from monotonic. Indeed, the number of hillocks increases with k_0 for $0.05 < k_0 < 0.12$ but decreases again with the apex-etching rate for $k_0 < 0.05$. These findings are confirmed from the statistical analysis of the resulting morphologies. This figure also shows the interface width, which characterizes the surface roughness, defined as

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

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 step. For $k_0 > 0.12$, the surface roughness is low and almost independent of k_0 despite the increasing number of apices. A further reduction of k_0 induces a rapid increase in roughness and reduction of the apex number. This trend is observed in the range $0.05 < k_0 < 0.12$ and it is related to the appearance of larger hillocks within a hillock-and-valley morphology. For $k_0 \sim 0.075$, the roughness reaches a maximum as large hillocks dominate the landscape.

For $k_0 < 0.05$, the roughness decreases, but finally the number of hillocks starts to increase. This can be interpreted as 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. While the appearance of hillocks is expected if apices are stable, the shown morphology dependence on the apex etch rate is far from obvious.

When two opposing kinks collide, they produce a small, one-particle hillock. It can quickly disappear if an etching event occurs, but it can grow if it remains stable while the surroundings are etched. If apex etching is too high, hillock formation is suppressed, as observed in Fig. 2. Conversely, if apex etching is too low, hillocks grow to finally constitute the whole pattern.

A hillock-and-valley pattern is stable only within a restricted range of the apex-etching rates. We are specifically interested in this morphology where hillocks form and coexist, scattered on a surface of limited roughness, because

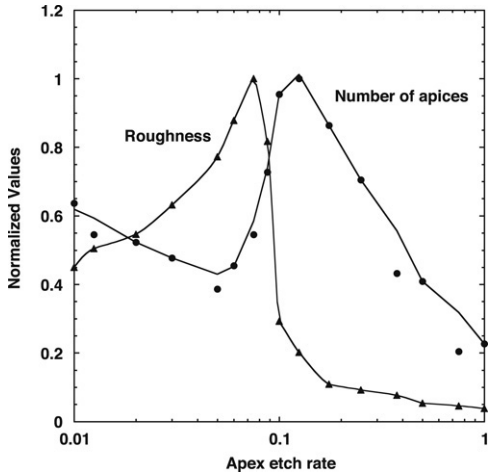

Fig. 3. Normalized number of apices and roughness as a function of apex-etching rate. Etching rates for kinks and step sites are 1 and 0.005, respectively. Both, the number of apices and the roughness presents a nontrivial dependence with the apex etch rate. When the roughness reaches a maximum the landscape is dominated by large hillocks.

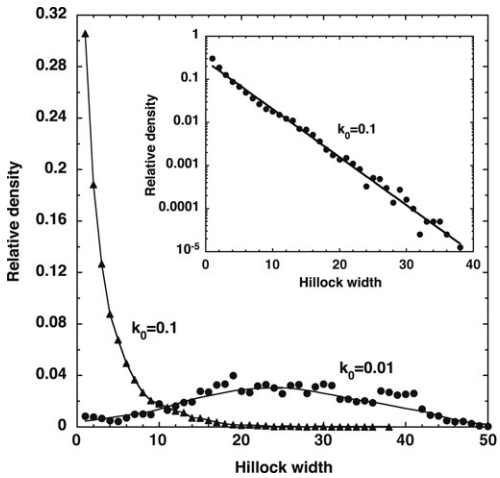

Fig. 4. Hillock-size distribution for apex etch rates of 0.1 and 0.01. Etching rate for kinks is always equal to 1 and the etching rate for step sites is always equal to 0.005. Distributions were obtained by averaging one-thousand patterns after reaching steady-state. The inset shows that the distribution for $k_0 = 0.1$ can be fitted with a decreasing exponential. This hillock size distribution indicates that hillock etching is faster than growing.

this is regularly observed in silicon etching. We will discuss next how the patterns are a consequence of several nonsimple interrelated mechanisms.

Monte Carlo results show that steps present hillocks of very different sizes. At first glance, it seems that hillocks can adopt any size at random (Fig. 2). However, Fig. 4 shows distinct distributions that are substantially different for $k_0 = 0.1$ than for $k_0 = 0.01$. These results indicate that there are important changes in the relevant mechanisms or in their roles. For $k_0 = 0.1$, the size distribution looks exponential. (The inset of Fig. 4 presents the distribution on logarithmic scale and a fitting with a straight line corroborates an exponential-like distribution.) Conversely, the hillock-size distribution for $k_0 = 0.01$ shows a Gaussian-like distribution. In what follows, we will focus on the results obtained for $k_0 = 0.1$.

The surface temporal evolution (not shown) demonstrates that small hillocks are continuously formed and annihilated. Conversely, large hillocks seem to propagate while their apices perform a random walk parallel to the step edge. After enough time, however, large hillocks can shrink and eventually disappear.

Since etching of a valley begins with the removal of a particle at a step site, two kinks are created that very rapidly "move" in opposite directions since kink etching is a much faster process than step site etching. Kink etching ends when they reach the valley limits determined by the nearest hillocks. In this way, the valley lowers its height by one unit and its width is reduced by two sites due to the RSOS rules. Etching continues when a new particle at a step site is removed and this kink formation is the limiting factor in valley etching. Such valley etching rates increase with the width of the valley as the number of available sites is larger. Eventually, this rate becomes independent of the valley size for very wide valleys.

If, during the kink etching at a valley, another particle is removed such that two kinks can collide, a new apex is created. This new apex is the smallest possible hillock of width one. Once formed, a hillock grows when the nearest valleys are etched. On the other hand, if the particle that constitutes the new apex is etched, the hillock is annihilated. In steady state, the rates of creation and annihilation of hillocks must be the same. Every time an apex is created, the valley in which this happens splits into two valleys of smaller size that etch slower. Every time an apex is annihilated, two valleys merge to form one larger valley that etches faster.

The rate at which a hillock is etched is controlled by k_0 since k_0 is exactly the etching rate for a hillock of width one. In larger hillocks, etching is more complicated because, once the apex is removed, the top of the hillock has three particles; two of them are in kink sites and one in a step site. Since the removal of kink particles is faster than apex particles, in a relatively short time a new apex forms at the top of the hillock. However, this makes the etching rate slightly slower than k_0. Note that the new apex can form in three different positions depending on the sequence at which the top particles are removed. This is why the apices perform a random walk in the parallel to the step edge as hillocks are etched.

So far, we have introduced the phenomena present in the etching model. We will now discuss how they determine the characteristics of a hillock-and-valley pattern, as in the case observed for $k_0 = 0.1$. For the hillock distribution to be stable, the rate at which hillocks of width w grow to become hillocks of width $w + 1$ must be the same as the rate at which hillocks of width $w + 1$ are etched to become hillocks of width w. In steady state, the hillock size distribution follows a decaying function with an exponential form indicating that hillock etching is faster than growing. This explains why hillocks do not grow monotonically with time but they reach a steady state distribution. Note that the hillock-etching rate is almost independent of the hillock size while hillocks grow at the rate valleys are etched, which depends on the valley size. Thus, hillocks must be etched faster than valleys which is responsible for the exponential-like distribution as a function of their size.

The above described mechanisms are not simply connected to produce the observed morphology. This is a much more complex system than expected as a consequence of two interrelated processes with feedback. On the one hand, the valley width determines the apex creation rate, which must be equal to the annihilation rate. This implies that the number of hillocks must be such that valleys have an average size for which creation and annihilation of unit hillocks is the same. On the other hand, the valley width determines the valley etch rate that together with the hillock etching rate are responsible for the hillock size distribution.

Fig. 5 shows a scheme with the relevant mechanisms and their interrelation. Apex creation depends on k_2 and the width of the valleys a. Apex annihilation depends on k_0. In steady-state, apex creation and apex annihilation must be equal. From this condition, the number of unit hillocks N_1 is determined. Thus, N_1 depends on k_0, k_2, and a. Valleys are etched at a rate V that depends on k_2 and a, and hillocks are etched at a rate H that is close to k_0. The difference between these etch rates, H–V, determines the hillock average size,W. Thus, the four described mechanisms are responsible for the steady-state hillock size distribution and then the surface morphology as the number and size of the hillocks determine the average valley width.

4. Conclusions

A simple, site-specific etching model shows the appearance of hillock-and-valley patterns for a one-dimensional substrate. A systematic study of the hillock formation shows an unexpected rich behaviour that is governed by several interrelated phenomena. We have analysed here the relevant mechanisms and their interconnections that determine the final morphology. At the same time, the surface pattern affects the processes of valley etching and hillock creation. Thus, it is not straightforward to analytically determine the resulting step morphology, especially because the mechanisms are not simple and nonlinear, and there are two feedback loops. Even to speculate on the effects of

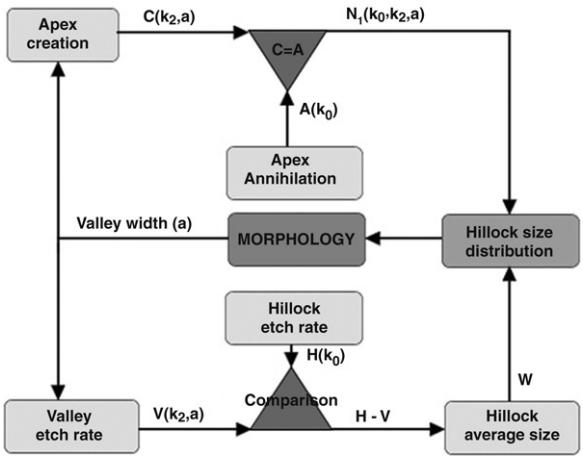

Fig. 5. Scheme showing the basic mechanisms responsible for the resulting surface morphology. Apex creation, apex annihilation valley and hillock etching are the four phenomena that determine the final morphology. The system is complex since the morphology affects apex creation and the valley etch rate.

changing the parameters of the model is not a simple task. The results presented here, for a relatively simple system, should guide the thinking for more complex systems.

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