In this thesis we describe experiments designed to probe spontaneous and directed surface evolution during annealing and plasma etching of three materials of high technological interest: silicon, nanoporous silica and photoresist.

Vicinal Si(111) surfaces provide a source of steps whose configuration we control via the introduction of a topographic pattern; this is done using combination of photolithography and reactive ion etching. We study the length scale dependence of self-organization of step bunches during annealing at ~ 1273 °C in ultrahigh vacuum (UHV), resulting from sublimation and diffusion, and the competition between effects due to the intrinsic stiffness of steps and their mutual interactions. We also show the results of numerical simulations on these surfaces based upon a simple model of step motion, which we compare with our experimental observations.
Nanoporous silica (NPS) is a heterogeneous material which is of potential use in micro/nanoelectronic applications requiring an insulator with a small dielectric constant. We investigate the stability of the NPS-plasma interface during etching, comparing the tendency for spontaneous pattern formation with the persistence of patterned perturbations. We study samples with various porosity (0 ~ 50 vol.% under low pressure C₄F₈/90%Ar plasma etching conditions. Our AFM characterization of unpatterned surfaces shows a monotonic increase in RMS roughness with etching time. Annealing etched NPS surfaces at temperatures over the range from 300 ~ 900 °C in UHV as well as in non-oxidizing environment produces no significant relaxation of etching-induced surface roughness. Statistical analysis using a height-height correlation function reveals that NPS surfaces do not show a simple scaling behavior during the technologically-relevant transient time regime. Etching of patterned surfaces reveals a persistent period of approximately 400 nm, which is ~ 4 times that which spontaneously appears during etching of unpatterned surfaces. Based upon this observation we investigate the possibility of period doubling, and find some evidence for it.

Lastly, we present preliminary results of surface morphological and compositional evolution of model photoresists for lithography at 193 nm and 248 nm wavelengths during etching using plasma and ion beam sputtering under a range of conditions. Surprisingly, our AFM characterization shows that there is no significant difference in roughness evolution between resists whose chemical backbone is qualitatively different, i.e. benzene-ring based 248 nm and acrylate-admatane based 193 nm polymers. The surface roughening however varies strongly with the position of a methyl group on the polymer backbone. Fourier transform infrared spectroscopy (FTIR), Ellipsometry and
XPS characterizations show that the polymers become dense at the early stages of plasma
/ ion beam exposure, possibly due to graphitization, cross-linking and hydrogen loss. We
compare these observations with molecular dynamic (MD) simulations of Ar$^+$ ion beam
sputtering.
EVOLUTION OF PATTERNED AND UNPATTERNED SURFACES DURING HIGH TEMPERATURE ANNEALING AND PLASMA ETCHING

By

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Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Dedication

To my parents, my uncle and aunt (Yoon’s family).
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Chapter 1 Introduction

1.1 Motivation

At the microscopic scale, all real crystalline surfaces contain steps and a finite density of kinks, producing roughness, as shown in figure 1.1. These defects are important in non-equilibrium processes on surfaces such as growth, sublimation and etching, all of which have been the subject of considerable technological and scientific attention. Each of these processes modifies existing surface roughness in different ways, depending on the details of the processing conditions [3.14].

In this thesis, we discuss the evolution of both nominally flat and lithographically patterned surfaces in three technologically important material systems, Si, nanoporous silica, and photoresist polymers, during high temperature annealing and plasma etching. Surface instabilities during such processes can be considered within the context of a moving boundary problem, where the surface protrusion grows with time (i.e. roughens). The classic example is the famous Mullins-Sekerka instability [1.1], which results from the competition between crystallization and either heat dissipation or the rejection of solutes.
Figure 1.1 Stepped surface with kinks
1.2 Ehrlich-Schwoebel effect

One of the best known mechanisms which drives surface instabilities is the Ehrlich-Schwoebel barrier. Ehrlich and Hudda [1.2] showed that the attachment of adatoms at a descending step-edge can be strongly inhibited by a kinetic barrier (E-S barrier) for crossing a descending step as shown in figure 1.2. This asymmetric attachment probability to ascending vs. descending step-edges (attachment rates \( K_- > K_+ \)), illustrated below, has been interpreted as the cause of bunching of steps and formation of stacks of islands (“mounds”) during MBE growth at low temperatures [1.3, 1.4].

![Diagram of Ehrlich-Schwoebel potential barrier at step edge](image)

**Figure 1.2** Schematic of Ehrlich-Schwoebel potential barrier at step edge.
The E-S barrier tends to stabilize uniform step trains against fluctuations in average spacing during sublimation, but as proposed by Bales and Zangwill can lead to a roughening of individual step edges [1.6].

Isolated atoms on terraces or at step edges are commonly referred to as “adatoms” (i.e. adsorbed atoms). The evolution of surface structure can be described by the motion of adatoms via diffusive motion, attachment from the vapor and sublimation from the surface. The diffusion of adatoms in the presence of an incident flux can be described in terms of their local concentration $c$ as follows:

$$\frac{\partial c}{\partial t} = D \nabla^2 c + F - \frac{c}{\tau}$$

(1-1)

where $t$ is time, $D$ is the adatom diffusivity, $F$ is the adatom flux from vapor, and $\tau$ is the average time that an isolated adatom spends on a terrace before sublimating into the vapor.

As mentioned above, flat terraces are bounded by steps; addition/subtraction of adatoms to/from a crystal occurs by attachment/detachment of adatoms at steps. The boundary conditions for adatom diffusion equation come from the relationship between the adatom flux toward the bounding step edges, the rate of attachment or detachment at the step edges, the permeation current of adatoms across the step. These can be described as follows:

$$\mp \hat{n} \cdot (-D \nabla c)_\pm = K_\pm (c_\pm - c_{eq}) + P(c_\pm - c_\mp)$$

(1-2)
, where \( \hat{n} \) is the unit normal vector at the step from the upper terrace (-) to the lower terrace (+), \( K_+ \) and \( K_- \) are the kinetic coefficients for attachment to the lower and upper terraces, respectively, and \( P \) is the permeability coefficient [1.7].

Alternatively, the evolution of a surface during growth or sublimation can be described at a coarser scale via the motion of steps. Weeks and his coworkers [1.8] proposed a simple 1+1 dimensional model in which the velocity of a step is written as a functional derivative of the individual step Hamiltonian, which includes terms containing both the step stiffness, its local curvature, and the step-step interaction free energy. Generalizing this to 2+1 dimensions, and including a simple expression describing the effect of sublimation yields the following for the velocity of a given point on a step:

\[
\frac{d\vec{S}}{dt} = \frac{\hat{n} \cdot \Gamma}{k_BT} \left( \frac{\tilde{\beta}}{R} + gh \left( \frac{1}{w_1^3} - \frac{1}{w_2^3} \right) \right) - \hat{n} \cdot \left( k^- \cdot w_1 + k^+ \cdot w_2 \right) \tag{1-3}
\]

Where \( \vec{S} \) is the trajectory of the step projected on the terrace plane, \( \hat{n} \) is local normal to the step edge within this plane, \( \Gamma \) the step mobility, \( \tilde{\beta} \) step stiffness, \( k_B \) the Boltzmann constant, \( T \) the temperature, \( g \) the step-step interaction coefficient, \( k^+ (k^-) \) is the adatom attachment/detachment rate to step edges from/to the step down (up) terrace. Equation (1-3) basically states that a step moves locally along the direction normal to the step edge due to the effect step stiffness \( \tilde{\beta} \), which is inversely proportional to the local radius of curvature \( R \), the step repulsion scaled by \( g \) but inversely proportional to the third power of the local distance to nearest neighboring steps \( w_1 (w_2) \), where \( w_1 (w_2) \) is the normal distance to nearest neighboring step in the step-up (step-down) direction, and the
sublimation of adatom from the neighboring terraces, which is estimated to be
\[ k^- \cdot w_1 (k^+ \cdot w_2) \] (See Fig. 2.14 in chapter 2).

The organization of the remainder of the thesis is as follows: In the remainder of this chapter we describe how our experiments are carried out. In chapter 2 we present results on lithographically patterned vicinal Si(111) surfaces, to introduce perturbations at well-defined length scales. The pattern allows us to probe the length scale dependence of the surface evolution which occurs during our annealing experiments, and to test the model described by Eq. (1-3) experimentally. While the above framework is useful for considering the evolution of crystalline surfaces during growth and sublimation, it is of limited use in describing the evolution of the surface of an amorphous or polymeric film. Here continuum models have often been employed, and much of the theoretical interest has been in the possibility of universal behavior, as described by scaling. We examine the evolution of two non-crystalline materials in the chapter 3 and 4 of this thesis and compare to these models. We also look for evidence of pattern formation at a preferred wavelength, using patterning once again to perturb the surface at a series of well defined lateral length scales.
1.3 Introduction to tapping mode AFM

Most of the characterization experiments I describe in this thesis were carried out using tapping mode atomic force microscopy (AFM). Here I briefly review this technique.

AFM is one of a family of techniques known as scanning probe microscopies (SPM) in which the lateral position of a probe is scanned across a surface and the probe-sample interaction or interactions are monitored [1.9]. AFM tracks the force or force gradient between the probe and sample under study, by measuring the either (1) the deflection or (2) the oscillation amplitude, phase or frequency of a flexible cantilever on which the probe is mounted [1.9 – 1.13]. As no current need flow, the technique effectively remedies one of the limitations of scanning tunneling microscopy: it can be used to characterize insulators. AFM can image conductors, semiconductors and insulators in vacuum, atmosphere as well as in liquid.

There are a number of modes in which an AFM can be operated [1.9 – 1.13]. Here we describe three common modes: contact-, non-contact-, and tapping mode AFM as I schematically show the difference in figure 1.3. Early experiments were carried out by monitoring the angular deflection of the cantilever to determine the force of interaction between the tip and underlying surface, usually adjusting the height of the supported end of the cantilever to keep this constant. This is commonly referred to as contact mode, as the tip sample separation is generally maintained within the repulsive regime corresponding to the short-range exclusion principle-derived force. A second mode, referred to as “non-contact” AFM is based upon application of a small oscillatory component to the vertical position of the supported end of the cantilever at a frequency close to resonance. In this case either the amplitude of the oscillation of the tip, the phase
shift between the tip and supported end oscillations or the resonance frequency is sensed, and the average vertical position of the supported end adjusted during lateral scanning to maintain this constant, resulting in a constant vertical force gradient. This mode has two principle advantages: (1) it is intrinsically less subject to low frequency noise and (2) the force of interaction between the tip and sample is typically much smaller than in contact mode. The latter is important when probing soft surfaces. A disadvantage is that there is a built in instability if the separation is such that the force gradient is equal in magnitude but opposite in sign to the spring constant of the cantilever: the tip abruptly jumps into contact with the surface.

Intermittent or “tapping” mode AFM works very much like non-contact mode, except that the trajectory of the tip brings it into intermittent contact with a sample surface. The position of the supported end of cantilever is again driven at or near its resonance frequency (typically ~ 300 kHz) with an amplitude ranging typically from 20nm to 100nm. In this case maintaining a constant oscillation amplitude or phase shift results in a constant tip-sample force gradient, averaged over one trajectory oscillation. The figure 1.4 shows how the tapping mode AFM works schematically.
Figure 1.3 Force vs. tip-to-sample distance in AFM operation.

Imaging the surface with tapping mode AFM provides some benefits over both contact mode and non-contact mode AFM: It gives better lateral resolution than non-contact mode and produces less damage to the surface than contact mode.
Figure 1.4 Schematic of tapping mode Atomic Force Microscopy.
We end this chapter with a brief mention of some issues influencing resolution in AFM scanning. In AFM the spatial resolution depends on the shape and size of the tip, as well as the separation between the tip and sample [1.9 – 1.13]. The apparent lateral extent of convex surface features is overestimated, and of concave features underestimated, due to a convolution of the surface topography with the tip shape as described in Fig. 1.5. This becomes important when the radius of the tip, typically approximately 5 ~ 10 nm, is greater than that features on the surface being probed, or when the height/width ratio approaches or exceeds 1.

The effective tip shape may change during an image, as the tip may pick up impurities as it contacts the surface; this can cause a change in the effective resolution. Tips with multiple asperities at the apex can result in multiple superposed images of surface features; if these are sufficiently close, the resolution is degraded.

Other factors influencing resolution are non-linear response of the Piezo materials used in the AFM scanner and environmental noise (vibration and electrical interference).
Figure 1.5 Examples of tip-sample convolution: (a) an overestimated convex surface feature, and (b) an underestimated concave feature.
Chapter 2 Length-scale dependence of the step bunch self-organization on patterned vicinal Si(111) surfaces

2.1 Introduction

There is considerable interest in systems which undergo self-organization, based upon a need to fabricate nanometer scale structures, at high densities, on a practical time scale. Among the approaches which have been explored for directing self-organization of structures at semiconductor surfaces, topographical patterning of a substrate followed by epitaxial regrowth, or annealing have received the most attention [2.1 – 2.4]. However, in spite of a number of experimental investigations which have been carried out on such systems, the substantial departure from equilibrium, and multiple types of kinetic barriers [1.2, 1.6, 2.5 – 2.7] have thus far prevented a detailed understanding of the evolution of topography during these processes.

In this chapter, we report on an investigation of a simple prototypical system which allows for a degree of directed self-organization, that of lithographically patterned vicinal Si(111) surfaces during high temperature annealing. We extend the approach reported by previous workers [2.1, 2.2] by studying the length-scale dependence of the topographical evolution. As discussed below, we observe a qualitative change in the nature of this evolution as the pattern length scale is increased, indicating the existence of a characteristic length scale in this system.
2.2 Experiment

2.2.1 Sample preparation

We use vicinal Si(111) wafers, miscut by 0.5±0.25° toward the [2 1 1] azimuth. On such surfaces the step density, at least at high temperatures [2.8, 2.9] depends on the step height and vicinal angle in a simple manner: specifically $\tan \theta \sim \theta = h / L$, where $h$ is the step height, $L$ is the terrace width, and $1/L$ is the step density. On Si(111) the minimum step height is 0.314 nm, corresponding to the separation between (111) “double-layers”. We pattern the surface with arrays of cylindrical pits, using photolithography followed by reactive ion etching. We effectively adopt a combinatorial approach, producing cylindrical pits whose diameters and center-to-center spacing we vary systematically with the diameter ranging from 0.7 to 8.0 µm, and the center-to-center spacing from 1.4 to 16 µm. An advantage of this approach is that it allows us to investigate the evolution of surface corrugations vs. two different characteristic lateral length scales independently. The mask for the photolithography process is shown in figure 2.1.
**Figure 2.1** Combinatorial approach: Systematic varying of pit diameters & spacing.
Before patterning we rinse the vicinal Si(111) wafers using a sequence of solvents: (1) acetone (2) methanol, and (3) isopropyl alcohol. We next spin coat them with the adhesion promoter, HMDS, followed by a positive photoresist (PR), OIR 906-10, while spinning at 6000 rpm for 60 sec. This produces a calculated resist thickness of \(~ 0.88 \mu m\). Next a so-called “soft bake” of the resist is performed at 90 °C for 60 s. The resist is then exposed to UV light (\(\lambda = 365 \text{ nm}\)) through a mask using a photolithographic stepper. The pattern transfer from the mask to the photoresist results from a UV exposure-induced solubility change of the resist in aqueous basic solution, i.e. “development”. Following this, the developed resist is “post baked” at 120 °C for 60 sec. We next expose the surfaces to an O\(_2\) plasma for 30 sec. in order to remove PR residues from the bottom of the pits which remain after development. Next the resist-patterned wafers are plasma etched in a reactive ion etching system (Plasmatherm model 790), using SF\(_6\) gas, at a flow rate of 10 sccm, a pressure of 10 mTorr, and a radio frequency source power of 50 W. The depth of the pits after etching is approximately 32 nm, with smaller diameter pits showing a very slightly smaller depth. We next remove the remaining resist, using cycles of chemical lift-off and oxygen plasma etching. A few such cycles reduce the level of residual resist to below what is detectable in atomic force microscopy (AFM) imaging, and produce only very slight changes in the dimensions of the pits. The overall sample preparation processes are summarized schematically in figure 2.2. Finally, the topography of patterned and cleaned samples is characterized using tapping mode AFM employing a single crystal Si tip whose diameter is \(~ 10 \text{ nm}\). We note in passing that the height/diameter ratio is always much less than 1 for our structures.
Figure 2.2 Summary of sample preparation for the cylindrical pit patterned Si(111) surfaces.
2.2.2 High temperature annealing of samples

Our high temperature annealing experiments on the patterned Si samples are conducted in an ion pumped ultra high vacuum chamber, whose base pressure is approximately $2 \times 10^{-10}$ mbar. The samples are out-gassed at temperatures between ~550 °C and 700 °C for several days to remove loosely bonded impurities after bake out of the chamber. Then the samples are heated to ~ 940 °C to remove the oxide. Finally each sample is heated to a temperature of $1273 \pm 5$ °C for a series of periods of time; these periods ranged from 15 seconds, to 480 seconds. We increase the temperatures from 940 °C to 1273 °C over a period of several seconds; we find that this heating procedure, combined with clamping the sample gently to the holder, produces few line of the defects associated with mechanical stress and large temperature gradient on surfaces. We carry out our annealing of the samples using a combination of the radiation heating from a tungsten filament behind the samples (i.e. opposite the patterned surface) and electron bombardment. Temperature was measured with a disappearing-filament pyrometer, correcting for the emissivity difference between Si and the W filament. After each annealing experiment at ~ 1273 °C for a given time, we quench cooled the samples to minimize changes on surfaces during cooling. Subsequently the samples are transferred through atmosphere to a tapping mode AFM (Digital Instruments dimension 3100) and the resulting topography measured. Although the surfaces oxidize, previous measurements by Tsai, et al. [2.10] indicate that the oxide is conformal to the starting surface.
2.3 Understanding of the surface evolution

There are numbers of effects that are known to contribute to the evolution of surfaces at high temperature, including diffusion in the presence of step-step interactions, step stiffness, possibly an Ehrlich-Schwoebel barrier [1.2] as well as sublimation. However as yet there is still no detailed quantitative understanding of the combined effect of these processes. A major goal of this part of my thesis is to achieve such an understanding.

Before discussing the results it is useful to introduce some nomenclature. In Fig. 2.3 we show a schematic of cross section through one of our pit patterned vicinal surfaces. There are two main types of steps which occur on these surfaces: (1) The vicinal miscut produces nearly straight (but nevertheless meandering [2.11, 2.12]) steps that we refer to as “vicinal steps”. (2) The patterning produce cylindrical pits which are bounded by closely spaced nearly circular steps we refer to as “loop steps”.

The arrows shown in figure 2.3 represent the motion of steps which would be produced if only sublimation were important. If that were so, the vicinal steps would always move in up-hill (i.e. step-up) direction under the influence of sublimation, whereas the loop steps would move parallel to the vicinal steps on up-hill side, but anti-parallel to the vicinal steps on down-hill (i.e. step-down) side. This latter effect can result in a local ‘step annihilation’ which is one of the modes by which the patterned structure can relax during annealing.
Figure 2.3 Step profile on a patterned vicinal surface, and step motion which would result if only sublimation were considered.
The above is an incomplete picture of step motion during high temperature annealing our patterned vicinal surfaces: we also need to consider diffusion of atoms in the presence of chemical potential gradient, including both step-stiffness and step interaction effects. The Gibbs-Thomson effect associated with stiffness will oppose the outward expansion of loop steps; since the change in chemical potential is inversely proportional to the radius of curvature of a circular step ($\Delta \mu \sim 1/r$); for small enough radius of curvature it will cause the loop steps to collapse, i.e. to move in opposite sense on the direction that indicated by short blue arrows in the figure 2.3.

Next we briefly consider step kinetics on the patterned vicinal surfaces during high temperature annealing. As indicated schematically in a figure 2.4, we need to include the effects of sublimation, line tension (step-stiffness), and step-step interaction on such patterned vicinal surface. We assume that the motion of steps relative to each other is restricted by condition that steps of the same sign do not cross; otherwise energetically costly overhangs would result. Pointed out by Chui and Weeks [2.13] this non-crossing of steps has a consequence on the interaction of steps. The fluctuations of the position of a given step are reduced by the presence of neighboring steps. This reduces the configurational entropy, and results in a repulsion term in the free energy per area which is proportional to the inverse cube of the separation between steps. A second mechanism for step interaction is the overlap of subsurface strain fields, which for neighboring steps of the same sign again produces a repulsion term in the free energy per area which is proportional to the inverse cube of the separation. The sign of this part of the interaction is expected to reverse and become attractive if neighboring steps have opposite sign, however.
Figure 2.4 Competing effects acting upon steps on a pit patterned vicinal surface during high temperature annealing: Sublimation; Line tension, which is related to the step stiffness; Step-step interaction. Here $\beta$ is the step stiffness, $g$ is the step-step interaction coefficient, and $l$ is the separation between steps in the Free E/Area equation.
Illustrative examples of influence of step stiffness at different pattern length scales are shown in a figure 2.5. It shows the surface plot of AFM Images after annealed for 30 sec. at ~ 1273 °C for the pit size of 1.4 um diameter and 2.8 um center-to-center spacing between the pits on the left panel, while the right panel shows part of surface patterned with pits of 4.0 um diameter and 8.0 um center-to-center spacing. For smaller pattern length scales, the line tension effect dominates, and leads to rapid relaxation to nearly straight step bunches. At larger pattern periods effect of line tension is less pronounced and the step bunches remain laterally corrugated during relaxation.

**Figure 2.5** Step stiffness effects vs. pattern length scale after 30 sec. annealing at ~1273 °C. On the left hand side is an AFM image of 1.4 um diameter – 2.8 um spacing, on the right hand side is an AFM image of 4.0 um diameter – 8.0 um spacing. The smaller period patterned surface shows the nearly straight step bunches after annealing, while the larger period patterned surface shows laterally corrugated step bunches after same amount of annealing.
A second effect which enters into the relaxation of the patterns is the step-step interaction. Our AFM images show two different types of indication of interaction, which can be seen in figure 2.6. At the up-hill side of the pits the inward relaxation of the initially tightly bunched loop steps which form the side-wall provides evidence for repulsive step-step interactions between steps of the same sign. By contrast, at the down-hill side there is a visible bowing-in of the step bunch, which suggests an attractive step-step interaction of steps with opposite signs. Attractive step-step interactions have been suggested theoretically, but as far as we know there has never been any experimental evidence to support them previously. As mentioned above, an attractive step-step interaction would allow for annihilation of steps locally.
**Figure 2.6** Step-Step Interaction Effects: Surface plot of AFM image for surface patterned with 8 um diameter pits spaced at 16 um.
2.4 Results

As illustrated in Fig. 2.5, the topographical evolution varies with the pattern length-scales during high-temperature annealing. In these experiments there are three quantities which we vary: pit diameter, spacing between the pits, and the annealing time; in this thesis we concentrate on patterns for which the initial diameter of the pits is one-half the center-to-center spacing (corresponding to the diagonal cells in figure 2.1).

We discuss the dependence on lateral length scale (i.e. pit diameter – spacing between the pits) first. Figure 2.7 shows a summary, in the form of AFM images, of the result of a fairly short anneal: ~ 15 sec. at ~ 1273 °C. The top left panel in the figure shows an AFM image from a region of the surface where the initial pattern consisted of 1.0 µm-diameter pits, spaced at 2.0 µm center-to-center. The image has been high-pass filtered to allow individual steps and step bunches to be seen, despite the large range of heights present in the original image. The pits on this part of the surface have entirely disappeared, and been replaced by a set of nearly straight step bunches whose spacing matches that of the original pattern, i.e., 2.0 µm. At the relatively larger period of structures atomically flat bottomed circular pits are visible in the image, with step bunches wrapping around the sidewalls on the “uphill” side. In addition, we observe the asymmetric intermediate loop shape with more curved step bunches in the periods 5.6 µm diameter – 11 µm pitch and 8 µm diameter – 16 µm pitch. The pits are again flat bottomed, but bounded by nearly semicircular steps, with flat edges on the uphill side of the pits, due to the small depth/diameter ratio for the pits in these cases. We find that the general features of the pattern length scale dependence of the surface evolution observed in this figure persist for surfaces annealed for longer times.
Figure 2.7 Length scale dependence on the topographical evolution after 15 sec. annealing at ~ 1273 °C.
Next, we present results for a fixed lateral pattern period, but increasing annealing time. As we continue to anneal the structure, we observe first that the pits completely disappear, due both to the annihilation events mentioned above, as well as inward collapse of loop steps driven by diffusion in the presence of the Gibb-Thomson effect. This disappearance leaves behind step bunches, which for short period structures quickly become nearly straight, but for longer period structures remain corrugated laterally. More protracted annealing eventually causes the amplitude of the sinusoid to relax. This can be seen in figures 2.8 and 2.9, which are for two different pattern length scales. The high-pass filtered AFM images shown in the figure 2.8 are for a pattern consisting of 2.8 µm diameter pits with a 5.6 µm center-to-center spacing. All the images are for a 20 µm x 20 µm field of view, for ease of comparison. After a relatively short annealing time, ~ 15 s, we still see flat-bottomed circular pits, around which step bunches wrap at the up-hill edges. This structure subsequently relaxes: first to nearly sinusoidal shaped step bunches by 65 s, and then to nearly straight step bunches by 120 s of annealing time. The high-pass filtered AFM images shown in figure 2.9 are for a larger pattern size: with 4.0 µm diameter pits spaced at 8.0 µm center-to-center; here the field of view of all the images is 30 µm x 30 µm. The topographical evolution as a function of annealing time shows a similar progression as for the smaller period structure. However, the lateral relaxation in this case occurs more slowly. Comparing AFM images for surfaces annealed for 30 s in figures 2.8 and 2.9, shows that for the 4 µm diameter – 8 µm spacing pits, all of the original flat bottomed pits are still present, whereas in the case of smaller 2.8 µm diameter – 5.6 um spacing the pits have almost all disappeared, and have been replaced by nearly sinusoidal step bunches.
Figure 2.8 Annealing time effect on evolution. High-pass AFM images for a pit pattern of 2.8 \( \mu \text{m} \) diameter x 5.6 \( \mu \text{m} \) spacing at \( \sim 1273 \, ^\circ \text{C} \). The images are for a 20 \( \mu \text{m} \) x 20 \( \mu \text{m} \) field of view.
Figure 2.9 Annealing time effect on evolution for a pattern made up of 4 μm diameter pits x 8 μm spacing at ~ 1273 °C. The high-pass AFM images are for a 30 μm x 30 μm field of view.
We next quantify the evolution of the surface topography based on our AFM measurements. We consider two different quantities to characterize the relaxation of the patterns. The first is the corrugation amplitude of the step bunches measured within the average surface plane, which we refer to as *in-plane corrugation*. In-plane corrugation is shown schematically by the dashed lines in the right panel of figure 2.10. To determine this, we visually pick out positions of step bunch crests and troughs from our high-pass AFM images. As shown in the left panel of figure 2.10, in-plan corrugation relaxes more slowly for larger pattern periods; this is qualitatively consistent with a decreasing effect of step-stiffness with increasing pit radius and separation.
Figure 2.10 (Left) In-plane corrugation of pattern relaxation vs. pattern length scale. The numbers indicate the initial pit diameter; the center-to-center spacing is twice the diameter. (Right) Illustration of determination of in-plane corrugation.
The second quantity of interest in the relaxation is the *out of plane corrugation amplitude* which is the amplitude within a plane defined by the surface normal and the azimuth perpendicular to the vicinal steps (i.e. the staircase azimuth). This can be measured from height profiles across our AFM images. Based upon symmetry considerations there are two obvious choices for the locations of such profiles along the vicinal step direction. First, of course, is across the center of neighboring pits; examples, for a pattern consisting of 2.8 µm diameter pits separated by 5.6 µm, are shown in figure 2.11 (a). These “across-center” profiles for small amount of annealing time show essentially flat bottoms of (111) orientation, while later ones relax to a nearly sinusoidal form. The other symmetric choice of profiles would be the midway between the pits, as shown in figure 2.11 (b). Because of the form of the pattern, initially there is no corrugation (aside from some very small extrinsic roughness) along this direction. In this case the profiles for smaller annealing time, the corrugation amplitude along the profiles is quite small. However, annealing drives the initially tightly bunched loop steps apart, and these interfere with the vicinal steps. The result is that the pattern spreads across the surface, and the corrugation amplitude measured in these “between pit” profiles approaches that measured across pit centers, as seen in the center panel of figure 2.11. By approximately 120 sec, the two measures of the out-of-plane corrugation converge afterwards relax essentially simultaneously. Based upon physical insight, we expect the relaxation of the out of plane corrugation to be driven in large part by the step-step interactions.

We summarize the out of plane corrugations along both directions for the varying length scales in a figure 2.12.
Figure 2.11 Relaxation of out of plane corrugation amplitude for a pattern consisting of 2.8 μm diameter pits with a 5.6 μm center-to-center spacing. (a) Profiles measured across pit centers, (b) profiles measured between pit centers. (Center) Summary of amplitudes vs. anneal time.
1.4 um Dia  
2.8 um Pitch

RMS Amplitude (Å)  
Anneal Time (sec)  

(b)  
2.0 um Dia  
4.0 um Pitch

RMS Amplitude (Å)  
Anneal Time (sec)
Figure 2.12 Out of plane corrugation with length scale variation (a) 1.4 um dia. – 2.8 um pitch, (b) 2.0 um dia. – 4.0 um pitch, (c) 4.0 um dia. – 8.0 um pitch, and (d) 8.0 um dia. – 16 um pitch.
Both the in-plane and out-of-plane/across-pit amplitudes show an approximate exponential decay with annealing time. We summarize the relaxation times both in plane and out of plane/across pits in the form of a log-log plot in figure 2.13. The slope of the logarithm of the out-of-plane time constant increases in this plot throughout the range of pattern length scales investigated. The in-plane relaxation time, on the other hand, is well fit over the entire range shown by a power law dependence on the lateral length scale, with an exponent of 3.86±0.14. Our observations are consistent with an in-plane relaxation time which increases approximately as the fourth power of the period of the pattern. A $\tau \sim \lambda^4$ is predicted for the case where relaxation is mediated by surface diffusion at a temperature above roughening [2.14]. Although the vicinal surfaces studied here are logarithmically rough, our observation of such a power law is perhaps surprising as the surface is not in equilibrium with a vapor phase, and there is a significant rate of sublimation at this temperature, approximately 1.4 bilayers/s [2.12]. The two time constants become equal by a pattern period consisting of pits of 8 $\mu$m diameter spaced at 16 $\mu$m, and there is the suggestion that the out-of-plane relaxation converges to the same dependence. However, more measurements at larger length scales are necessary to confirm that this is indeed the case.
Figure 2.13 Summary of time constants for decay of in-plane (solid circle) and out-of-plane (open squares) corrugation amplitudes as a function of initial pit diameter. Dashed line shows a best fit to a power law dependence for the in-plane relaxation time, with an exponent of $3.86 \pm 0.14$. 
2.5 Discussion

The pronounced difference in the relaxation times in-plane, and out-of-plane corrugation amplitudes that we observe at small pattern lengths might be explained by at least two possible sources of asymmetry. The first is the difference in the surface stiffness along the vicinal direction, where it is determined by step-step interactions, and at right angles to this, where it is determined by step stiffness. The second is a difference in the diffusivity along steps and across terraces.

To understand our observations quantitatively and judge the relative contribution of these effects requires modeling the motion of steps across the surface including both diffusion, which is driven by the effects of step stiffness and step interactions, and sublimation. In the following section we present the results of simulations based upon a very simple model [1.8, 2.15] describing the velocity of steps in including the first source of asymmetry. Here we point out that a strong variation with pattern length in the relaxation rate of the in-plane corrugation can be understood qualitatively based upon the Gibbs–Thomson effect, which produces a term in the free energy which is inversely proportional to the radius of curvature. The size dependence of this effect leads to two important differences between the way small-period and long-period structures relax: (1) This radius is negative for the loop steps which bound the pits, and thus the Gibbs–Thomson effect drives diffusion of atoms from the larger loop steps to the smaller ones. This curvature-mediated diffusion opposes sublimation, which tends to drive steps in the uphill direction. Small pits disappear mainly via diffusion, while large pits instead disappear via annihilation with vicinal steps; a much larger in-plane corrugation immediately after the pits disappear results in the long-period structure case due to the
greater number of “horseshoe shaped” steps which form during these annihilations. (2)

Subsequent to the disappearance of the last loop steps, for long-period structures the relaxation of the in-plane corrugation is much slower than for small-period structures. We expect the characteristic length scale we observe in Fig. 2.10 to depend on temperature, and thus it should be possible to vary the pattern period at which the in-plane and out-of-plane relaxation times coincide by varying the annealing temperature.

Finally, we note that the eventual relaxation to a uniform step train suggests that diffusion of atoms under the influence of a repulsive step-step interaction for steps of the same sense is important; sublimation alone cannot explain this effect. This same observation allows us to rule out a strong Ehrlich–Schwoebel barrier [1.2], which would result in step bunching. Surprisingly, our observations show that even at a temperature of 1273 °C, where sublimation drives our patterned Si surfaces well out of equilibrium, the final configuration is consistent with what would be expected based upon relaxation to a minimum energy configuration.

2.6 Summary of Experimental Results

In the previous sections we describe the results of a combinatorial approach toward controlling the evolution of topography during high-temperature heating of Si. Lithographically patterned arrays of cylindrical pits of different diameters and spacings on 0.5 ° miscut Si(111) surfaces were annealed at ~ 1273 °C for times ranging from seconds to minutes. Straight steps due to miscut locally annihilate with loop steps at the “downhill” side of the pits and partially unwrap, leading to both in plane and out of plane
corrugations. Ex-situ AFM observations show the existence of a critical pit separation, set by the competition between sublimation pressure on the steps, their intrinsic stiffness and their mutual interactions; above it straight steps wrap around pits, leaving a pronounced corrugation within the surface plane, beneath it straight step bunches quickly form, with a pronounced corrugation perpendicular to the surface plane. Our observations of step bowing on the downhill sides of the pits provide evidence of attractive interactions between steps of different signs.

Most interestingly, we find a pronounced asymmetry in the evolution of the pattern within the vicinal plane and perpendicular plane for small lateral spatial periods, but a convergence to a symmetric relaxation for lateral periods $>\sim 16 \mu$m for annealing carried out at 1273 °C.

2.7 Numerical simulations on patterned vicinal Si(111) surfaces during high temperature annealing

2.7.1 Introduction

In earlier sections in this chapter we show the experimental results of difference in surface evolution between smaller length scale patterns and larger length scale patterns on vicinal Si(111) surfaces during annealing at $\sim 1273$ °C. There we observe that the annealing of smaller length scaled patterns causes a complete disappearance of the original pits in fairly short annealing time. In agreement with the earlier work of Ogino [2.1], in their place are straight step bunches whose spacing is that of the original pattern. A longer anneal causes a relaxation of these straight step bunches to a uniform
step train. As we increase the length scale of the pattern both the rate, and the nature of
the evolution of the surface begin to change. The slower evolution is not so surprising,
given that it involves transport of atoms across the surface as well as sublimation. Even
once the pits disappear, the evolution is qualitatively different than at the smallest
periods. The step bunches remain sinusoidal as the overall structure relaxes. We also
consider the effects which come into play in determining the characteristic length scale
which separates the regimes in which bunch waviness relaxes faster than bunch height,
and that in which they decay together.

We summarize numerical simulation results on the Si(111) vicinal patterned
samples to compare it with experimental results [2.16] in this section. As a starting point
we consider the problem in terms of the contributions to the free energy of a stepped
surface. As we already considered in experimental parts, the important physical
parameters in the evolution of such surfaces are the step stiffness and the step-step
interaction (See in the equation (2-1)).

\[
\text{Free Energy / Area: } f = f_0 + \frac{\beta}{l} + \frac{gh}{l^3}
\]

(2-1)

Where \( \beta = \beta + \frac{\partial^2 \beta}{\partial \phi^2} \) (\( \beta \) is the step stiffness), and \( l \) is the separation between steps.

Making a step creates additional broken bonds, and bending that step creates more broken
bonds still. The free energy contains a term which is proportional to the step density, i.e.
the step creation free energy. This is related to the stiffness. The second important
contribution, the step-step interaction has both an entropic and elastic contribution, but
both fall off like \( 1/l^3 \) as shown in the equation (2-1). The step-step interaction is
repulsive between steps of the same sign both due to the fact that they don’t cross and the
overlap of the strain fields. It has been suggested that the interaction between steps of
opposite signs might be attractive, and in fact we see some possible evidence from this
from the inward bowing of the steps (in Fig. 2.6), and also from our simulations.

We have carried out extensive numerical calculations adapting the model
suggested by John Weeks and his coworkers [1.8]. In this model the local velocity of a
point on a given step is written as mobility times a functional derivative of a step
Hamiltonian as described in figure 2.14. It depends explicitly on the step stiffness and
step-step interactions, and also has a term corresponding to sublimation. If there is an
asymmetry in the probability of a detaching adatom moving onto the terraces above and
below the step, the two coefficients are different. Such an asymmetry would result from
an Ehrlich-Schwoebel barrier, which would be expected to cause step bunching during
sublimation. Our observations show relaxation to a uniform step-train we see no evidence
for such a barrier, and thus set the two coefficients equal (i.e. $\kappa^+ = \kappa^-$). To allow for step
annihilations we take the interaction between opposite sign steps to be attractive-for
simplicity we merely reverse the sign of the coefficient.

The starting values for $\Gamma$, $\tilde{\beta}$, $g$ and $\kappa$ are extrapolated from the values obtained
from Metois’ experiments [2.12] under near equilibrium conditions at 900 °C and
1100 °C. Step parameters for Si(111) surfaces proposed in previous works at 900 °C
[2.20, 2.21] and at 1270 °C [2.22] under direct current heating are summarized in table
1.1 and 1.2 for comparison.
\[
\frac{d (x_n, y_n)}{dt} = \frac{\Gamma}{kT} \left( \vec{\beta} \cdot \frac{1}{R} + gh^3 \cdot \left( \frac{1}{w_1^3} - \frac{1}{w_2^3} \right) \right) \cdot \hat{n} - \left( k^+ \cdot w_2 + k^- \cdot w_1 \right) \cdot \hat{n}
\]

\textbf{Figure 2.14} Mesoscopic model for step kinetics [1.8]. Here \( \Gamma \) is the step mobility, \( \vec{\beta} \) is the step stiffness, \( g \) is the step-step interaction coefficient, \( \kappa^- \) and \( \kappa^+ \) are the kinetic coefficients for attachment to the upper and lower terraces, and \( W_1 \) and \( W_2 \) are the upper terrace and the lower widths, respectively.

\[\mathbf{\kappa^+ / \kappa = 1} \]

No Schwoebel Barrier

Hard Core Step Repulsion

- No Step Crossing
Parameters | $d$ (Å) | $q$ (e) | $\Gamma$ (Å$^3$/s) | $D_s$ (Å$^2$/s) 
--- | --- | --- | --- | --- 
A | 100000 | 0.006 | $3 \times 10^7$ | $5.2 \times 10^{11}$ 
B | 5000 | 0.006 | $4 \times 10^7$ | $3.4 \times 10^{10}$ 
C | 100 | 0.03 | $3 \times 10^6$ | $5.2 \times 10^9$ 
D | 10 | 0.2 | $2 \times 10^9$ | $3.5 \times 10^8$

**Table 1.1** Si(111) step parameters proposed at 900 °C under local mass transport limit in Ref. 2.20 and 2.21. Here $d$ is defined by $d = D_s / \kappa$ where $D_s$ is the adatom diffusion rate, and $\kappa$ is the attachment/detachment rate. $q$ is an effective charge of the adatoms, and $\Gamma$ is the step mobility. $\Gamma = 2 c_{eq} a^3 \kappa (c_{eq} a^2 = 0.2$ ML) is used; the step interaction parameter $g$ was estimated as approximately 0.015 eV/Å$^2$ at 900 °C.

Parameters | $\beta$ (meV/Å) | $\kappa c_{eq} a^2 F / kT$ | $q$ (e) 
--- | --- | --- | --- 
 | 28 | $6.5 \text{ s}^{-1} - R_e$ | 0.13

**Table 1.2** Si step parameters proposed at 1270 °C in Ref. 2.22. Here $c_{eq}$ is the equilibrium adatom concentration on terraces, $a^2$ is the area of a single atomic cell on the surface, and $F$ is the force acting on each adatom ($F = qE$). $R_e$ is the sublimation rate, and it is approximately 2 ML/s at 1270 °C.
2.7.2 Results

We firstly show the results of two different simulations for the smallest period structure we have studied, 700 nm diameter pits separated by 1.4 um and for a structure 4x as large, already in the transition region between the small scale and large scale behaviors we see. The figure 2.15 (a) is the simulated starting surface of 0.7 um diameter – 1.4 um spacing between the pits, and (b) is the simulated starting surface of 2.8 um diameter – 5.6 um spacing between the pits. Although only a single pit is shown, periodic boundary conditions are used, so that the effect of neighboring pits is included. In the simulation sequences, we observed that there are two modes by which loop steps disappear. The smallest loops collapse due to diffusion driven by the curvature, while the large loops annihilate with vicinal steps. We also see a difference in the disturbance of the vicinal step spacing midway between pits in the two cases. The overlap of the disturbances is much greater in the small period case-this is a significant part of the origin of the difference in the subsequent relaxation. As shown in the inserted AFM height images in Fig. 2.15, the smallest period structure causes nearly straight step bunches ((a)), while the larger period structure causes sinusoidal step bunches due to far more step annihilations ((b)) after same amount of annealing, 30 sec. in this case.
Figure 2.15 Two examples of simulations on circular pit patterned Si(111) surface in both top-down and cross-sectional views: (a) 0.7 um diameter – 1.4 um separation, and (b) 2.8 um diameter – 5.6 um separation. Insets are the AFM height images of the surface after 30 sec. annealing at ~ 1273 °C.
In figure 2.16 we show a summary of experimental results, in the form of high-pass filtered AFM images, as a function of pattern length scale as well as annealing time to compare with simulated images of the starting surfaces for the same small period, intermediate period and large period structures after a 30 second and 65 second anneals in figure 2.17. The insets in Fig. 2.17 show the high pass AFM images that we measure for comparison. We can see that the simulation captures all of the qualitative features of the evolution, across the entire range of periods. To make a more quantitative comparison, we extract from the simulations the same in plane and out of plane corrugation amplitudes we measured in our AFM images. These are shown in semi-log plots as normalized in-plane (or out-of plane) corrugation vs. time in second in Fig. 2.17. As you see the asymptotic behavior is decaying exponential, and the time constants increase with spatial period, in qualitative agreement with what we observe experimentally (See Fig. 2.16 (b)).
Figure 2.16 Summary of experimental results of surface evolutions on effects of length scale and annealing time. (a) The top panel shows the three pattern length scales from different parts of the surface after 30 sec. annealing at ~ 1273 ° C: 1.4 um pit diameter – 2.8 um separation between pits, 4.0 um pit diameter – 8.0 um separation between pits, and 8.0 um pit diameter – 16.0 um separation between pits (from left to right). The middle column images show the evolution on fixed length scale at 4.0 um pit diameter – 8.0 um separation between pits with increased annealing time. (b) Log-log plot of decay time constant as a function of pit diameter for both out-of-plane corrugation (OOP) and in-plane corrugation (IP).
Figure 2.17 Simulated structures after a 30 second and 65 second anneals. The insets show the high pass AFM images that we measure for comparison. The summary plots are the extracted simulations of the same in plane and out of plane (OOP) corrugation amplitudes we measured in our AFM images.
2.7.3 Discussion

In this section we interpret our simulation results qualitatively in terms of in-plane (IP) and out-of-plane (OOP) corrugations by comparing our experimental results. In figure 2.18 we show a detailed comparison between the simulated and measured decay times vs. length scale. The model successfully captures the different dependences of the two decay times for the smallest structures, as well as their convergence for the larger period structures. It underestimates the exponent for the asymptotic dependence, giving ~ 2.8 rather than 4.

In the simulations, the difference between regimes can be understood qualitatively as follows: Shortly after beginning the anneal the step-step interaction drives the closely bunched loop steps outward in a shock wave, propagating the original shape of the pits. The larger overlap of shock waves for the smaller period structure results in a disturbance in the step spacing which extends all the way out to the mid-plane between pits, while for the larger period structures the step spacing is uniform here. At the uphill apices of the pits where the steps are closely bunched a given step is effectively pinned by its neighbors. The driving force for the change in step position comes largely from the curvature of the steps away from these apices, where its motion is relatively unhindered due to the larger step separation in the disturbed regions between pits.

We can also make rough approximations as to the characteristic length scales bounding the small period, transitional and large period behaviors. For the small period structure the step stiffness term in the velocity equation dominates the step interaction term. Once the pit disappears the steps in the bunch take on an approximately sinusoidal shape. An inspection of the simulation and a little insight suggest that the small period
regime corresponds to amplitude $A \sim w$, the average step spacing. This gives a characteristic lower bounding period of $\sim 2.2$ um-close to what we observe. In the opposite limit, it is the step-step interactions which dominate. The appropriate characteristic amplitude is related to the shape of the pit, specifically the pit depth divided by the sine of the vicinal angle. This gives a characteristic upper spatial period of 15 um, again close to what we observe.
Figure 2.18 A detailed comparison between the simulated and measured decay times vs. pit diameter from both in-plane (IP) and out-of-plane (OOP) corrugations analysis. Also the characteristic lower and upper bounding periods are estimated by using the step kinetic parameters $\Gamma, \beta, \text{and } g$ as 2.2 µm and 15.5 µm, respectively. Where $A$ is the amplitude of the sinusoid, $w$ is the average step spacing, $\theta$ is the miscut angle, $d$ is the depth of pit, and $L$ is the period (i.e. twice of pit diameter).
Finally we consider the size of the parameters which give optimum agreement with the experiment as shown in figure 2.19. The velocity equation contains the product of the step mobility and stiffness and the product of the mobility and step interaction parameter. For simplicity we used the step mobility extrapolated from measurements of step fluctuations at 900 °C and 1100 °C by Metois [2.12]. We fit to the step relaxation times and last loop step disappearance times to get the step interaction parameter and step stiffness. Both values (black filled markers with a dotted circle in Fig. 2.19) are very low compared to the extrapolated values: approximately two orders of magnitude lower. Seemingly this discrepancy should be attributed to the nonequilibrium conditions under which we did our annealing.
\[
\frac{d(x_n, y_n)}{dt} = \frac{\Gamma}{kT} \left( \tilde{\beta} \cdot \frac{1}{R} + gh^3 \cdot \left( \frac{1}{w_1^3} - \frac{1}{w_2^3} \right) \right) \cdot \hat{n} - \left( k^+ \cdot w_2 + k^- \cdot w_1 \right) \cdot \hat{n}
\]

**Figure 2.19** Step kinetic parameters for simulation [2.12, 2.17 – 2.19]. The velocity equation contains the product of the step mobility and stiffness and the product of the mobility and step interaction parameter. For simplicity we used the step mobility extrapolated from measurements of step fluctuations at 900 °C and 1100 °C by Metois [2.12].

One last point is that although the step-step interaction is apparently very small, it is necessary to get agreement with our experiments. Turning it off causes a very large increase in the out of plane relaxation times—well out of the range observed in our experiments.
Chapter 3 Evolution of roughness and wavelength selection during fluorocarbon plasma etching of Nanoporous Silica

3.1 Introduction

There is considerable interest in the development of low-k dielectrics for high speed devices for which the RC time constant is rate limiting [3.1]. While integrating copper metallurgy in place of traditional aluminum has reduced the resistance component of the RC time delay, reducing the capacitance component will involve integration of a new insulating material with a lower dielectric constant (k) than the incumbent silicon dioxide dielectric materials [3.2]. The low-k dielectric material can either be inorganic, organic, or a hybrid combination, and are deposited by chemical vapor deposition (CVD) or by spin coating [3.2, 3.3].

An appealing candidate for these applications is a nanoporous silica (NPS), consisting of a SiO$_2$ matrix into which gas-filled pores are dispersed. Introduction of the pores lowers the dielectric constant of the nanoporous film since the dielectric constant of air is 1.0. One of the unique features of a porous material is the ability to control porosity by varying the volume density of pores, with a value of $k \sim 1.9$ is achievable at a porosity of 50% and hence tailor the performance of the material to meet the requirements of successive generations of future integrated circuits [3.4]. The porosity is tuned by changing the amount of sacrificial copolymers called porogens into the low-k matrix resin. The porogens volatilize during thermal curing (> 400 °C) of a NPS film leaving nano-size pores. Figure 3.1 shows a summary of how NPS film can be produced.
Defining the location and extents of insulator regions on a device requires patterning, with lithography followed by plasma-based etching being the standard approach for contiguous SiO$_2$ [3.6], and also resist stripping and post-etch cleaning processes commonly utilize the plasma. An issue of some concern is thus the stability of the NPS/plasma interface during plasma etching. A roughening of the etch front will result in unwanted variations in the thickness of the insulator making it difficult to control critical dimensions. Therefore, we set out to study the evolution of surface roughness during plasma etching of NPS and contiguous pattern formation during etching of NPS.

Recently Hua et al. reported on the results of etching methyl-silsesquioxane (MSQ) derived NPS with C$_4$F$_8$-based plasmas under both ion-poor and ion-rich conditions [3.4]. They found that in the former case a relatively thick fluorocarbon polymer layer builds up on the NPS surface, and that the pores in the top ~ 200 nm of the NPS are infiltrated, increasing its dielectric constant. In contrast, for an ion-rich plasma containing C$_4$F$_8$/90%Ar TEM images showed no obvious infiltration of the pores and most importantly the dielectric constant maintained its low value after etching. These

**Figure 3.1** Processing steps to produce Nanoporous silica films [3.5].
latter conditions however produced much rougher etch-fronts. Controlled generation of nanoscale roughness has the potential for great technological impact in the development of nonwetting surfaces [3.7, 3.8], low friction coatings [3.7, 3.8], wafer bonding [3.8, 3.9] and light-trapping films for high-efficiency solar cells [3.10]. There is thus considerable interest in the development of materials and processes for which surface roughness of a controllable amplitude and spatial period can be easily achieved. Interestingly, transmission electron microscopy images of etched NPS show some indication of spontaneous pattern formation [3.4]. Such an effect is potentially useful as a means of self organization of a rippled structure at a preferred wavelength.

In this chapter we describe a series of experiments on plasma etching of both pristine and patterned NPS, designed to both characterize the lateral size dependence of the roughening which occurs, and to probe this system for instability to spontaneous pattern formation. We first describe our experimental procedures. We then present experimental results for unpatterned surfaces, and then for lithographically patterned surfaces.

3.2 Experiment

Our MSQ-derived NPS films, for which the empirical formula is \((\text{CH}_3\text{-SiO}_{3/2})_n\), are 400 nm in thickness, with pore sizes of between 2-3 nm. A schematic of our sample, which has a layer of NPS deposited on a Si substrate with sandwiched structures, is shown in figure 3.2. The surfaces are etched in a reaction chamber employing inductively coupled plasma (ICP) geometry with Ar-rich Fluorocarbon plasma [3.4, 3.11]. A low
pressure of 10 mTorr is used, so that the ion mean free path is large relative to the characteristic size of features on the surface. The self bias voltage is set at -125 V, gas flow rate at 50 sccm, and an RF source power at 600 W. To improve our understanding of plasma-surface interactions, we employ a shutter approach [3.12] where a sample is etched for a time period which increases progressively along the sample (gradient etch) using a moving shutter. Using this shutter approach we can obtain the entire etching history along the sample in a highly controlled fashion. Both prior to and after each etching experiment we characterize the topography of the NPS surface using the tapping mode AFM (DI dimension 3100) described in chapter 1. In addition, at each stage of our experiments we measure the NPS film thickness using a single wavelength (632.8 nm) ellipsometry; this allows us to determine both the etching rate, and the depth of the modified surface layer. We use NPS films with the porosities 10 %, 15 %, 30 %, and 50 % for “blanket etch” experiments. And for comparison, we perform the same experiments to the conventional SiO₂ film, which is assumed as 0 % porosity, and organosilicate glass (OSG), which contains relatively low porosity of ~ 7 %.
We also investigate experiments on lithographically patterned surfaces, in order to probe the possibility of presence of a preferred length scale set by the system during etching. We produce our patterns, consisting of a series of various nm-sized/spaced square pits by using electron beam lithography followed by plasma etching; the lithography is done using a scanning electron microscope (SEM, JEOL Model 6500F) controlled by lithography software (Nabity NPGS). We vary both pit size and spacing between the pits (Pattern design details are shown in Appendix C). Due to proximity effects, the minimum pattern size we could reliably produce was ~ 140 nm. Here we only focus on results for NPS samples with 30% porosity. The plasma etching conditions were held fixed, using the parameters described above for the blanket etch surface experiments. An initial 16 second etch was used for patterning we define as a starting surface, which depth is about 33 nm. Having multiple patterns on a single wafer

![Diagram of blanket NPS sample structures.](image)

**Figure 3.2** Schematic drawing of blanket NPS sample structures.
minimizes the nearly inevitable etching variation from sample to sample and allows collecting accumulated surface information from the staring surface. Subsequently the patterned surfaces were cleaned, and their topography measured. Finally, additional plasma etching of the samples was carried out for steps of 32 seconds; we performed sequential etches on the same samples, using the pattern to navigate to particular individual features on the surface after each etching step.

3.3 Results

Plasma etching NPS under the conditions described above results in a very rough surface; the overall rate at which the surface roughens increases monotonically with porosity as showed in figure 3.3, and at a rate at least an order of magnitude faster than either contiguous SiO$_2$ or organosilicate glass [3.4]. Lazzeri et al. [3.13] reported that surface roughness strongly increases with NPS porosity, however no surface roughness develops on OSG and bulk SiO$_2$ even after prolonged C$_4$F$_8$/90%Ar plasma treatment. The threshold porosity for excess roughening is about 10 %, meaning that the porosity values above 10 %, significant bulk and surface modifications including roughness of NPS dielectrics are observed [3.13]. These results are consistent with our experimental results summarized in figure 3.3. It is known that porous materials are etched faster than non-porous materials like SiO$_2$ because of their intrinsic sponge-like fragile structures (i.e. less mass density), so that higher porosity yields higher etching rate.

In figure 3.4 we show representative AFM images for the etched surfaces. The size of each image is 2 µm x 2 µm; the vertical scale extends for 0 - 40 nm for all the
images, for ease of comparison. Dramatic surface morphological changes can be observed as both etching time and porosity are increased. By contrast, only a very slight change in surface morphology during etching of bulk SiO$_2$ (0 % porosity) was observed over the etching time range we studied.
Figure 3.3 Summary of AFM scanning results on blanket samples: Plasma etching induced surface roughness vs. plasma etching time as a function of porosity. The additional box includes the etching rate of each surface depending on the porosity.
Figure 3.4 Summary of representative AFM images after plasma etching with C₄F₈/90% Ar at 10 mTorr, 600 W source power, and -125 V self-bias voltage. The etching was performed gradually along the long edge of each sample for 0 ~ 70 sec. using a Si shutter. The percentage in each image indicates porosity of NPS. SiO₂ is assumed to be 0 % porosity.
Conventionally, the roughness of such films is characterized by calculating the height-height correlation function:

\[
G(\vec{R}) = \left\langle \left( h(\vec{r}) - h(\vec{r} + \vec{R}) \right)^2 \right\rangle
\]  

(3-1)

where \( h \) is the local height of the surface, \( \vec{r} \) and \( \vec{R} \) are two dimensional translation vectors lying within the average surface plane, and the average is over the entire image. \( G \) measures how the correlation in height between different parts of the surface falls off with distance due to roughness. It is frequently assumed that the structure of rough surfaces result is self-affine [3.14, 3.15]. Based on this assumption, scaling theory would predict that the height-height correlation function should show a power-law dependence on distance, \( G \sim R^{2\alpha} \), for \( R \) much smaller than a characteristic value called the correlation length \( \xi \). For \( R >> \xi \), \( G \) is predicted to saturate at a value of \( 2w^2 \), i.e. twice the square of the RMS roughness. In addition, if scaling theory applies both the RMS roughness and the correlation length should show power law dependences on the etching time: \( w \sim t^\beta \) and \( \xi \sim t^{1/z} \), where the three exponents should be related according to \( \beta/\alpha = 1/z \) [3.15].

It is not obvious that simple scaling theory should describe the structure resulting from the etching of a heterogeneous material like NPS. To determine whether models based upon this theory are applicable to this complex process we calculated the height-height correlation function for samples of different porosities over a series of etch times. We show the examples of height correlation functions as a function of etching time calculated from 30% porosity NPS in figure 3.5. In the plots, the level of saturation (i.e.
twice the square of the RMS roughness) as well as correlation length ($\xi$) increase with
time. Similarly, we measured the height correlation functions for the samples with
different porosities. In figure 3.6 (a) we show another example of the measured height-
height correlation function, for a 15 % porosity sample after etching for 43 s. The solid
line shows a best fit to the functional form suggested by Sinha, et al. [3.16]

\[
G(R) = 2w^2 \left( 1 - \exp\left( - \frac{R}{\xi} \right)^{2\alpha} \right)
\]

which has the proper behavior in the limiting cases. The fit of this form to our calculated
values is generally good, although the data show a more rapid fall off than the fit for the
smallest separations. This could be an effect due to the finite AFM probe radius, which
should smear out roughness on very short length-scales. The data also show a damped
oscillation about the saturation value, which is not predicted by simple scaling theory.
The first minimum is for $R \sim 100$ nm.
Figure 3.5 Height correlation functions as a function of plasma etching time for 30 % porosity NPS.
Figure 3.6 (a) Height-Height correlation function vs. lateral distance (open circles) for an unpatterned 15% NPS sample after etching 43 s in C₄F₈/90%Ar, calculated from a 2 μm field of view AFM image, and fit to form from reference [3.16] for self-affine structure (solid curve). Insert: AFM image of the same surface (0.75 μm field of view). (b) Asymptotic values of roughness exponent α (filled circle), RMS roughness vs. time exponent β (closed vertical diamonds), correlation length vs. time exponent 1/z (filled square) and ratio of β/α (open square) vs. porosity. Dashed line shows value of 1 predicted by flux re-emission model [3.14] for all exponents.

From fits like that shown in Fig. 3.6 (a) we have determined the apparent value of the roughness exponent α. Aside from some scatter α is approximately equal to 1, independent of porosity, as shown by the filled circle in Fig. 3.6 (b). This corresponds to the maximum value predicted by self-affine theory, and to a very rough surface [3.15]. Interestingly, Monte Carlo simulations based on the recently proposed “flux reemission model” [3.14] for the evolution of a generic surface during reactive ion etching, predict a value of α ~ 1, in agreement with our observations. This is a non-local model, in which a radical or ion which is incident upon a surface either reacts with the surface, etching it, or
is re-emitted, possibly interacting with the surface multiple times, leading to the following height equation:

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h - k \nabla^4 h - \sqrt{1 + (\nabla h)^2} \left( S_0 F_0(\vec{r}, t) + S_1 F_1(\vec{r}, t) + \ldots \right) + \eta$$  

(3-3)

Here the first term corresponds to evaporation and condensation induced smoothing \((n>0)\), the second term to surface diffusion, the third, nonlinear term to etching, and the last term to stochastic noise \([3.14]\). The Monte Carlo simulations further predicted that both the RMS vs. time exponent \(\beta\) and the correlation length vs. time exponent \(1/z\) should also be approximately equal to 1 \([3.14]\). This prediction however is in pronounced disagreement with our results: the apparent asymptotic values that we extract for both these exponents decrease with increasing porosity, with values dropping to well below 1 for the most porous samples. Furthermore, as seen by comparing the measured values of \(1/z\) (filled square) with the measured ratios of \(\beta/\alpha\) (open square) in Fig. 3.6 (b) we find that the more general prediction for self affine structures, that \(\beta/\alpha = 1/z\), is not
reproduced over the range of etching times that we have studied. It may be that our measurements reflect the *transient*, rather than steady state behavior. For our films, it is not possible to extend the etching experiments substantially; by 64 s we have etched more than half way through the 400 nm thick NPS film for the highest porosity. Further, it is likely to be the transient response which is of most interest in device fabrication using NPS.

In summary, our results show that the time-evolution of the roughness of NPS during plasma etching for etch depths of up to a few hundred nm is not well explained either by the flux reemission model [3.14] or more generally by models which assume self-affine behavior [3.15].

We now turn to the question of spontaneous pattern formation during plasma etching of NPS, which was suggested both by the TEM images in ref. [3.4] and by the damped oscillation in the height-correlation function in Fig. 3.6 (a). The figure 3.7 shows the AFM image vs. TEM cross-sectional image from the blanket 30 % porosity NPS surfaces after etching. A TEM image of an etched NPS indicates a preferred wavelength as about 100 nm. However, the cross sectional TEM images in ref. [3.4] did not allow for full 2 + 1 dimensional mapping of the topography of the etched surface, and with an AFM image it is hard to determine the preferred wavelength. Also, it is not possible based upon them whether in fact wavelength selection takes place.
Figure 3.7 Evidence for wavelength selection during $C_4F_8/90\%Ar$ plasma etching of NPS (30 % porosity): (a) AFM image of a blank surface after etching for ~ 47 sec., and (b) TEM cross-sectional images after etching from Ref. [3.4].

To investigate this intriguing possibility, we have used a combination of lithographic patterning and atomic force microscopy imaging to examine the evolution of the NPS surfaces during $C_4F_8/90\%Ar$ plasma etching, as a function of lateral length scale. For this we adopt the technique of pre-patterning to introduce perturbations at a series of well defined wavelengths [2.3, 2.4]. This approach is particularly well suited to probing the tendency of moving interfaces toward pattern formation, a phenomenon which has been reported during both plasma etching of Si(001) [3.17] and in ion sputtering of semiconductor [3.18] and insulator surfaces [3.19]. We pattern the NPS surfaces using electron beam lithography followed by etching in ICP chamber, creating arrays of square pits on the surface whose width and spacing we vary from cell to cell, but maintaining a
fixed width/spacing ratio of 1:2 and an initial depth of ~ 33 nm as described in Fig. A.1. Some of AFM images of a patterned area, subsequent to removal of the resist are shown in figure 3.8. These are 30 % porosity surfaces, containing 140 nm wide pits, spaced at 280 nm center to center; due to proximity effects this was the smallest pattern we successfully produced. We also include the AFM images from 280 nm width – 560 nm center to center spacing and from 400 nm width – 800 nm center to center spacing. In Fig. 3.8 we summarize the patterned surface evolution after additional etch durations of 32 s, 64 s, and 96 s in vertical direction for each patterned surfaces. The induced roughness visibly increases with time. For 140/280 nm pits after 96 sec. we noticed AFM tip effects, so the image is excluded in the summary.
Figure 3.8 AFM summary of e-beam patterned NPS (30% porosity) surfaces. We pattern the surface with the arrays of square pits with varying in size by maintaining a fixed width/spacing ratio of 1:2. And then we etched the “pre-patterned” surfaces at various time periods.

In figure 3.9 we show the evolution of height profiles measured across a row of pits for the same series of etching times for the various pit sizes. An advantage of this patterning-based approach is that it allows us to return to the same part of the surface after each etch step, and thus follow the evolution of individual structures. As seen in the profiles, etching produces profound changes in the topography. For the smallest structure,
140 nm wide x 280 nm spacing (Fig 3.9 (a)), deep trenches form at the edges of the pits by 32 s. The dominant effect for increased etching time is an inward motion of the sidewalls which coalesce to single downward pointing cusps by an etching time of 64 s. Figs. 3.9 (b), and (c) show sequences of profiles for larger patterns: 200 nm width x 400 nm spacing, and 560 nm width x 1120 nm spacing. For the largest period structure, trenches again form initially at the sidewalls; in this case additional etching produces a different mode of evolution, with downward pointing spikes forming between pits and nearly obscuring the initial pattern by 64 s. For the 400 nm period structure, the mode of evolution of the structure is evidently intermediate between the two extreme cases, and results in persistence of the amplitude. This can be seen even more clearly in figure 3.10, where we plot the amplitude of the fundamental Fourier component as a function of the pattern period, for the initial surface and three additional etch steps. The initial patterning produces some variation with period, with an ~ 30 % increase in the amplitude of the shortest period structure. Subsequently, for the smallest period structure amplitude falls off approximately linearly, to approximately 2/3 of its initial value by an etch time of 64 s. For the longest period structure the decay is more abrupt, saturating at a value approximately 20 % of the initial amplitude by 32 s. In striking contrast is the behavior for the 400 nm period structure: the amplitude remains constant up to the longest etch time studied.
Figure 3.9 Evolution of height profiles vs. etching time: pattern sizes for (a) 140 nm width x 280 nm spacing, (b) 200 nm width x 400 nm spacing, and (c) 560 nm width x 1120 nm spacing from the 30 % porosity NPS. In both the smallest and the largest pattern periods, the formation of micro-trenches at the side walls of pit bottoms is dominant at initial stage of etching.
Figure 3.10 Summary plot of the amplitude of fundamental Fourier component as a function of pattern period. This shows an existence of a persistent length scale at ~400 nm period during Fluorocarbon plasma etching of NPS (30% porosity), where the pattern amplitude persists regardless of etching duration we studied.
3.4 Discussion

A question which arises concerns the value of this persistent wavelength; it is approximately 4 times that of the first minimum in the height-height correlation function shown in Fig. 3.6 (a). An interesting possibility is that there is a series of (meta)stable wavelengths, and that period doubling can occur. We in fact see some evidence for this, as illustrated in figure 3.11 (b) ~ 3.11 (d). These are gray scale representations of a second height correlation function, defined as

\[ g(\vec{R}) = \langle h(\vec{r} + \vec{R}) \cdot h(\vec{r}) \rangle - \langle h \rangle^2 \]  

(3-4)

Where \( h(\vec{r}) \) is the local surface height and \( \langle \cdot \rangle \) represents the ensemble average over \( \vec{r} \).

They are for the 400 nm period-patterned NPS region, i.e. that which shows a persistent amplitude. We also add an unpatterned NPS surface for the comparison. The periodicity in the square array of spots seen in Fig. 3.11 (b) reflects that of the initial pattern. In an unpatterned sample (Fig. 3.11 (a)), however, there is no such periodicity instead only one maxima peak is shown up. After certain amounts of etching the correlation map looks quite different. A striking change occurs after 32 sec of etching (Fig. 3.11 (c)): a second set of spots has appeared between those for the patterned surface. This second periodicity is induced by the etching; further etching (64 s, Fig. 3.11 (d)) shows that this second periodicity is persistent as well.
Figure 3.11 The mapped images of cross term in height correlation function \( g \) for the as patterned and etched surfaces for the pits with 200 nm width x 400 nm spacing. (a) An unpatterned NPS surface is included for the comparison. (b) Starting surface, (c) 32 s etched surface, and (d) 64 s etched surface. The starting surface shows the nice square periodicity, set by initial patterning. In an unpatterned sample, however, there is no such periodicity instead only one maxima peak is shown up. After 32 s etching the additional maxima appeared, indicating that there are series of stable wavelengths. Further etching, 64 s also similarly shows the second periodicity, possibly something-like period doubling is going on.

Pattern formation generally requires the competition of at least two effects, one of which destabilizes the interface and the second of which smoothes it out over short distances [1.1]. The profiles shown in Fig. 3.9 suggest that such a competition exists during the plasma etching of NPS. We now consider what these effects might be. It has been suggested [3.14] that smoothing during reactive ion etching could be mediated by

\[
g(\vec{R}) = \langle h(\vec{r}) \cdot h(\vec{R}) \rangle - \langle h \rangle^2
\]

Cross term in \( G \):
evaporation-condensation, surface diffusion or a combination of the two. In the related case of room temperature sputtering of amorphous surfaces it is thought that viscous flow might be promoted by ion impact [3.20]. We expect that a combination of these effects might be important in the evolution of the shortest period structures seen here. The etching induced roughening which destabilizes the interface is likely to be more complex than for the ion sputtering case, as evidenced by the qualitatively different topography which evolves. The linear height equation suggested for the latter case [1.1, 3.20] cannot explain the downward pointing cusps, which indicate a breaking in the up-down symmetry [3.21] of the system, and require a nonlinear term like that included in the flux re-emission model [3.14]. The lack of agreement between our observations and the predicted time dependence in that model, and most importantly the dramatic proliferation of spikes in the AFM profiles suggest that the nanopores play an important role. An intriguing possibility is that the pores might act as nucleation sites for the formation of nanotrenches which percolate through the matrix, and then spread outward, with the shape of the trenches setting a preferred spacing. Numerical simulations of the etching of NPS are needed to see if such an effect indeed explains the observed profound roughening of this technologically important material during plasma etching.

3.5 Conclusions – Pattern Formation

Finally we consider the difference between the persistent pattern length of 400 nm seen in Fig. 3.10, and the value of ~ 100 nm suggested by the dip in the height-height correlation function. One possibility is that there are more than two competing effects, as
discussed above, resulting in more than one maximum in the evolution rate with size. A second interesting possibility is that multiples of a stable period show transient stability, and that further etching might result in multiple period doubling. Further investigations to distinguish between these possibilities are in progress.

3.6 Evolution of roughness during annealing of plasma etched NPS

Above we have shown that the surface of nanoporous silica roughens strongly, and monotonically with plasma etching. This conclusion poses challenges to the possible application of this material into nanoscale electronics. It would be desirable to find a way to cure the roughness created by the plasma etching. In this section we describe our investigations of the possibility of relaxing the roughness on NPS surfaces induced by plasma etching by subsequent annealing.

For these experiments we worked with NPS samples with the porosity of ~ 36 %, whose starting thickness is approximately 230 nm, deposited by spin casting on Si(100) wafer. We also perform similar annealing experiments on e− beam patterned NPS (36 % porosity).

Both unpatterned and patterned samples were prepared using Ar+ sputtering in a reactive ion etching (RIE) chamber to roughen the surface for annealing. Then annealing experiments were conducted in both an UHV (ultra high vacuum) chamber and in a rapid thermal annealing (RTA) oven in air. The annealing processes in both environments are schematically shown in figure 3.12.
We investigated the effect of annealing at temperatures ranging from \( \sim 300 \, ^\circ C \) to \( \sim 900 \, ^\circ C \), and annealing times ranging from minutes to tens of minutes. Temperatures were measured using a calibrated thermocouple below 500 \( ^\circ C \) and by IR Pyrometer above 500 \( ^\circ C \). After each annealing step we measured the topography of the resulting surfaces with AFM.

Figure 3.12 The schematic descriptions of annealing processes performed on NPS (36 \% porosity) samples. (a) The vacuum chamber is pumped down to approximately \( 2 \times 10^{-8} \) torr. The sample is then heated with a tungsten filament in conjunction with electron bombardment; (b) The sample is heated on a Silicon wafer while forming gases (H\(_2\) and N\(_2\)) are introduced into the oven in order to prevent oxidation during heating. The temperature is controlled by a thermocouple fixed to the base of the wafer and an infrared pyrometer.
We summarize some of representative AFM images of as Ar\(^+\) sputtered and annealed surfaces in both UHV chamber and RTA oven in figure 3.13. We divide AFM images depending on their annealing temperatures, so that we summarize relatively lower temperature (300 ~ 700 °C) in Fig. 3.13 (a) and relatively higher temperature (800 ~ 900 °C) in Fig. 3.13 (b). During low temperature annealing there is little to no change in RMS roughness or surface morphology. While the high temperature annealing, the two annealing processes appear to similarly modify the NPS surface under corresponding conditions.
**Figure 3.13** Summary of AFM scanning on the 36 % porosity NPS surfaces after as Ar$^+$ sputtered and after annealing treatments in either UHV chamber or RTA oven in air. The inserted captions indicate the sputtering time in RIE and the annealing time and temperature in either environment. (a) No or very little changes in surface morphologies during low temperature annealing processes, here $\omega =$ RMS roughness; (b) similar surface morphology changes during high temperature annealing processes: 800 °C vs. 900 °C.
To confirm this observation, the height-height correlation functions were calculated from our images to statistically characterize other parameters which might indicate a change in the surface. In figure 3.14 we show some examples of measured height-height correlation functions from the surfaces before and after annealing at 700 °C in RTA oven and at 800 °C in UHV chamber. We extracted roughness parameters including such as $\omega$, $\xi$, and $\alpha$ from the correlation plots; an example is shown in Fig. 3.14. These are summarized as a function of annealing time in figure 3.15. From the figures 3.14 and 3.15 we see that the RMS roughness ($\omega$) and correlation length, $\xi$, decrease, while the roughness exponent, $\alpha$, remains about the same. We also perform the numerical simulations on the high temperature annealed surfaces as shown in Fig. 3.15 as gray and black dotted / solid lines. We compare our results with the predictions of the quasi-phenomenological Edward-Wilkinson continuum equation (Equation (3-5)), which has a diffusion-like form, but is identified with smoothing due to sublimation and recondensation [3.22]:

$$\frac{\partial h}{\partial t} = V + \nu \nabla^2 h + \eta$$  \hspace{1cm} (3-5)$$

where $\nu$ is the surface tension term, $\eta$ is the space- and time-dependent stochastic noise, and $V$ is the constant average velocity of the propagating surface. Numerical simulations using the Edward-Wilkinson equation for sublimation, and that for surface diffusion predict reduction in the RMS roughness, however the simulations predict an increase in the correlation length and roughness exponent which are not consistent with the experimental results.
Figure 3.14 Examples of height-height correlation functions for the NPS samples (36 % porosity) annealed in RTA oven and in UHV chamber. The annealing temperatures and durations are noted in the plots. (a) annealed in RTA oven at 700 °C up to 25 min., and (b) annealed in UHV chamber at 800 °C up to 30 min.
Figure 3.15 Summary of height-height correlation function analysis of annealed NPS samples after Ar$^+$ sputtering. The scaling exponents are summarized as a function of annealing times and annealing temperatures, especially the results at high temperatures are compared with EW theory and we find out the reduction in RMS roughness may be due to sublimation.
We also carry annealing experiments on e− beam patterned NPS sample with the same porosity of 36% for comparison with blank ones. Patterned samples allow for the characterization of identical areas on one sample. This e− beam patterned sample is annealed with RTA at 900 °C for two consecutive runs of 5 minutes each as summarized in figure 3.16. The major changes seen here is the reduction in pit depth and the changing morphology at the pit edge. These changes may be again due to sublimation of the NPS surface during annealing.

In summary, our experimental results show that a simple annealing procedure is of limited effectiveness in relaxing etching induced roughness on NPS. Our results show however that the morphology of NPS is a very stable material at high temperatures, which may prove useful in high temperature applications.
Figure 3.16 RTA annealed patterned NPS sample: (a) AFM images of areas with 570 nm and 410 nm width square pits after annealing at 900 °C for 10 min. (b) line profiles of 570 nm and 410 nm width square pits. As annealing time increases, the pit depth decreases in both pattern sizes.
3.7 Summary

Here we summarize the important results and conclusions of this part of thesis.

Firstly, we observe the NPS roughens monotonically with time and porosity during plasma etching. And the scaling theory does not describe the etched NPS surfaces well at least over the time range we investigated.

Our patterning and etching experiments reveal the evidence of a persistent wavelength at $\sim 400 \text{ nm}$. It is not so clear what mechanism is involved for this. One possibility could be the preferred periodicity set by nanotrenches, nucleate at pores during plasma etching and have a preferred spacing.

A most interesting result is an indication of period doubling even at persistent wavelength (400 nm). In order to clarify this issue, we need to investigate the smaller periodicities.

Annealing in vacuum and in non-oxidizing environment produces similar changes in the surface morphology of NPS during annealing. Low temperature annealing ($300 \text{ }^\circ \text{C} \sim 700 \text{ }^\circ \text{C}$) shows no obvious signs of curing the surface roughness caused by plasma etching processes, while high temperature annealing ($800 \text{ }^\circ \text{C} \sim 900 \text{ }^\circ \text{C}$) does reduce the surface roughness of the NPS surface, potentially due to sublimation of the material.
Chapter 4 Nanotechnological Manufacturing: Nanostructured Polymers Designed for Plasma/Energetic Beam Templating of Materials

The third major part of this thesis concerns the morphological stability of the surface of model resists during plasma etching. Here we describe our preliminary results, investigating the morphological and chemical evolution of unpatterned resist surfaces. I also present as an appendix our first attempts at creating patterns on the surface of one of these films, polystyrene, use AFM-based nanolithography; this process will serve as an enabler for further investigations of the length scale dependence of morphological evolution of resist during both etching and annealing, in analogy to the work I presented in Chapters 2 and 3.

4.1 Morphological and chemical evolution of model polymers during plasma etching

4.1.1 Introduction

Controlled patterning of materials at the nanometer scale will be one of the fundamentals of future nanotechnological manufacturing. The current demand for making devices with decreasing dimensions drives the development of photolithography with shorter wavelength light sources, novel techniques such as nanostamping, and new photoresist materials. One of the least understood elements for nanoscale patterning is the interaction of the plasma species and the organic molecules during pattern transfer. In particular, it would be desirable to understand the chemical, morphological and
topographic changes induced by these interactions in the macromolecules themselves and macromolecule-defined nanoscale features.

A crucial consideration in the development of resists of next-generation lithography is the stability of the resist-plasma interface during plasma etching. Roughening of the interface leads to line edge roughness, which ultimately will limit the minimum feature size achievable. In this work we seek to understand the relationship between the rate at which model resists roughen during etching and their chemical structure. In addition, we explore how roughening relates to the tendency of a resist to undergo cross-linking vs. chain-scission in the presence of ionizing radiation.

4.1.2 Experiment

We investigate the evolution of the surface roughness and of chemical composition of five prototypical model resists. This is a collaborative investigation, with synthesis carried out by Professor C. Grant Willson’s group at University of Texas, inductively coupled plasma (ICP) etching done in a special homebuilt and well-characterized reactor by Professor Gottlieb Oehrlein’s group at University of Maryland [4.1], Ar ion bombardment studies carried out by Professor David Graves’ group at the University of California at Berkeley, and characterization carried out by our group. In figure 4.1 we show the chemical structures of the five model polymers we study: polystyrene (PS), Poly(4-Methyl Styrene) (P4MS), poly(α-Methyl Styrene) (PαMS), poly(3-hydroxy-1-adamantyl methacrylate) (HAMA), and poly(3-hydroxy-1-adamantyl acrylate) (HAdA). Parallel studies of the effect of pure ion sputtering are carried out using a high vacuum system and employing a noble gas beam to sputter the films over a
range of incident angles. We characterize the topography, density and composition of the surfaces of these resists using a combination of atomic force microscopy (AFM), ellipsometry, x-ray photoelectron spectroscopy (XPS) and infrared fourier transform microscopy (IRFTM) is done before and after etching.

In our first investigations we have studied plasma etching of two groups of resists: aromatic ring (polystyrene)-based and adamantine-based polymers, which are model structures for photolithography using light at a wavelength of 248 nm and 193 nm, respectively. Each group has the nearly same Ohnishi parameter [4.2], which is a common measure of the resistance of the polymers during plasma etching, defined below.

\[
\text{Ohnishi Parameter (OP)} = \frac{N}{N_C - N_O} \propto \text{Etch Rate}
\]

, where \(N\) = total \# of atoms in a monomer unit, \(N_C\) = total \# of carbon atoms in a monomer unit, and \(N_O\) = total \# of oxygen atoms in a monomer unit.

Figs. 4.1 (a) - 4.1 (c) show the chemical structure of polystyrene and its derivates; their monomeric structure consists of a simple aliphatic chain (i.e. carbon-carbon backbone) and an aromatic ring. The main difference among the three variants shown is the presence or absence of a methyl group (CH\(_3\))- and its position relative to the aromatic ring. We chose these variants, as it is known that the addition/positioning of the CH\(_3\) group to the aliphatic chain can be used to change the tendency of polymer upon exposure to ultraviolet radiation from cross-linking (which is the case for the PS and P4MS) to chain-scission (for P\(\alpha\)MS).
Figs. 4.1 (d) and 4.1 (e) on the other hand show the chemical structure of HAMA and HAdA. Once again in this case the addition of the CH$_3$ group changes the response of the polymer to UV radiation, from cross-linking for HAdA to chain-scission for HAMA.

Polymers with similar structure have the nearly same values of Ohnishi parameter, and based upon a simple phenomenological model, they should have similar resistance to plasma etching. A crucial, but unresolved question involves how the rate of roughening during etching depends on the structure of the polymer, and whether the Ohnishi parameter is useful in this regard. A related question involves the effect of the methyl group on the tendency to roughen.
Figure 4.1 Schematic of chemical structures of 248 nm wavelength model polymers (a) – (c), and 193 nm wavelength model polymers (d) and (e). Here $M_n$ = molecular weight, DP = degree of polymerization, and OP = Ohnishi Parameter.
Our model polymers are spun onto a Si substrate with an average starting thickness of ~ 400 nm, and then plasma etched with various gas combinations in an ICP reactor. Most of our results are for either C₄F₈/90% Ar or pure Ar. For both plasma gas chemistries we set the gas flow rate at 50 sccm, the operating pressure at 10 mTorr, and the self-bias voltage at -100 V. For C₄F₈/90% Ar plasma, we use a RF source power 800 W. For pure Ar ion sputtering instead we use a source power 400 W in order to maintain the etching rate below 100 nm/ min.

Figure 4.2 shows the schematic of the ICP chamber used in our experiments. The etching time normally ranged between 0 ~ 60 seconds. In some cases we etched the surface uniformly for a given time, while in others we used a moving Si shutter to vary the etching time across the surface of a resist film [3.12]; This latter approach allows for ease of following the evolution of the film vs. etching time under controlled conditions. In this shutter approach, we gradually expose part of the sample along its long side as shown in figure 4.3.
Figure 4.2 Cross-sectional view of schematic of the inductively coupled plasma chamber used in this work.

Figure 4.3 Plasma etching using a moving shutter.
4.1.3 Results

The etched model polymers were characterized with tapping mode AFM to follow their morphological evolution. In figure 4.4 we show example results of the surface evolution of model polymers under C\textsubscript{4}F\textsubscript{8}/90\%Ar plasma etching. Comparing the etching rates (in nm/min.), the Ohnishi model seems to hold more or less for the polymers with similar structures. An exception is that while P4MS and P\alpha MS have the same chemical composition and Ohnishi Parameters, they show quite different etching rates. The strong effect of the chemical structure on its response to the plasma can be also seen in the AFM images in Fig. 4.4. While all of the surfaces get rougher with increasing etching time, however, when the methyl group is positioned at the aliphatic chain (i.e. for the cases of P\alpha MS and HAMA), the surface roughens significantly faster.
Figure 4.4 Representative AFM images of five prototypical resists after gradient etched with C₄F₈/90% Ar. The data scale is between 0 and 20 nm for all the images, for ease of comparison. The polymers with a methyl group on the aliphatic chain show the significant roughening rates than others in the same group.
This is confirmed by our quantitative analysis of the AFM images. We show the RMS roughness as a function of etching time in Fig. 4.5 and 4.6. In the summary plots, we show that for both PαMS and HAMA, the addition of a CH$_3$ group to the α position of the aliphatic chain results in a significant increase in the rate of roughening during etching as compared to the other polymers.
Figure 4.5 RMS roughness vs. thickness removed for 248 nm wavelength model polymers after plasma etching with C₄F₈/90%Ar. PαMS shows much higher RMS roughness than PS and P4MS within the same etch duration, 0 ~ 60 s.

Figure 4.6 RMS roughness vs. thickness removed for 193 nm wavelength model polymers after plasma etching with C₄F₈/90%Ar. HAMA shows much higher RMS roughness than HAdA within the same etch duration, 0 ~ 60 s.
This trend, of increased roughening for a structure including a methyl group at the α position, also holds during pure Ar etching, although the absolute surface roughnesses are smaller for a given amount of etching (See Fig. 4.7 and 4.8). This is perhaps surprising: it is frequently observed that ion bombardment of surfaces results in material in a rough or “rippled” surface. Interestingly, we observe that increasing the ion fraction of the etching gas for these model polymers results in smoother surfaces.
Figure 4.7 RMS roughness vs. thickness removed for 248 nm wavelength model polymers after pure Ar ion bombardment.

Figure 4.8 RMS roughness vs. thickness removed for 193 nm wavelength model polymers after pure Ar ion bombardment.
A complicating issue in plasma etching involves the effect of trace contaminants. In particular, ion discharges tend to sputter material from remote regions of the reaction chamber. Our XPS analysis for early studies revealed Al and O$_2$ contamination, presumably from inadvertent ion bombardment of the Al anode and quartz coupling window. In subsequent experiments we essentially eliminate these contaminants by covering the electrode and quartz window with a Si wafer and Kapton tape, respectively. We find that this reduces the contamination levels to beneath what is detectable in XPS. This also allows us to test the sensibility of both the etching, and roughening rates to the presence of these elements (See Appendix D for C$_4$F$_8$/90%Ar etching case). As shown in a summary plot in figure 4.9, the roughness trend is qualitatively reproducible, i.e. P$_2$MS shows higher roughening rate than PS and P$_4$MS, and HAMA shows higher roughening rate than HAdA. But the overall roughening rates for 248 nm wavelength model polymers are lower than the values shown in Fig. 4.7. We caution that this latter result might be caused by other factors, as the investigation carried out here was not systematic. The 248 nm wavelength model polymers shown in Fig. 4.7 were etched on a different day than the 193 nm wavelength model polymers shown in Fig. 4.8, and we cannot completely exclude other trace contaminants which might have been present during one of these experiments. However, the later results summarized in Fig. 4.9 are based on etching experiments performed on the same day. We conclude that the qualitative difference, of the effect of the presence or absence of an $\alpha$ methyl group on rate of roughening is robust in the presence of at least trace Al and O impurities.
Figure 4.9 Semi-log plot of RMS roughness vs. etching time for both 248 and 193 nm wavelength model polymers after pure Ar ion bombardment. The overall roughening trend is repeatable.

Our preliminary results clearly show that the chemical structures of the polymers strongly affect their performance as resists. In particular, the position of the CH$_3$ group clearly affects the rate at which the surface roughens under plasma etching.

Besides the morphological evolution of the polymer surfaces, we have investigated the evolution of the chemical composition of our model polymers during plasma etching using the ATR (Attenuated total internal reflection) mode FTIR spectroscopy. ATR-IR spectroscopy allows identifying chemical elements and chemical structures by using an attenuated total internal reflection, which penetrates through the
thin film in a range of a few microns. The chemical bonds can be vibrated as a result of
infrared absorption, and different elements compose the chemical bonds are assigned to
unique wave-numbers.

Our preliminary ATR-IR spectroscopic observations on model polymers etched
with $\text{C}_4\text{F}_8/90\%\text{Ar}$ show the decreased CH bond concentration in all 248 nm model
polymers. This is also observed in $\text{Ar}^+$ sputtered model polymers. This result is consistent
with ellipsometry and XPS measurements, and molecular dynamics (MD) simulation
(MD simulation was done by professor Graves’s group at University of California,
Berkeley) as shown in figure 4.10. In our IR spectroscopy analysis, we have monitored
the intensity of C-H peaks as a function of etching time. In addition to the common peaks
from the aromatic ring and the linear backbone chain, there peaks from the methyl group
are also present in the spectra obtained from P4MS and PαMS. We can also see decrease
in C-H peak heights both at linear chain and pendant of PS-based polymers from XPS
analysis (Fig. 4.10 (b)), and increase in index of refraction at the early stage of plasma
etching (indicated by blue dotted line in Fig. 4.10 (c)) from ellipsometry measurements
for all three materials. In Fig. 4.10 (d) we observed significant decrease of hydrogen near
PS surface from the depth profile as a result of more than thousand Ar ion impacts with
100 eV. Near surface region of a simulated image after Ar ion bombardment also showed
very dense graphite-like layers. Here we can draw one common conclusion: the plasma /
ion beam exposures result in hydrogen loss and material densification possibly due to
cross-linking of polymers, graphitization, etc. Further investigation is needed to correlate
the chemical evolution to the different morphological evolution in chain-scission from
cross-link polymers.
C-H Aromatic out-of-plane bending

PS
CH
2
C ( )
H
Crosslink

CH stretching vibration bands

(a)

(b)

(c)

XPS Intensity (a.u.)

0 10 20 30

F2s
O2s
C2s
σ (pendant C-H), C2s
σ (chain C-H), C2s
σ (pendant C-H, C-C)
σ (pendant C-H)
π orbitals
π orbitals

Binding Energy (eV)

0 10 20 30 40 50 60

0.000
0.005
0.010
0.015
0.020
0.025
0.030

0 10 20 30 40 50 60

0.000
0.005
0.010
0.015
0.020
0.025
0.030

800W, -100V

Etching Time (sec)

Index Change

800W, -100V

Etching
**Figure 4.10** Chemical compositional analysis / simulation results for 248 nm model resists: (a) IR spectra from PS as a function of etching time, (b) X-ray photoelectron spectroscopy (XPS) spectra, (c) Single wavelength ellipsometry ($\lambda = 632.8$ nm) measurements before and after $C_4F_8/90\%$Ar plasma etching, respectively, and (d) Molecular dynamics simulation: cross-sectional view of $Ar^+$ bombardment on PS with given conditions.
Figure 4.11 shows FTIR spectra for HAMA before and after C₄F₈/90%Ar plasma etching as a function of etching time. We recognize in these spectra peaks from the C-H stretching from both the C-C backbone and the adamantane structure. The other feature that is as easily recognizable is the CO single bond and CO double bond stretching. Here we monitor those peak heights as a function of etching time for both HAMA and HAdA. And then we normalize the peak heights with the initial values before etching. The summary plots are shown in figure 4.12. Both plots in Fig. 4.12 we compare the CO intensities to that of the C-H stretching from CH₂ bonds. The main difference between HAMA and HAdA, based on these two plots, seems to be that for HAdA the signal from both the CO double bond and CO single bond seem to higher compare to the signal from the CH stretching with etching time. It may imply that the C-O and C=O bonds were etched less than the C-H bonds. And for HAMA, the C=O bond signal evolves almost the way the CH signal does (Fig. 4.12 (b)), and the C-O bond seems to decay slightly faster at the beginning of etching than that of C=O bond. Lastly, there are no differences in the rate of decreasing between CH stretching from symmetric and asymmetric CH₂ vibrations. Still remaining to be done is to tie these differences to what we observed from the roughness evolution of these two polymers.
Figure 4.11 FTIR spectra from 193 nm wavelength model resist, HAMA before and after C₄F₈/90%Ar plasma etching as a function of etching time. For C-H bond stretching vibrations are caused both from the adamantane structure and the linear backbone chain. CO single bond and CO double bond are also shown clearly.
Figure 4.12 chemical compositional evolutions with etching time on 193 nm model resists after C₄F₈/90%Ar plasma etching. Both plots show the normalized peak height vs. etching time for (a) C-H and C-O stretching, and (b) C-H and C=O stretching. ATR-IR spectra clearly show the decrease in CH and CO bonds.

4.1.4 Discussion

We analyze AFM images from etched model polymers using the height-height correlation function. In addition to providing information about the lateral length scale of roughness from surfaces, this statistical analysis allows us to compare the detailed evolution of the surface roughness with models based on simple scaling theories for kinetic roughening. The typical shape of the correlation function we obtain is shown in Fig. 4.13; this was from an AFM image obtained after fluorocarbon plasma etching of PmMS. It generally follows the shape predicted by theories for self-affine roughness:
there is a power law regime at smaller lateral distances, but it flattens out at larger
distance. As for the etched NPS surface presented in Ch. 3, we have fitted these
calculated height correlation functions to empirical formula suggested by Sinha et al.
[3.16] in order to extract the scaling exponents $\alpha$, $\beta$, and $1/z$. The value $\alpha$ is estimated to
be approximately 1 for all the samples after etching with both pure Ar and C$_4$F$_8$/90%Ar
discharges indicating surfaces are very rough (See Fig. 4.14).

Figure 4.13 Height correlation functions calculated from C$_4$F$_8$/90%Ar etched PαMS as a
function of etching time. As a reminder I included the definition of height correlation
function and scaling parameters, $\alpha$, $\omega$, and $\xi$. 

\[
G(r,t) \equiv \left[ h(\bar{r} + \bar{r}' , t) - h(\bar{r}' , t) \right]^2
\]

\[
G(r,t) \equiv 2[w(t)]^2 f\left( \frac{r}{\xi(t)} \right)
\]

\[
f\left( \frac{r}{\xi(t)} \right) = \left( \frac{r}{\xi(t)} \right)^{2\alpha}, \quad \frac{r}{\xi(t)} << 1, \quad \alpha \sim 1
\]

\[
f\left( \frac{r}{\xi(t)} \right) = 1, \quad \frac{r}{\xi(t)} >> 1
\]
Figure 4.14 Roughness exponent, $\alpha$, estimated by fitting the height correlation functions to Sinha’s equation. It approximately equals to 1 for all the samples we study in both gas chemistries.

As shown in Fig. 4.15 the “growth” exponent, $\beta$, is extracted from the power-law dependence of the RMS roughness with etching time ((a)). Similarly, the dynamic exponent, $1/z$, is extracted from the power-law dependence of the correlation length with etching time ((b)). Even though they both show power law dependences with time, they do not follow the prediction of the scaling theory, i.e. $1/z$ is not equal to $\beta/\alpha$. This lack of agreement is shown in Fig. 4.15 (c). The results imply that the simple scaling theory does not apply to the surface evolution we observed over the time we etched.
Figure 4.15 Estimated scaling exponents, $\beta$ and $1/z$. Both exponents along with alpha approximately equal to 1 from the Monte Carlo (MC) simulation based prediction [3.14]. We show one of representative examples of (a) $\ln \omega$ vs. $\ln t$, where the slope is beta, and (b) $\ln \xi$ vs. $\ln t$, where the slope is $1/z$. (c) comparison of calculated $1/z$ and $\beta/\alpha$ for 248 nm model resists. The self-affined surface is assumed that $1/z$ should equal to $\beta/\alpha$, however they are not same and are far away from the MC simulation predicted value 1 in our experimental results.
4.2 Summary

We have reported that during etching in C₄F₈/90%Ar the presence vs. absence of substitutional methyl groups and their position relative to the aromatic ring in polystyrene derivatives has a pronounced effect on the rate of roughening. In particular poly-α-styrene (PαMS) roughens fastest, un-substituted polystyrene (PS) at an intermediate rate, and poly(4-methylstylene) (P4MS) most slowly in 248 nm wavelength model resists. Similarly, poly(3-hydroxy-1-adamantyl methacrylate) (HAMA), where the methyl group is added to the backbone, shows the higher roughness than HAdA, which has no methyl group added to either the adamantane pendent or the backbone. Interestingly, the trends were similar in pure Ar⁺ sputtering: polymers with a methyl group added to the alpha position of the aromatic ring showed again higher RMS roughness than other polymers.

In addition to the morphological evolution of 5 model polymers, we have investigated chemical evolution of these materials during etching via ATR-IR spectroscopy, ellipsometry, XPS and molecular dynamics simulations. And we have found out that these materials become dense after energetic ion beam or plasma exposure and that could be graphitization, hydrogen loss and/or cross-linking of polymers.

For more quantitative analysis of roughened surfaces using both gas chemistries we have used height-correlation function analysis. Our analysis results turned out that these etched model polymers do not follow scaling behavior within the time scale we explored.
4.3 Appendix: Nanolithography on PS

4.3.1 Introduction

As we mentioned in section 4.1 the consideration of line edge roughness (LER) is significantly important in developing new resist materials, since it will directly affect the performance of devices by transferring the LER from the resist mask to the underlying active layer. Thus, we consider making nanometer scale patterns to extend our understanding from our studies in blank samples. As a starting point we have attempted to pattern polystyrene (PS) samples by using an AFM. We will discuss the detailed procedures in experimental part.

Similar to earlier two chapters here we seek to determine whether a characteristic length scale exists during heating, by prepatterning a polymer surface. This is inspired by the observation that etched unpatterned surfaces show a damped oscillation in height-height correlation function (see Fig. 4.13), which is not predicted in conventional correlation function. In these first attempts we perturb the nominally flat topography of a PS surface with well defined pattern periods using an AFM tip.

4.3.2 Experiment

Due to limited resolution in patterning down to ~ 140 nm using our e− beam lithography facility, we have considered to do AFM-based nanolithography. AFM-based nanopatterning has a distinct advantage over the STM because AFM as fabricating and imaging tool can be used for insulating as well as conducting materials.

In this preliminary study, we have designed and fabricated a sample mounting stage which allows heating and it is shown in figure 4.16. A homemade resistive heater is
sandwiched between the PS sample and an aluminum heat sink. The Al heat sink was
designed for insuring effective heating and cooling. Also four tantalum-tungsten (TaW)
spring tabs are used to hold the sample firmly. The overall height of the sample mounting
stage is 1.2 cm, the width of the stage is 4 cm x 4 cm, and the dimension of resistive
heater is ~ 2 cm x 2 cm. The heating is done by a DC power supply with maximum
voltage of 20 V and maximum current of 3 A. We measure the temperature by using a
thermocouple, which is mounted directly onto the sample surface. The temperature
accuracy based on our measurements is about 70±6 °C. However, center of the sample
surface should be hotter than the thermocouple reading because the thermocouple was
placed at the edge of the sample and there must be temperature gradient along the sample.
Figure 4.16 A picture of experimental set-up for nanometer patterning, imaging, and heating of samples using a DI AFM dimension 5000. An enlarged picture shows the details of sample mounting stage.
The nanolithography was done by a commercial AFM (digital instruments (DI) Dimension 5000) by adopting the NanoScript™ macro language. Lithography uses C++ program along with NanoScript™ macro Litho functions to manipulate the tip relative to the sample surface [4.3]. All the patterning was conducted at room temperature in the air, and regular Si tips with tip radius 10 nm, cantilever length 125 um, force constant 40 N/m, and resonant frequency 300 kHz were used for both patterning and imaging the surfaces in tapping mode. The lithography programs direct the microscope to inscribe or move items on the sample surface [4.3]. This function is designed for a closed loop XY scanner, and standard contact mode tips (Silicone Nitride tips) are recommended by manufacture, Veeco. However, we have performed our experiments using an open loop XY scanner, which causes significant piezo drift effects during patterning. After several trials we were able to successfully make arrays of diamond-shaped trench patterns. Figure 4.17 shows an AFM image of our first successful patterns where the field of view is 5 um x 5 um and the nominal size of the diamond is 1 um.

For more effective and practical patterning we have developed C++ complier for this purpose by using an industry standard complier supplied by Veeco, so that we can make arrays of patterns easily and quickly.
Figure 4.17 An AFM image of 2 x 2 diamond patterns drawn by a Si tip on PS surface. The scan size is 5 um x 5 um, and the nominal size of the patterns is 1um. Array of patterns are made by changing X & Y offset of the piezo tube scanner manually.

4.3.3 Results

Figs. 4.18 and 4.19 show patterns consisting of 4 x 4 arrays of roughly cylindrical nano-holes at the nominal sizes of 90 and 30, respectively created on PS. We have also created patterns consisting of arrays of holes of other diameters: 50, 70, 110, and 220 nm. Since the patterning is done by indenting the tip to the surface and scratching out defined area by moving the tip back and forth several times, it causes material piles up in both shoulders – not necessarily symmetric – of the nanohole. In our first attempts we set the center-to-center spacing between the holes by 3x larger than the nominal size of the hole, to reduce overlap of disturbance between neighboring pits. We have in addition investigated the optimal indentation depth of the tip. We recycle the sample for additional processes and collect accumulated information from same areas, so that we can observe
evolution of patterns qualitatively. A third important issue is the temperature during lithography; for the pattern shown in figure 4.18, the surface was heated to ~ 70 °C, beneath the glass temperature of ~ 95 °C for PS. Annealing of the surface may help to define better shape of the holes leading to sinusoidal periodic structures. We find indeed that annealing the surfaces at ~ 70 °C causes partial relaxation of the patterns. The changes during annealing are more dramatic at the smallest patterns we study, nominal size of 30 nm as shown in figure 4.19; this is expected based on diffusion mediated relaxation. In Fig. 4.19 we show both height profiles (Red circled areas) and 3D height images; as seen from the figure these shallower and smaller nanoholes relax to nearly smooth surface.
Figure 4.18 3D AFM images of a nanohole pattern, 90 nm nominal size on PS surface. The sequential heating at ~ 70 °C from 1 min. up to 5 min. shows the array of patterns relaxes. Vertical data scale of all the images is 100 nm. The large scale scratches at top right are a navigational aid.
**Figure 4.19** 3D AFM images of nanoholes, 30 nm nominal size on PS surface: As patterned vs. 1 min. annealed at ~ 70 °C. We also include the height profiles along with 3D height images. Both images show the dramatic relaxation of nanoholes. Vertical data scale of all the images is 25 nm.
We summarize our early attempts at AFM-based nanolithography on PS and annealing in figure 4.20. Results are for as patterned, after a first annealing step at ~70 °C for 1 min., subsequent annealing for 2 more minutes at same temperature and then a final anneal of 2 more minutes. After each anneal we shut off power for fastest cooling; all of the images were taken at room temperature. The 30 nm nominal size holes almost disappeared by 5 min. The 50 nm nominal size holes also were relaxed, but the patterns are still visible, while the larger holes seemed to show little or no change within 5 min. annealing except 110 nm holes. We are using the standard Si tip for tapping mode AFM, and its radius is less than 10 nm, so the nominal pattern size 110 nm should be made easily. Our result might be caused by a blunt tip, which may be adhered by more material – more adhesive force – due to its larger surface area than a sharp tip. Another possible explanation for this might be the combination of tip and surface defects such as scratches or impurities in the area we patterned.
Figure 4.20 AFM height images of nanometer scale patterns made by Si tips on PS surface. The top panel shows the as-patterned surface, and each column for each pattern shows the annealed structure at ~ 70 °C for a minute to 5 min. All the images were taken at room temperature after each anneal.
4.3.4 Discussion

For quantitative understanding of our AFM images shown in previous section we obtained line profiles of each pattern by drawing a line across the center of the holes. The measured line profiles as a function annealing time for each pattern is shown in Fig. 4.21. The nominal pattern size is shown bottom of each profile. The smallest hole, nominal size 30 nm, relaxes quickly within one minute annealing from the ripple like shape to much less corrugated surface. However, for the larger sizes 70, 90, and 220 nm we observe very little change in depth with annealing. This is summarized in figure 4.22. There the patterns with nominal sizes 30 and 50 nm show linear decrease in pit depth with annealing time, whereas the pit depths are persistent at the nominal sizes 70, 90, and 220 nm. Further investigations are required to quantify the relation between the characteristic relaxation time and spatial period.
Figure 4.21 Height profiles measured across the center of a row of pits on a patterned PS surface. The nominal pattern size is shown bottom of each profile, and the center to center spacing of each pattern is 3xx larger than pattern size. Different colored lines represent different annealing time, and the as-patterned profile means no annealing.
Figure 4.22 Measured pit depth of nanoholes made by AFM tips vs. nominal pit size. The patterns with nominal sizes 30 and 50 nm show linear decrease in pit depth with annealing time, whereas at the nominal sizes 70, 90, and 220 nm, the pit depths are persistent.
Chapter 5 General conclusions

In this chapter we summarize general conclusions from three major works presented in this thesis. We have studied 3 technologically important materials: Si, Nanoporous Silica (NPS), and Resist polymers. In each case, we explored the length scale dependence of the evolution of the surface during etching or annealing. Our general approach in this work has been comparing observations of apparent characteristic length scales on unpatterned surface with systematic observations on patterned surfaces across these scales. We find that the interpretation of the length scale dependence of the evolution of the surface is aided considerably by this approach. A general remark is that the observation of a characteristic length scale in each of these systems points to competition between at least two effects; in the annealing experiments these are different terms in the free energy of a stepped surface, while in the etching experiments the effects are kinetic, with one effect destabilizing the flat surface, and the second smoothing it at short length scales.

In chapter 2, we described that the length scale dependence on the evolution of cylindrical pit patterned vicinal Si(111) surfaces during high temperature annealing at ~1273 °C for varying amounts of time. The smaller pit structures consist of nearly straight step bunches within a short annealing, while the larger pit structures consist of nearly sinusoidal step bunches even longer annealing. In order to understand our observations quantitatively we considered two step kinetic effects which require modeling the motion of steps across the surface including both diffusion, which is driven by the effects of step
stiffness and step interactions, and sublimation. For the smaller pit structures diffusion driven by curvature governs the evolution, i.e. straighten out as soon as the annealing begins due to inward collapse of loop steps resulted in Gibbs-Thompson effect; whereas the repulsive step-step interaction effect governs the evolution of larger pit structures during high temperature annealing. And the larger pit structures are relaxed mainly by step annihilation of the steps with opposite signs in down-hill side. These observations of length scale dependence on the evolution agreed semi-quantitatively with the numerical simulations based on the mesoscopic step kinetics model. Finally, we note that the eventual relaxation to a uniform step train suggests that diffusion of atoms under the influence of a repulsive step-step interaction for steps of the same sense is important; sublimation alone cannot explain this effect. This same observation allows us to rule out a strong Ehrlich–Schwoebel barrier [1.2], which would result in step bunching during sublimation. Surprisingly, our observations show that even at a temperature of 1273 °C, where sublimation drives our patterned Si surfaces well out of equilibrium, the final configuration is consistent with what would be expected based upon relaxation to a minimum energy configuration.

In chapter 3, we investigated the roughness evolution of blanket NPS samples and the wavelength selection in nanometer scale patterned NPS samples both during ion-rich fluorocarbon plasma etching. We found that NPS roughens dramatically during plasma etching under ion rich conditions. And the scaling theory does not describe the etched NPS surfaces well at least over the time range we investigated probably we are at transient regime. In addition, we found the evidence from our patterning experiments of
wavelength selection at 400 nm, while our correlation function analysis and cross-sectional TEM image suggest a persistent wavelength at approximately 100 nm. Although the continuum model which has been applied to explain rippling during ion sputtering might be applicable here, it does not obviously include the effect of micro-trenching, which seems to be the dominant effect during plasma etching of NPS. An intriguing speculation is that the nanopores might actually nucleate micro-trenches. Most interestingly we found an indication of period doubling even at persistent wavelength (400 nm). In order to clarify this issue, we need to investigate the smaller periodicities. A further interesting speculation is that patterning the surface at a persistent wavelength might stabilize it against fluctuations at other length scales, in analogy with driven “chaotic” systems.

In chapter 4, we studied how the chemical structures of model resist polymers affect the surface evolution during C₄F₈/90%Ar plasma etching and Ar ion sputtering. We found that the polymers with the methyl group positioned on α position of the aliphatic chain roughen at much faster rate than the other cases under both gas chemistries. Our unpatterned polystyrene surfaces show some sign of a preferred modulation at ~ 70 nm; we anticipate that surfaces patterned at a wavelength near this might show persistence in topographical amplitude. We expect that this will have implications on line edge roughness, and the stability of patterned features during plasma etch based pattern transfer. It may well dictate an optimum length scale for such features. As a first attempt we have also patterned polystyrene surfaces with the arrays of holes,
which ranges from a few tens nanometers to a few hundreds nanometers, using nanoscraping method with an AFM.
Chapter 6 Future work

In this chapter we mention possible future work which would extend our current understanding regarding the three systems I described in earlier chapters.

Chapter 2 Length-scale dependence of the step bunch self-organization on patterned vicinal Si(111) surfaces

Firstly, we can test our insights as to what sets the lower- and upper limits of ranges of length scale dependence of the self-organization of step bunches on patterned vicinal Si(111). Two relatively easy experiments would involve varying the vicinal angle (θ) and pit depth (d). By increasing the vicinal angle of the surface, we expect the lower bounding limit to move to left in Fig. 2.18. While if we increase the pit depth, we expect the upper bounding limit to move to right in Fig. 2.18.

We could also perform same experiments on singular Si(111) wafers in order to understand the role of nominally straight steps during evolution. The permeability of adatoms might be possible on surface during annealing.

It would be of considerable interest to carry out annealing experiments over a range of different temperatures. This would allow us to probe the temperature dependence of the effective step stiffness and step interactions. A limitation is that if we anneal such a patterned vicinal surface much lower than 1200 °C, we expect to see high density of SiC pinning sites, which hinder the motion of steps, due to not sufficiently clean surface, while we if we anneal the surface at much higher temperature void island
growth will compete with step flow, so that the voids act as sink of adatoms and may change overall evolution we observed.

Chapter 3 Evolution of roughness and wavelength selection during fluorocarbon plasma etching of Nanoporous Silica

From our etched surface characterization using a cross term in height correlation function (G2) analysis clearly showed that we need to try smaller length scales for preferred wavelength selection during C₄F₈/90% Ar plasma etching. An alternating technique such as nanoscraping using an AFM, described in section 4.3 in chapter 4 allows us to test smaller pattern length scales on such surfaces.

Chapter 4 Nanotechnological Manufacturing: Nanostructured Polymers Designed for Plasma/Energetic Beam Templating of Materials

Even more so than surface roughness, line edge roughness significantly affects the possibility of dramatic decreases in critical dimensions we can achieve; furthermore the performance of microelectronic devices as the roughness value is comparable to the intrinsic roughness of polymer molecules. The nano-patterning techniques described in section 4.3 in chapter 4 should allow us to test the length scale dependence of line edge roughness, and the persistence of patterned features at the scale of 10’s of nm. We expect that the studies begun in this thesis will have considerable impact in the optimization of resist chemistries and etching parameters for extending critical length scales downward.
Appendix A

Sample cleaning procedures for Si (111) patterned samples:

1) Acetone jet (i.e. pressurized Acetone gun) cleaning → Acetone soak cleaning in an ultrasonic cleaner for ~ 30 min.

2) NMP (N-Methyl-2-Pyrrolidone = C₅H₉NO) solution soaking @ 80 °C for 30 min. → Rinse the samples with Acetone - Methanol - IPA - DI water

3) Asher (O₂ plasma, Pressure 5 Torr, RF power 500 W):
   (i) Conditioning. – STRIP recipe for 2 ~3 min. using a Si sacrificial piece
   (ii) Ashing – STRIP recipe for 1 ~ 6 min.

4) Acetone soak cleaning in the ultrasonic cleaner for 2 ~3 min. → Rinse the samples with DI water
Appendix B

Patterned NPS sample preparation procedure:

1. Spin casting (positive e− beam resist, 950 PMMA A4) on the sample at 5000 rpm, 60 seconds. → PMMA thickness is ~ 110 nm

2. Soft bake at 180 °C for 5 minutes

3. Deposit ~ 10 nm of Al layer using thermal evaporation

4. Perform e− beam lithography (SEM, JEOL Model 6500F)

5. Remove Al layer using OPD 4262 (Basic solution for positive resist development) for 1 minute → DI water rinse

6. Develop PMMA layer by MIBK/IPA (1:3 vol. ratio) for 20 seconds and then rinse the sample in IPA for ~ 20 seconds

7. Plasma cleaning to remove PMMA residues near the patterns: dandescum recipe – O₂ plasma for 15 seconds


9. Lift-off with NMP (1-methyl-2-pyrrolidinone, C₅H₉NO)
Appendix C

Nanometer size square pattern design details for electron beam lithography on NPS

Figure A.1 Optical microscopy image of patterns on NPS films after developing, and a detailed schematics of our design for e-beam lithography. For the smaller size pits in the rectangular box we varied the e-beam dose, so that we could selectively inspect the best patterns.

We vary both pit size and spacing between the pits. We attempted to produce a minimum square size of 50 nm as shown in figure A.1, however, the minimum pattern size we could produce was ~ 140 nm due to proximity effect.
Appendix D

Roughness evolution of model resist polymers during C₄F₈/90% Ar plasma etching:
Effect of trace Al contaminants

As we discussed in section 4.1.3 in chapter 4 we have tested the sensibility of both the etching, and roughening rates to the presence of Al contaminants during C₄F₈/90% Ar plasma etching (there is no significant evidence of quartz window erosion in this case as seen in pure Ar ion sputtering case.). Figure A.2 shows that the roughness trend is qualitatively reproducible in both groups of model polymers, i.e. PαMS shows higher roughening rate than PS and P4MS, and HAMA shows higher roughening rate than HAdA. And both 248 nm and 193 nm wavelength model polymers get roughen nearly the same range from about 0.4 nm up to about 7.4 nm in this case. Thus, the trace of Al contaminants during C₄F₈/90% Ar plasma etching on these model polymers does not hold significant effect in surface roughness evolution.
Figure A.2 Overall summary plots of RMS roughness vs. etching time for (a) 248 nm and (b) 193 nm wavelength model polymers after C₄F₈/90%Ar etching: presence vs. absence of Al contaminants.
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Chapter 2


Chapter 3


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Chapter 4
