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Non-Equilibrium Nanoscale Self-Organization

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Executive Summary

Self-organized one- and two-dimensional arrays of nanoscale surface features (“ripples” and “dots”) sometimes form spontaneously on initially flat surfaces eroded by a directed ion beam in a process called “sputter patterning”. Experiments on this sputter patterning process with focused and unfocused ion beams, combined with theoretical advances, have been responsible for a number of scientific advances. Particularly noteworthy are (i) the discovery of propagative, rather than dissipative, behavior under some ion erosion conditions, permitting a pattern to be fabricated at a large length scale and propagated over large distances while maintaining, or even sharpening, the sharpest features; (ii) the first demonstration of guided self-organization of sputter patterns, along with the observation that defect density is minimized when the spacing between boundaries is near an integer times the natural spatial period; and (iii) the discovery of metastability of smooth surfaces, which contradicts the nearly universally accepted linear stability theory that predicts that any surface is linearly unstable to sinusoidal perturbations of some wave vector.

1. Introduction

The ability to understand and control the properties of matter on nanometer length scales is a major thrust in materials chemistry and physics today. Mastery of fundamental science at this length scale will have profound implications for a wide variety of future discoveries and applications in the chemical and biological sciences as well as in materials science and condensed matter physics. In this program we studied the phenomenon of “sputter patterning” in nanoscale morphology evolution during ion irradiation and have begun to develop a conceptual framework for understanding it at the fundamental level.

Nanoscale surface morphologies spontaneously develop from uniform ion irradiation of an initially flat surface in a non-equilibrium self-organization process termed “sputter patterning”. Spontaneous self-organization processes such as this have no fundamental throughput limitations and have been used to create patterns with lateral feature sizes as small as 15 nm, and good short-range order [1] as shown in Fig. 1. As in most self-organization processes, the major challenge is the flexibility one has over the resulting pattern. A combination of “top-down” approaches for flexibility and “bottom-up” approaches for size and throughput is likely to be a successful strategy for mass production of functional nanoscale devices. The importance of the “bottom-up” approaches will be determined to a significant degree by the answer to the question, “how much control do we have over the morphology?” A great deal of fundamental work must be done before this question can be answered directly.

In a related phenomenon, ion irradiation permits morphology control on the single-digit nanometer level and is consequently termed “ion beam nano sculpting”. Solid state nanopores with diameters of molecular dimensions have been fabricated this manner [2], as discussed further in §1.3. The resulting intellectual property [3], the Aziz portion of which was supported by a past DOE program, has been licensed by Agilent. It is being used in the development of one type of biomolecule detector the mass production of which is deemed feasible by this method.

In the current program we have had significant success in delineating the applicability of the standard theory of sputter morphology evolution, have made several important advances, and have identified serious shortcomings in our understanding ranging from the inadequacy of the theory for the evolution of tall, steep features to the lack of universality of a linear instability, contrary to predictions.

2. Background and Technical Progress

2.1 Formation of Sputter Patterns

An ion beam for sputter erosion is a very common processing tool used in the semiconductor industry and in surface science research groups, usually to clean surfaces in an ultra-high vacuum (UHV) environment. However, it is known that under some conditions a spontaneously-arising sputter pattern topography arises that often takes the form of one-dimensional ripples or two-dimensional arrays of dots. The periodicity is understood to arise as a result of a kinetic competition between the surface roughening effect of the ion beam and morphological relaxation.

There is a significant body of experimental and theoretical work on ion-stimulated formation and relaxation of self-organized nanoscale features on solid surfaces [4-85]. Fig. 2 shows representative surface morphologies on Si, including regular and irregular one-dimensional ripples formed at off-normal ion beam incidence [4-6], and also transient two-dimensional ripple morphologies. For sputter patterns on Si, the in-plane length scales (wavelengths) are typically of order 100 nm, whereas the out-of-plane length scales (amplitudes) are of order 10 nm. Although features with ~100 nm length scale are formable lithographically, spontaneously self-organized ripples and dots as small as 15 nm have been formed in other materials systems such as GaSb [74] and SiO₂ [28]. We are studying larger

Fig. 1. “Quantum dots” on GaSb, fabricated by normal-incidence sputter patterning. From Facsko et al. [1]. Image 500 nm x 500 nm. Dots as small as 15 nm have been reported.

Fig. 2. Sputter patterns formed on Si. (a) highly aligned parallel mode ripples on Si(111), from Brown et al [4], (b) wavy perpendicular ripples on Si(001) [5], (c) wavy perpendicular mode ripples on Si(111), from Brown et al. [6], (d) two dimensional dot arrays on Si(111), from Brown et al. [6]; (e) ripples in a-Si formed by uniform FIB rastering. Projected ion beam direction is from bottom to top in all images. AFM scan size for (a)-(d) is 10 microns. Scale bar in SEM image in (e) is 1 micron.

lateral length scales in Si because of the availability of *in-situ* probes, e.g. optical diffraction techniques [5,86] and Focused Ion Beam (FIB)-Scanning Electron Microscopy (SEM) [75,76] and because Si is a monatomic system amenable to atomistic modeling. As a result we can learn much more about the fundamental aspects of the phenomenon with measurements at these length scales. Our objective has been a fundamental understanding that permits us to answer the question, "How much morphology control can one attain without having to write each individual feature?"

A significant new discovery [73,75] has been sputter patterning under uniform rastering of a focused ion beam (FIB), which is a machine typically used to micromachine surfaces in computer-controlled patterns. The rapid feedback possible with *in-situ* real-space imaging in a FIB instrument has accelerated the understanding of the phenomena believed to be common to both focused and unfocused ion irradiation. Not only has this observation of pattern evolution under FIB irradiation served as an excellent test of theory and motivated new theory, it has also lead to entirely unanticipated discoveries, as shown in Fig. 3 [75].

Fig. 3. SEM image of Ge "nanograss" formed by uniform rastering with 30 keV Ga^+ FIB. (a) incident angle 90 degrees; (b) incident angle 60 degrees

2.2 Guided self-organization by templating

Methods for the fabrication of large areas of nanoscale features with controlled period and intra-period organization are of interest because of the potential for high-throughput mass production of nanoscale devices. Due to their potential in this regard, much recent attention has been devoted to self-organization processes [1,87-91], in which processing causes the spontaneous emergence of a nanoscale pattern. The short-range order can be quite high [1,88,89] but some envisaged applications require long-range order, which is destroyed by uncontrolled topological defects arising spontaneously from the self-organization process. A potentially successful hierarchical fabrication strategy is the fabrication of controlled features at a small, but lithographically tractable, length scale by methods such as conventional mask or optical standing wave lithography, in order to guide a self-organization process at the finest length scale [92-99]. Topographic patterning has been used for templating the local disorder in 2D self-assembled monolayers [100] and for templating defect organization or elimination in 3D colloidal crystallization [101,102]. Topography has also been used to manipulate semiconductor quantum dot placement, composition, and strain through its effect on stress [103] and surface energy and mobility [104]. 3D short-range ordering of grown-in quantum dot short-period superlattices can result from multilayer growth [87,89]; nanoscale topographic templating of the first layer could dramatically accelerate the development of order and lead to true long-range order. Lithographically- and Focused Ion Beam (FIB)-patterned topographies have recently been used to template quantum dot growth in linear chains [99], periodic 2D lattices [97], and in more complex configurations promising for novel nanoelectronics architectures such as quantum cellular automata [105]. The finest features have been templated by serial writing with the FIB, a prohibitively expensive process for mass production that might be circumvented by the

hierarchical fabrication strategy. Self-organized sputter-ripple topographies have been used to template metal islands [106] and colloidal particles [107] in linear chains.

In our program, we have measured the influence of patterned boundaries on a Si(001) substrate in guiding self-organized sputter ripples [77]. We showed that the long-range order of the features can be greatly enhanced by this lateral templating approach (Fig. 4). The emerging pattern can be manipulated by changing the boundary spacing and misorientation with respect to the projected ion beam direction. We developed a scalar figure of merit, a dimensionless topological defect density, to characterize the degree of order of the pattern. At small boundary separation, the greatest order is observed when the separation is near an integer multiple of the spontaneously arising feature size. The defect density is exceedingly low up to a critical misorientation angle, beyond which topological defects develop in proportion to the incremental misorientation. These results suggest the potential utility of lateral templating ion irradiation-induced topographic patterns for high throughput fabrication at sub-lithographic length scales. For example, the GaSb results of Facsko *et al.* (Fig. 1.1) give us grounds for optimism that the templating technique might be used to create long-range ordered arrays of “quantum dots” with uniform size well below 100 nm in layers of GaSb on narrower-gap substrates. *No theory has been shown to predict the lateral templating effect and the behaviors we have documented, or to address the maximum distance between template boundaries over which it is possible to deterministically set the pattern that evolves within the intervening area.*

Fig. 4. First demonstration of lateral templating under ion beam sputtering [77]. AFM topographs of sputter-rippled Si(001) just outside (left) and inside (right) lithographically templated region of same sample. High regions are white.

2.3 Single biomolecule detectors

The insight gained by our studies of sputter patterning is proving to be an essential first step in developing the materials science base required for the design of sensitive and reliable nanopore molecular detectors (Fig. 1.5). In collaborative work with J.A. Golovchenko (Harvard), we guided experiments and developed an adatom-diffusion model (Fig. 6) that successfully predicts many aspects of the ion-sputter-induced closing of nanopores in SiN membranes [2] that are being used as single molecule detectors for biopolymers such as DNA [2,108] (Fig. 1.7) and are envisaged as DNA sequencers $\sim 10^6$ times faster than those in current use [109]. The model, which embodies the current, limited status of our understanding of the ion beam nano sculpting process, is an extension of the model we developed of the atomistic processes occurring in sputter rippling of Si(001) [5]. The adatom diffusion model posits that the spatiotemporal evolution of the concentration field $C(\mathbf{r}, t)$ of surface-diffusing mobile species (“adatoms”) created by the ion beam is governed by the following partial differential equation (PDE):

$$\frac{\partial}{\partial t} C(\mathbf{r}, t) = fY_1 - \frac{C}{\tau_{\text{trap}}} - fC\sigma + D\nabla^2 C, \quad (1)$$

Fig. 5. a) Pore area determined by ion beam current transmitted through nanopore vs. dose. b) TEM image of initial ~60 nm pore in a 500 nm thick Si₃N₄ membrane made by focused ion beam. c) TEM image of sample after subsequent unfocused 3 keV Ar⁺ ion irradiation during which pore fills with electron transparent (~10 nm thick) membrane; final diameter 1.8 nm.

where f is the ion flux, Y_1 is the number of adatoms created per incident ion, τ_{trap} is a time constant for annihilation by fixed traps, σ is the cross section for adatom annihilation by direct ion impingement, and D is the adatom diffusivity. Adatoms that diffuse to the edge of the pore fill it in. The model successfully accounts for several observations including (a) the measured time-dependence of the nanopore area during irradiation; (b) the decreased effectiveness of nanopore closing, per ion, at higher fluxes due to increased beam-induced "adatom" annihilation; (c) the increased effectiveness of nanopore closing, per ion, if the same flux is delivered in pulses separated by "offtime", to the same total fluence; (d) the strong temperature-dependence of the closing rate; (e) the existence of a maximum size pore that can be closed under ion exposure. Representative results are shown in Fig. 5(a).

In this research program we examined the closure kinetics of nanopores in SiO₂ and have found that although they close under ion irradiation, they behave very differently than the nitride nanopores. The instantaneous

Fig. 6. Kinetic processes in model.

Fig. 7. Detection of folding configurations in solution of individual double-stranded DNA molecules using ion-sculpted 10 nm nanopore. Current vs. time traces determine position of folds in molecule, from Li et al. [108]. Cartoons show folding configurations of molecules translocating nanopore from left to right: fat parts block more current.

Fig. 8. Temperature-independent ion beam sculpting of SiO₂ nanopores.

rate of closure seems to be independent of temperature (Fig. 8) and dependent on the prior history of the pore's radius - thus a 5-nm pore that started at 10 nm has a faster instantaneous closure rate than a 5-nm pore that started at 20 nm. In this case one must consider the possibility that ion stimulated viscous flow [71,110], possibly in conjunction with ion-stimulated compressive stress [111,112], mediates morphology evolution in this system.

We anticipate that different classes of materials may be found in which different mechanisms mediate transport. For example, surface-confined viscous flow via an ion-enhanced fluidity has been identified as the transport mechanism in sputter rippling of SiO_2 with keV ion beams [28,71]. Our nanopore-closing results on amorphous SiN are quantitatively consistent with our surface diffusion model and qualitatively inconsistent with at least one key aspect of the ion-enhanced fluidity mechanism, namely the observed dependence of closure-per-ion on flux and on offtime between ion pulses: in current models for ion-enhanced fluidity, only the ion fluence matters and not its temporal dependence. Results in SiO_2 are also qualitatively inconsistent with this same key aspect of the ion-enhanced fluidity mechanism in its current form [113]. It is more difficult to envisage viscous flow as an important mechanism in materials that remain crystalline under ion irradiation, in either single-crystal or large-grain polycrystal form, as metals do at typical temperatures and Si and Ge do at sufficiently high temperature.

Other nanoscale devices would be possible if ion beam nano sculpting could be made to work with other materials besides the insulators SiN_x and SiO_2 , such as metals, or composites of metals and nonmetals. We have discovered that nanopores in metallic glass close under ion irradiation.

Additionally, amorphous silicon (a-Si) nanopores close under ion irradiation, as shown in Fig. 9. With further understanding, it may be possible to find conditions under which metals, semiconductors, and insulator close at the same rate, thereby permitting the integration of dissimilar materials into nanodevices. An envisaged device for rapid DNA sequencing is shown in Fig. 10.

Fig. 9. Ion beam closure of amorphous silicon nanopore. (a) area vs. time as pore closes under unfocused Ar^+ irradiation. (b) TEM image of pore after irradiation was stopped. Initial diameter ~ 200 nm and thickness ~ 250 nm, final diameter ~ 100 nm and thin enough to be electron transparent.

The discovery of nanopore closing in a-Si is of great *fundamental* significance; hence it is a high priority for future research. *Amorphous Si is the perfect model system for understanding nanoscale morphology evolution under ion irradiation:* we can make sputter ripples; we can close nanopores; it's amorphous and single-element and so we should be able to model its behavior theoretically without unknown and confounding anisotropy and composition effects; and it's amenable to molecular dynamics simulations with classical potentials in this ion energy regime, thereby permitting an understanding all the way down to the atomistic level.

Fig. 10. Envisaged insulating nanopores articulated with metallic contacts for molecular detection by tunneling. Top: fabrication by conventional methods of large (~ 30 nm) pore and aligned metallic leads. Bottom: ion stimulated closure of pore under conditions where metal and insulator are transported at identical rates creates aligned metal contacts for sequencing single-stranded DNA by electron tunneling.

2.4 Theory of Sputter Pattern Formation

The rate of recession of an eroding surface (excluding surface relaxation and noise) can be written as

$\partial h / \partial t = -V_n \sqrt{1 + b^2}$, where $b \equiv \partial h / \partial x$ is the local slope of the surface and V_n is the speed normal to the surface (Fig. 11). Generally, V_n is a function of the surface slope, curvature, and higher order derivatives of the morphology. The Sigmund theory of sputtering [114,115], which is the starting point of just about every theoretical treatment of sputter patterning, asserts that V_n at point A at position x on the surface is proportional to the power arriving at x from the collision cascades resulting from ions impinging on the surface at all other points x' , as shown in Fig. 11. The speed of erosion at x , with coordinates $(x, y, h(x, y))$ is then given by an integral over all points x' :

$$V_n(x, y) \propto \iint dx' dy' E(x, y; x', y'), \quad (2)$$

where $E(x, y; x', y')$ is the power reaching x from the ion impingement at x' . Sigmund modeled the distribution of deposited energy as centered a distance a below the impingement site (along the initial ion direction) and decaying outward as a Gaussian with an ellipsoidal shape. $E(x, y; x', y')$ then depends on the relative height, lateral distance and direction of x and x' with respect to the incident ion beam direction. If we define the ion trajectory to be in the $-z$ direction then

$$E(x, y; x', y') = (\text{const.}) \exp \left(-\frac{[h(x', y') - a - h(x, y)]^2}{2\sigma^2} - \frac{[x' - x]^2 + [y' - y]^2}{2\mu^2} \right). \quad (3)$$

We shall refer to the r.h.s. of Eq. (2) as the *Sigmund sputter integral* and Eq. (3) as the *Sigmund kernel*. Note that the only materials parameters controlling morphology evolution in the Sigmund theory are a , σ , and μ (parameters such as the surface binding energy merely scale the rates for all points on the surface by a multiplicative factor through the proportionality sign in eq. (2)).

2.4.1 Linear stability theory

Bradley and Harper (BH) [13] performed a linear stability analysis of a flat surface undergoing erosion according to the Sigmund kernel. By expanding $h(x, y)$ for small curvature, slope difference, and height difference from a planar surface, they found that the leading order instability arises from the curvature coefficient of the sputter yield. As can be seen from Fig. 11, concave regions of the surface, such as A, are closer to the energy deposition maxima than convex regions and so erode faster. Their resulting PDE for the change in height (relative to the average height) with time, simplified here to include only one independent spatial dimension, is

Fig. 11. Sigmund theory of sputtering. Iso-energy contours are illustrated. Average ion range is a ; longitudinal and transverse straggling are σ and μ . As illustrated by red arrows, some energy from ions impinging at all points contributes to erosion at point A. Concave regions such as A are closer to the energy deposition maxima than convex regions and thereby erode faster.

Fig. 12. Variation of the curvature coefficient S of the vertical erosion rate in eq. (3) with inclination angle. Linear instability ($S < 0$) exists at all angles. Mode with most negative value of S is expected to dominate topography. Adapted from Feix et al. [78].

$$\frac{\partial h(x,t)}{\partial t} = S \frac{\partial^2 h}{\partial x^2} - B \frac{\partial^4 h}{\partial x^4} \quad (4)$$

where the curvature coefficient S is negative, leading to instability. The last term represents classical Mullins/Herring [116,117] isotropic surface relaxation back toward flatness via surface diffusion - a stabilizing term. As a linear PDE, Eq. (4) can be solved using Fourier methods. The amplitude of each Fourier component of the surface morphology $h_q(t)$ with wavenumber q should grow or decay exponentially with rate constant $R(q) = -Sq^2 - Bq^4$. BH theory thus predicts a maximal value of $R(q)$ at a fastest growing spatial frequency $q^* = (-S/2B)^{1/2}$, so after a while the surface should be dominated by sinusoidal ripples with spatial period $\lambda^* = 2\pi/q^*$.

In two independent spatial dimensions, Bradley and Harper solved for the stability with respect to sinusoidal perturbations with wavevector either parallel or perpendicular to the direction of the projected ion beam on the surface ("parallel mode" and "perpendicular mode", respectively, Fig. 1). As shown in Fig. 12, *all surfaces, at all angles of inclination θ , are predicted to be linearly unstable to perpendicular mode ripples*, whereas all surfaces below a certain inclination angle are predicted to be unstable to parallel mode ripples. Where instabilities to both modes arise, the resulting topography is expected to be dominated by the mode with the most negative value of S .

BH theory has been tested in several ways and has been found to describe some aspects of evolution but not others. We have shown some of the successes and limitations of the model for Si(001) [5,67]. One commonly observes amplitude saturation at large enough values, which must necessarily come from nonlinear terms missing from a linear stability theory, but in some materials, such as Si(001), saturation is occurring at surprisingly small slopes ($\sim 10^\circ$) that are difficult to understand [67]. However, by far the most confounding observation is that experimentally, *some surfaces appear to be absolutely stable against the BH instability*.

One common example of the curious failure of BH theory is for normal-incidence unfocused ion irradiation, where an instability with a characteristic length scale is predicted but rarely observed [75] (with a few notable exceptions, e.g. [74]). Beyond this, the experimental conditions for stability are not clear. We now have evidence that under certain conditions the sputter instability is actually a *sputter metastability*, i.e., an initially flat surface is metastable. In Fig. 13, we show a sequence of images taken during FIB irradiation of a rectangular pit in Si. A sharp boundary separating rippled and flat "phases" sweeps across the pit bottom. The existence of the flat "phase" is evidence for stability against infinitesimal perturbations. The rippled phase "nucleates" along the edge of the pit (a large perturbation) and consumes the flat phase by the passage of a sharp interface. Because the silicon surface becomes amorphous virtually instantaneously upon FIB irradiation, the evolution we are seeing is characteristic of an amorphous surface: surface free energy should be isotropic and cannot be a cause of "faceting".

Because the BH linear stability results are a rigorous consequence of eqs. (2)-(3), one must examine the validity of the Sigmund theory underlying just about every treatment of morphological development. Recently Feix *et al.* [78] reported molecular dynamics simulations of the sputter erosion of copper crystals by 5 keV Cu. They looked at the spatial distribution of sites from which the sputtered atoms were emitted with respect to the point of impact and found that Eq. (2) describes their results pretty well (assuming V_n is proportional to the atom emission rate, which they tracked), except that the Gaussian ellipsoid kernel, Eq. (3), needed to be replaced by a kernel of a somewhat different form. This permitted them to explain a reduction in sputter yield with increasing angle at very high angles, which is not explained by Sigmund theory (see Fig. 17), but otherwise the results of Sigmund theory seem to be qualitatively unchanged. In particular, with a modified sputter kernel of Feix *et al.*, the qualitative features of Fig.

Fig. 13. Sputter metastability. Time sequence of FIB sputtered Si morphology evolution. At 78 min., two "phases" are evident: metastable flat phase is being consumed by sputter rippled phase.

12 remain the same: all surfaces at all inclinations *should* exhibit a linear instability.

We have accumulated reasons to believe that ion-stimulated surface mass transport is the key element that has been neglected; that, as a consequence, V_n is *not* proportional to the atom emission rate; and that including this effect will create a term $S' \partial^2 h / \partial x^2$ that can overwhelm the first term on the r.h.s. of eq. (4), thereby becoming the predominant source of linear stability or instability. *If this is correct, it will revolutionize the theory of sputter erosion.*

2.4.2 Nonlinear perturbative approach

Enhancements to BH theory have been made to include noise [24,28], nonlinear effects at larger amplitudes [62,72,79-85], and the identification [48] of a fourth-order “effective surface diffusion” term $-D_{xx} \partial^4 h / \partial x^4$ through which we can understand how patterns may form even when surface diffusion is essentially turned off at low temperature where $B = 0$.

The inclusion of nonlinear effects is an area of very active research. An important advance was made by Makeev and co-workers [72], who developed from the Sigmund kernel a general expression for V_n in terms of arbitrary topography and the parameters a , σ , and μ describing the ion collision cascade in the solid. To obtain solutions, they then expanded V_n in powers of slope and derived an erosion equation of the form (for simplicity we report only the most noteworthy terms in a one-dimensional version although the actual theory is for two independent spatial dimensions)

$$\frac{\partial h}{\partial t} = S_x \left(\frac{\partial^2 h}{\partial x^2} \right) + \xi_x \left(\frac{\partial h}{\partial x} \right) \left(\frac{\partial^2 h}{\partial x^2} \right) + \Omega_1 \frac{\partial^3 h}{\partial x^3} - D_{xx} \frac{\partial^4 h}{\partial x^4} + \frac{\lambda_x}{2} \left(\frac{\partial h}{\partial x} \right)^2. \quad (5)$$

where S_x , ξ_x , and Ω_1 are roughening prefactors determining the anisotropic erosion rate, D_{xx} describes ion induced effective (fourth-order) diffusion, and λ_x controls the early stages of nonlinear evolution. Makeev *et al.* solved for these ion-related coefficients as functions a , σ , and μ . Solutions to the two-dimensional counterpart of Eq. (5) have been obtained for shallow ripples [72,81] and self-affine surfaces [80].

Makeev *et al.*'s small-slope expansion, Eq. (5), cannot be used to describe our observed lateral templating of sputter ripples (Fig. 4) because experimentally the initial surface possesses regions of widely differing slopes and very high amplitudes. *What is needed in such cases is a non-perturbative approach that can handle large excursions in inclination angle.*

2.4.3 Erosion of tall, steep features

Methods of micro and nanofabrication of three-dimensional (3D) structures are of increasing interest due to their importance for the creation of compact 3D devices and their assembly into functional 3D systems. Examples include micro-electromechanical systems, 3D integration of electronic microprocessors, 3D information storage, and

Fig. 14. Example of tall, steep features that cannot be modeled with a perturbative approach. Single crystal diamond curved tip microindenter fabricated by FIB, from Adams *et al.* [118]. High-magnification view on the right shows three different morphologies, including rippled “phase” and flat “phase”.

Fig. 15. (a) SEM image of an initial circular pit in Si with 3 mm diameter and 0.5 mm depth. (b) The wall of the enlarged pit is still sharp after uniform ion exposure.

photonic band gap waveguides. Direct fabrication with the FIB itself is already a commercial production technique for expensive components such as AFM tips; it is also used for the fabrication of prototype devices and it is feasible to use the FIB for fabricating templates for the molding of replicas. Understanding and controlling the effects of the FIB on the morphology evolution of tall, steep features is therefore an area of active research [118-121].

We discovered a new regime of ion beam sputtering that occurs for sufficiently steep slopes [122]. High slopes propagate over large distances without dissipating the steepest features. Both the propagation velocity and the dynamically selected slope are universal, independent of the details of the initial shape of the surface. The SEM image in Fig. 15 shows a pit with steep side walls that has been micromachined into silicon using a Focused Ion Beam, and to the right the same pit, with sides that have not smeared out, after uniform ion irradiation of the entire wafer. The left panel of Fig. 16 shows predictions of the new theory of sputter morphology evolution that is valid for arbitrarily large slopes when the curvature is small. Under uniform ion irradiation the pit wall, initially at $t=0$, propagates laterally and, for this particular set of conditions, evolves to maintain a uniform slope that is steeper than the original slope. (The theory also predicts that sufficiently shallow slopes dissipate, which is the conventionally observed behavior.) The experimental sequence in Fig. 16, obtained with an optical profilometer, shows striking confirmation of the predictions of the theory. An important implication of the transition from dissipative behavior to propagative behavior at high slopes is that a structure (e.g. line or dot) can be fabricated at a large length scale and, with uniform ion irradiation, reduced to a smaller length scale while preserving, or even sharpening, the steepest features.

To treat tall, steep features, we developed from the Sigmund sputter kernel a small-curvature approximation that is valid for *all* slopes. Combining this with Mullins-Herring fourth-order surface smoothing mediated by surface diffusion results in a nonlinear PDE called the advection-diffusion equation,

$$\frac{\partial b(x,t)}{\partial t} = -C \frac{\partial b}{\partial x} - S \frac{\partial^2 b}{\partial x^2} - B \frac{\partial^4 b}{\partial x^4}, \quad (6)$$

Fig. 16. (left) Theoretical profile evolution. Red curves: solution of advection-diffusion PDE; black curves: numerical integration of Sigmund sputter integral. (a)-(d) Experimental profiles illustrating propagation of shock front with decreasing height and increasing size of trailing "snail's foot" or rarefaction wave. The arrows are for illustrative purposes and do not signify a quantitative one-to-one correspondence between theoretical and experimental profiles.

Fig. 17. Sputter yield of flat surface vs. incidence angle. Adapted from Vasile [120]. Dashed curve: full Sigmund sputter integral (Gaussian ellipsoids). Solid black: with Yamamura correction due to reflection at grazing incidence [120,123]. Applying Bradley-Harper analysis to large amplitudes assumes all coefficients are constant at their initial value, e.g. illustrated here for an initial slope of 30° . Red curve: Makeyev et al.'s quadratic expansion in powers of slope. The entire black curve goes into our theory; shock fronts result in the region where the curvature is downward and so will not result from the Bradley-Harper approach or the Makeyev et al. approach.

where $b \equiv \partial h / \partial x$ is the slope, $C = C(b) \equiv \partial Y / \partial b$ turns out to be the propagation speed, and Y is the sputter yield (atoms removed per incident ion, see Fig. 17). The solutions of this equation predict behavior that can be understood as the propagation of a shock front that self-selects a stable slope; the mathematical structure of the solutions is the same as that previously observed in thin-film fluid flows. We undertook this study because we believed that it would afford a good test of the Sigmund kernel, but the shock front behavior turns out to be a generic feature of the non-monotonic behavior of the sputter yield vs. slope. As the slope increases, the center of the energy deposition gets closer to the surface; hence the sputter yield increases with slope. But at high enough slope, the sputter yield turns down again due to effects such as reflection at grazing incidence [123] and possibly to deviations of the true collision cascade shape from Gaussian ellipsoids [78]. This qualitative behavior of the sputter yield vs. slope, combined with the kinetics of surface diffusion, turns out to be sufficient for propagative rather than dissipative solutions to the morphology evolution equation arising from the Sigmund sputter kernel and fourth-order diffusion.

2.5 Surface morphological relaxation and nanostructure stability

2.5.1 Non-classical smoothening kinetics observed for crystalline surfaces

The recent work of Makeev *et al.* and our aforementioned theoretical effort are focused on a better understanding of the sputter yield and its nonlinear dependence on elements of the surface topography. These and other analytical treatments generally assume surface diffusion mediated smoothening governed by the final term in Eq. (4), $B \partial^4 h / \partial x^4$, where B contains the surface diffusion coefficient. This term comes from the Mullins-Herring [116,117] theory known to be valid for surfaces above the thermodynamic roughening transition temperature. It assumes a spatially uniform concentration of mobile species on the surface. However, we have shown that under thermal annealing conditions after the ion beam is turned off, *sputter rippled surfaces obey non-classical relaxation kinetics inconsistent with $B \partial^4 h / \partial x^4$* [66,124-126]. As are most crystalline surfaces under typical materials processing conditions, these surfaces are well below their roughening transition temperature. Non-classical effects appear to be responsible for the change of the decay kinetics of the corrugation amplitude $A(t)$ from exponential decay to inverse linear,

$$A(t) = \frac{A(0)}{(1 + kt)}, \quad (7)$$

where k is a wavelength and temperature dependent rate constant.

2.5.2 Nonclassical Relaxation theory for stepped and faceted crystalline surfaces

In a related NSEC-supported collaboration with D. Margetis (MIT) and H.A. Stone (Harvard) we have developed a new continuum theory of morphological relaxation for non-faceted crystalline surfaces with arbitrary morphologies composed of step trains in two independent spatial dimensions. From fundamental equations governing adatom transport between steps, a continuum partial differential equation has been derived. The input is the standard [127,128] expression for the surface free energy γ per unit area projected on a “basal plane” of high crystallographic symmetry,

$$\gamma(h(x, y)) = g_0 + g_1 |\nabla h| + \frac{1}{3} g_3 |\nabla h|^3, \quad (8)$$

where g_0 is the terrace free energy, g_1 is the step line tension, $|\nabla h|$ is the step density, and g_3 represents the strength of step-step interactions. g_1 and g_3 , as well as the adatom diffusivity D , are assumed to be azimuthally isotropic. From this follows a general expression for the chemical potential μ for any stepped, non-faceted surface profile,

$$\mu = -\Omega g_1 \left[\nabla \cdot \frac{\nabla h}{|\nabla h|} + \frac{g_3}{g_1} \nabla \cdot (|\nabla h| \nabla h) \right], \quad (9)$$

where Ω is the atomic volume. An expression of mass conservation is then combined with a kinetic equation relating the adatom current density to the chemical potential gradient. The result is a nonlinear PDE for the time-evolution of $h(x, y, t)$. The novel aspect of this theory is that the current density and the chemical potential gradient do not have to be parallel to each other, as has been assumed in previous work [129-131]. Rather, they are related

by a mobility that is a tensor because current in a direction orthogonal to the steps contains fundamentally different barriers (step traversal barriers) than current in a direction parallel to the steps, and neither may be neglected for non-axisymmetric profiles.

For the decay of non-axisymmetric structures such as the imperfect sputter ripples we produced experimentally on Si(001) under our DOE program, (Fig. 2(b)), *the predicted decay behavior is inverse linear in time, Eq. (7), just as we observed experimentally* [66]. Additionally, the predicted decay for highly perfect lithographically-fabricated corrugations is exponential in time, as is observed experimentally by Blakely and coworkers [132] and predicted by 1D theory [133]. With this development, which resolves a major controversy over the decay kinetics of non-classical corrugated surfaces [66,124,125], we have laid the foundation for PDE-based descriptions of a wide variety of non-classical 2D surface morphology evolution processes. In related work we have shown how this PDE can be combined with appropriate boundary conditions at the edge of a facet [129,130] to predict the evolution of prototypical faceted shapes, and can be combined with appropriate boundary conditions at a grain boundary to predict the evolution of grain boundary grooving [134].

These results suggest the question of whether *during sputtering* this non-classical capillarity is important in the evolution of crystalline morphologies under ion irradiation. It is conceivable that the ion bombardment creates a non-singular kinetically rough surface with a spatially uniform concentration of mobile species, in which case the second term on the r.h.s of Eq. (4) might still be appropriate. However, it is difficult to ascertain whether this is indeed the case. Hence we believe that the behavior of amorphous surfaces, where ion stimulated morphology evolution should definitely obey classical relaxation kinetics, must be understood before further progress on crystallographic surfaces is possible.

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