Phase separation in ion-irradiated compound semiconductors:
an alternate route to ordered nano-structures

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Abstract

In recent years, observations of highly-ordered, hexagonal arrays of self-organized nanostructures on binary or impurity-laced targets under normal-incidence ion irradiation have excited interest in this phenomenon as a potential route to high-throughput, low-cost manufacture of nanoscale devices or nanostructured coatings. The currently-prominent explanation for these structures is a morphological instability driven by ion erosion discovered by Bradley and Shipman; however, recent parameter estimates via molecular dynamics simulations suggest that this erosive instability may not be active for the representative GaSb system in which hexagonal structures were first observed.

Motivated by experimental and numerical evidence suggesting the possible importance of phase separation in ion-irradiated compounds, we here generalize the Bradley-Shipman theory to include the effect of ion-assisted phase separation. The resulting system admits a chemically-driven finite-wavelength instability that can explain the order of observed patterns even when the erosive Bradley-Shipman instability, and in a relevant simplifying limit, provides an intuitive instability criteria that agrees qualitatively with experimental observations on pattern wavelengths. Finally, we identify a characteristic experimental signature that distinguishes the chemical and morphological instabilities, and highlights the need for specific additional experimental data on the GaSb system.

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I. INTRODUCTION

Among the many nanoscale patterns that have been observed on ion-irradiated surfaces [1, 2], the discovery of hexagonal arrays of high-aspect ratio dots on Ar\textsuperscript+ -irradiated GaSb [3] has sparked a flurry of experimental and theoretical study into spontaneous pattern formation as a potential route to “bottom-up” fabrication of nanoscale devices. The mathematical study of such patterns is a mature field known as bifurcation theory, and the ingredients necessary to produce long-range hexagonal order are well known [4, 5]. First, one needs isotropic physics, which is readily achieved by irradiating the sample at normal incidence, or by rotating it during off-normal bombardment. Second, one needs a destabilizing mechanism that produces a finite wavelength bifurcation – a transition in the linearized equations from stability to instability that occurs first for perturbations of a finite wavelength. This kind of bifurcation leads to instabilities in which the unstable wavenumbers are bounded both above and below by stable wavenumbers; the resulting narrow band of unstable modes generically produces some kind of ordered pattern at long times.

Unfortunately, none of the early models of ion irradiation predicted a narrow-band instability [6, 7], suggesting a need for the incorporation of additional physical effects. Two candidates that initially seemed promising were a “damping” term proposed to stand for long-range atomic redeposition [8] and biaxial compressive stress injected by the ion beam (see [6, 7] for a comprehensive discussion). However, recently both mechanisms have been ruled out as sources of a narrow band [9, 10]. In parallel with these theoretical struggles, persistent difficulty obtaining consistent results between labs has led to a re-examination of the experimental results. It was found that dots, originally also observed on irradiated pure silicon [11, 12], disappeared from that system when impurities and geometric artifacts were carefully removed [7, 13, 14], and conversely, that the systematic addition of impurities to a clean system causes dots to appear [15–18]. This has led to the strengthening conclusion that two-component materials are the necessary ingredient to produce ordered quantum dots [19].

This growing consensus has caused increasing interest in theoretical treatments of irradiated materials with two components, in which coupled PDEs simultaneously describe
both the morphology and the concentration evolution. Extending the pioneering work of Shenoy, Chan, and Chason [20], Bradley and Shipman (BS) have recently introduced such a theory for irradiated binary compounds exhibiting the first physically-grounded finite-wavelength bifurcation [21, 22], making it a foundation for current understanding of these structures. However, in order to explain the structures, the model makes several strong assumptions. First, it requires that any finite-wavelength bifurcation be driven primarily by the erosive instability identified by Bradley and Harper [23], which implies that surfaces should be unstable even in the absence of a second species. Second, it requires a strong component of preferential redistribution, in which one target atom is redistributed much more strongly than the other. Last, it assumes chemical diffusion of the standard, Fickian type.

As will be shown below, all three assumptions of the Bradley-Shipman theory may be fairly questioned, with some evidence to the contrary existing in each case. This suggests the consideration of alternate physical mechanisms to explain the ordered structures in irradiated binary compounds. Here, based on a growing body of experimental [24–27] and numerical [24, 28] evidence in a variety of irradiation regimes, we propose a generalization of the original BS theory that admits the process of phase separation. We find that our model admits a finite-wavelength bifurcation even when the assumptions of the BS theory are not fulfilled; in addition, it provides a clear experimental signature distinguishing it from the Bradley-Shipman mechanism. In a plausible and particularly useful limit of nearly equal redistribution of the two species, we obtain an intuitive approximation of the instability criteria, which shows that the presence of the ion beam fundamentally changes the nature of the instability relative to other phase-separating systems.

II. BRIEF REVIEW OF THE BRADLEY-SHIPMAN MODEL

In order to provide proper historical and mathematical context, and because our treatment of phase separation builds upon it, we begin by very briefly summarizing the recent work of Bradley and Shipman [21, 22] for binary compounds irradiated at normal incidence, highlighting those results that we will refer to directly in our generalization.
A. Model

The Bradley-Shipman model tracks the evolution of a height field \( z = h(x, y, t) \) describing the irradiated surface, and concentration fields \( c_A(x, y, t) \) and \( c_B(x, y, t) \) of two components \( A \) and \( B \). Under the effects of normal-incidence ion bombardment, one material is preferentially eroded until a steady state is reached, in which the surface is receding with constant velocity \( v_0 \) and with constant surface concentrations \( c_{A,0} \) and \( c_{B,0} \) of \( A \) and \( B \) atoms, respectively. Perturbations to this steady state are then investigated by setting

\[
\begin{align*}
  h(x, y, t) &= -v_0 t + u(x, y, t) \\
  c_A(x, y, t) &= c_{A,0} + \phi(x, y, t) \\
  c_B(x, y, t) &= c_{B,0} + (1 - \phi(x, y, t))
\end{align*}
\]

where \( u(x, y, t) \) and \( \phi(x, y, t) \) describe the perturbations to the height and concentration field of species \( A \). After some significant analysis (Eqs. (3)-(13) of Ref. [22]), and the neglect of a few terms based on physical considerations, the authors obtain the following linearized equations for the evolution of \( u \) and \( \phi \):

\[
\begin{align*}
  \frac{\partial u}{\partial t} &= -A\phi + C\nabla^2 u - D\nabla^4 u \tag{1} \\
  \frac{\partial \phi}{\partial t} &= -A'\phi + B'\nabla^2 \phi + C'\nabla^2 u \tag{2}
\end{align*}
\]

The coefficients in Eqn.(1) for the height evolution are defined via

\[
\begin{align*}
  A &= P_0\Omega \left[ \Lambda'_A(c_{A,0}) - \Lambda'_B(c_{B,0}) \right] \\
  C &= \Omega \left[ (\mu_A(c_{A,0}) + \mu_B(c_{B,0})) - \alpha (\Lambda_A(c_{A,0}) + \Lambda_B(c_{B,0})) \right] \\
  D &= [c_{A,0}D_A + c_{B,0}D_B] \frac{n_s\Omega^2\gamma_s}{k_B T} > 0
\end{align*}
\]

and those in Eqn.(2) for the concentration evolution, via

\[
\begin{align*}
  A' &= \frac{P_0\Omega}{\Delta} \left[ c_{B,b}\Lambda'_A(c_{A,0}) + c_{A,b}\Lambda'_B(c_{B,0}) \right] > 0 \\
  B' &= \frac{n_s\Omega}{\Delta} \left[ c_{B,b}D_A + c_{A,b}D_B \right] > 0 \tag{4} \\
  C' &= \frac{\Omega}{\Delta} \left[ c_{B,b}\mu_A(c_{A,0}) - c_{A,b}\mu_B(c_{B,0}) \right]
\end{align*}
\]
Here $P_0$ is the power deposited by the ions per unit surface area on a flat surface, $\Omega$ is the atomic volume (taken to be the same for both species), $n_s$ is the total number of mobile surface atoms per unit area on the surface, $\gamma_s$ is the surface energy, $k_B$ is Boltzmann’s constant, $T$ is the temperature, $\Delta$ is the amorphous film thickness, $c_{A,0}$ and $c_{B,0}$ are the concentration of $A$ and $B$ atoms in the film at steady state, $c_{A,b}$ and $c_{B,b}$ are the concentration of $A$ and $B$ atoms in the bulk, $D_A$ and $D_B$ are the diffusivities of $A$ and $B$ atoms, $\Lambda_A (c_A)$ and $\Lambda_B (c_B)$ are proportionality constants linking the deposited power to the sputtering rate, and $\mu_A (c_A)$ and $\mu_B (c_B)$ are proportionality constants describing preferential redistribution of material, an effect first proposed in the Bradley-Shipman model, and playing a critical role therein.

We have continued to employ the assumption of BS that the mobilities of the two species are equal, which eliminates a term $B \nabla^2 c$ in Eqn. (1). In addition, those authors neglect a term $D' \nabla^4 h$ in Eqn. (2), because it does not seem to affect numerical simulations much. (If one replaces surface diffusion with ion-enhanced viscous flow [29] as the dominant surface energy relaxation mechanism, this neglect becomes rigorous.) In a slight deviation from the definitions in the BS model, we have defined coefficients in such a way that zeroth- and fourth-order terms in Eqs. (1)-(2) have negative sign, whereas second-order terms have positive sign. In an additional slight deviation, we assume without loss of generality that the species labels $A$ and $B$ are chosen in such a way that $\Lambda_A' (c_{A,0}) > \Lambda_B' (c_{B,0})$, so that the coefficient $A$ in Eq. (1) is positive. This will greatly simplify a discussion of experimental signatures in Section V below.

B. Stability Analysis

Because the surface is irradiated at normal incidence, the system is isotropic, with no preferred orientation. Therefore, to determine the presence or absence of an instability, and its general characteristics, it is sufficient to consider a one-dimensional perturbation. (The ultimate long-time morphology of the pattern, of course, depends on careful study of superimposed modes [5, 21, 22] in the presence of nonlinearities.) Without loss of generality, one may orient this instability in the $x$-direction, giving
\[
\begin{bmatrix}
u \\
\phi
\end{bmatrix} = e^{ikx+\sigma(k)t} \begin{bmatrix} u_1 \\
\phi_1
\end{bmatrix},
\]

(5)

where \(k\) is the wavenumber of the perturbation, \(\sigma(k)\) the growth rate of that perturbation, and \(h_1\) and \(\phi_1\) are undetermined constants describing the relative phases and magnitudes of the height and concentration modulations. Inserting the perturbation (5) into the governing equations (1)-(2), one obtains, in matrix form,

\[
\begin{bmatrix}
\sigma + Ck^2 + Dk^4 & A \\
C'k^2 & \sigma + A' + B'k^2
\end{bmatrix} \begin{bmatrix} u_1 \\
\phi_1
\end{bmatrix} = 0.
\]

(6)

For a solution \([u_1, \phi_1]^T\) of this equation, the determinant of the matrix must be zero, giving the dispersion relation \(\sigma(k)\) in the quadratic form

\[
\sigma^2 + \tau\sigma + \Delta = 0,
\]

(7)

where \(\tau(k)\) and \(\Delta(k)\) are respectively the trace and determinant of (6) when \(\sigma = 0:\)

\[
\tau(k) = A' + (C + B') k^2 + Dk^4
\]

(8)

\[
\Delta(k) = (CA' - AC') k^2 + (CB' + DA') k^4 + (DB') k^6.
\]

(9)

For the purpose of identifying stability properties, it is sufficient to consider only the root \(\sigma_+(k)\) associated with the '+' sign in the quadratic formula, which gives the growth rate of the faster-growing solution:

\[
\sigma_+(k) = \frac{1}{2} \left(-\tau + \sqrt{\tau^2 - 4\Delta}\right).
\]

(10)

The value of \(k\) that maximizes \(\sigma(k)\) - denoted \(k_{\text{max}}\) - is called the most unstable mode; if \(\sigma(k_{\text{max}}) < 0\), then all modes decay and the steady solution is stable, whereas if \(\sigma(k_{\text{max}}) > 0\), then at least some modes grow and the steady solution is unstable. A set of parameters at which \(\sigma(k_{\text{max}})\) changes from negative to positive is called a bifurcation point. If the bifurcation occurs for some finite value \(k_{\text{max}} \neq 0\), the bifurcation is said to be finite-wavelength, since the most unstable mode has a finite wavelength of \(\lambda = 2\pi/k_{\text{max}}\). However, if it occurs for \(k_{\text{max}} = 0\), it is said to be longwave, because the wavelength of the most unstable mode
approaches infinity. Beyond the bifurcation point, finite-wavelength bifurcations exhibit a narrow band of unstable modes, with stable modes at both larger and smaller values of $k$. This leads generically to ordered arrays of stripes, squares, or hexagons. On the other hand, longwave bifurcations tend to exhibit instability for all wavelengths larger than a critical value, leading to disordered kinetic roughening phenomena [4, 5].

C. Discussion: Requirements for a Finite-Wavelength Bifurcation

A full analysis of Eqn. (10) is contained in Refs. [21, 22]. Here, we obtain only a few results relevant to what follows, in a rigorous but qualitative way emphasizing intuition. In particular, an instability with a narrow band of unstable modes must have stable modes as in both of the limits $k \to 0$ and $k \to \infty$, so these limits merit brief examination.

In fact, all well-posed physical problems should exhibit $\lim_{k \to \infty} \sigma^+ (k) < 0$; i.e., that very-small scale perturbations are stable. Otherwise, the system would be expected to exhibit variation on infinitely-small scales, violating the continuum hypothesis and suggesting that additional physical terms were necessary in the model. From Equations (8)-(10) a simple asymptotic expansion reveals that

$$\lim_{k \to \infty} \sigma^+ (k) \approx -2 (DB') k^2 + O(1).$$

(11)

Because it is assumed that $D > 0$ we see that equations (1)-(2) are well-posed as long as $B' > 0$, which is also assumed within the model. This amounts to an assumption that chemical diffusion is of the standard, Fickian type.

To achieve a narrow band of unstable wavenumbers, it is also necessary that the long waves in the limit $k \to 0$ be stable. Again, a simple asymptotic expansion of Eqns. (8)-(10) in the limit as $k \to 0$ reveals that

$$\lim_{k \to 0} \sigma^+ (k) \approx -\frac{1}{A'} (CA' - AC') k^2.$$

(12)

This leads immediately to a requirement for narrow-band instabilities of

$$CA' > AC'.$$

(13)

A general feature of Eq. (10) is that a mode is only unstable if either $\tau < 0$ or $\Delta < 0$ [5]. Together with the limits just considered, this allows us to easily summarize the main
assumptions that the BS theory requires in order to explain ordered structures. First, under the restriction (13), and because the parameters $D$, $A'$, and $B'$ are all positive by definition, we see that the only way to achieve $\tau < 0$ or $\sigma < 0$ is if the coefficient $C$ is sufficiently negative to drive the instability. This is a notable criteria, because $C < 0$ implies the existence of an erosion-driven morphological instability [23] even in the absence of concentration modulations ($\phi_1 \equiv 0$). Second, if the coefficient $C$ must be negative, then to satisfy Eq. (13), the parameter group $AC'$ must be sufficiently negative to stabilize the long waves, with $|AC'| > |A'C|$. This implies a critical role to be played by preferential redistribution, as characterized by the parameter $C'$, in which one atomic species exhibits much larger displacements within the collision cascade [21][22].

III. GENERALIZATION TO INCLUDE PHASE SEPARATION

The preceding summarized analysis clearly highlights the essential requirements of the Bradley-Shipman theory for producing ordered patterns: (a) an erosion-driven instability indicated by $C < 0$, (b) strong preferential redistribution indicated by $|AC'| > |A'C|$, and (c) ordinary Fickian chemical diffusion indicated by $B' > 0$. We now illustrate why each of these assumptions might be questioned, and in response, propose a generalization of the BS theory which admits the process of phase separation.

A. Motivation

Elsewhere [30], we have used molecular dynamics simulations to estimate the values of $\{A, C, A', C'\}$ for the representative and much-studied GaSb system, by extending the theory of crater functions [31, 32] to the regime of binary materials. Our simulations suggest that, contrary to the requirements of the BS theory just described, the coefficient $C$ is positive, implying the absence of the erosive morphological instability of Bradley and Harper. In addition, we found that the parameter group $|AC'| \ll |A'C|$, suggesting that preferential redistribution plays a negligible role in the dynamics of this system. Indeed, for the parameters we estimated, all terms in Equations (8)–(9) are positive, which means the theory should in fact predict stable, flat surfaces instead of the ordered structures that are
Figure 1. (a) The phase diagram of crystalline GaSb, from [33]. (b) Schematic of a plausible free energy function for amorphous GaSb at low temperatures, based on (a).

frequently observed. This provides strong motivation for the consideration of alternative instability mechanisms to drive these patterns.

Our starting point is to note that Ref. [21, 22], and all subsequent models to date, assume the solute flux due to diffusion is taken to be the simple Fickian one. However, there is ample evidence to suggest that this is not always the case. For GaSb specifically, the presence of the line compound at the 50/50 composition line in the phase diagram depicted in Fig 1a suggests that a free-energy diagram of amorphous GaSb at low temperatures would have a qualitative shape like the curve depicted in Fig 1b. For such a free energy, any significant preferential sputtering of one component will rapidly leave the film in an energetically unfavorable configuration, in which chemical energy would be reduced by phase separating into regions of 50/50 GaSb, and smaller regions of the excess component in nearly pure form. Normally, the low temperatures typically associated with ion irradiation are far below those needed for thermal segregation, but it is known that the ion beam induces an effective mobility in the target atoms that is many orders of magnitude higher than for an un-irradiated target [29]. Indeed, numerical phase-field simulations for irradiated GaSb exhibited structures qualitatively similar to those seen experimentally [28] (a pattern repeated in other irradiation regimes [24]), but so far phase separation during ion bombardment has not been explored analytically. This strongly motivates the development and exploration of a model incorporating phase separation.
B. Model

Though perhaps unable to explain pattern formation in GaSb due to parameter values outside of the pattern-forming regime, the Bradley-Shipman model powerfully demonstrates the ability of the coupling between height and composition displayed in Eqs. (1)-(2) to admit a variety of instability types. The increased complexity of the dispersion relation finally provided a way for the emergence of a finite-wavelength bifurcation, overcoming a fundamental barrier in all models of pure materials [7]. Therefore, to study phase separation in irradiated systems, we will not define an entirely new model, but will instead generalize the existing model of Bradley and Shipman [21, 22] using well-known results from the field of phase separation [34].

We begin by assuming that the ion beam creates a single amorphous phase with a free energy in the standard form

\[
E(c) = \int_S \left[ F(c) + \frac{\bar{\varepsilon}}{2} |\nabla c|^2 \right] dS ,
\]

where \( F(c) \) is a concentration-dependent Gibbs free energy of mixing qualitatively like that in Figure (1)b, and \( \bar{\varepsilon} \) describes a phase boundary energy that penalizes sharp concentration gradients. From here, a local chemical potential \( \mu(c) \) is defined variationally as

\[
\mu(c) = \frac{\delta E}{\delta c} = F'(c) - \bar{\varepsilon} \nabla^2 c .
\]

Next, we assume a diffusive flux \( j_D \) of species \( c \) in the direction of steepest decrease in the chemical potential;

\[
j_D = -\bar{D} \nabla \mu ,
\]

where \( \bar{D} \) is an ion-enhanced diffusional mobility. Finally, conservation of mass leads to terms in the concentration evolution equation of the form

\[
\frac{\partial c}{\partial t} \propto -\bar{D} \nabla j_D = \bar{D} \nabla^2 \left[ F'(c) - \bar{\varepsilon} \nabla^2 c \right] .
\]

With this generalization of the diffusive flux, the (linearized) equations governing the evolution of perturbations \( u \) and \( \phi \) to height and concentration fields become

\[
\frac{\partial u}{\partial t} = -A\phi + C \nabla^2 u - D \nabla^4 u ,
\]

\[
\frac{\partial \phi}{\partial t} = -A'\phi + B' \nabla^2 \phi + C' \nabla^2 u - E' \nabla^4 \phi ,
\]
which are nearly identical to Eqs. (1)- (2), except that a term proportional to $\nabla^4 \phi$ has been added to Eqn. (19). In addition, most of the coefficients of these equations are unchanged from the prior values in Eqs. (1)- (2), except that the coefficients $B'$ and $E'$ are redefined via

\begin{align}
B' &= \frac{\Omega}{\Delta} \tilde{D} F'' (c_0) \\
E' &= \frac{\Omega}{\Delta} \tilde{D} \tilde{\varepsilon},
\end{align}

where for simplicity we have followed Eq.(11) of Ref.[22], which assumes that diffusion is constrained to the surface. We note that simple Fickian diffusion, as employed in the Bradley-Shipman model [21, 22], is recovered by this model if $\tilde{\varepsilon} = 0$ and $F(c) = \frac{1}{2} c^2$, in which case the chemical potential is simply proportional to the concentration. However, we see from Eqn. (20) that if $F'' (c_0) < 0$, diffusion will now generate fluxes up the gradient of concentration - this is precisely the regime of phase separation.

C. Potential Application to other regimes

Finally, although we have primarily in mind here the GaSb system because of the availability of parameter estimates for that system [30], various modifications of the equations derived by Bradley and Shipman to describe this system have subsequently also been employed to describe related irradiation regimes - for instance, those describing simultaneous co-deposition of contaminant [35, 36], or the (net growth) regime of ion beam assisted deposition (IBAD) where the total deposition rate of all atomic species exceeds the sputter rate due to ion irradiation [37]. However, like the original Bradley-Shipman model on which they are based, these models all assume simple Fickian diffusion. It is therefore natural to wonder whether these additional regimes might profitably be generalized to the phase separation case.

In fact, there is strong experimental evidence of phase separation in each regime (which also partly motivates the present inquiry). For instance, in the regime of erosion with simultaneous co-deposition of metal impurities, Hoffsass et al. [27] have recently demonstrated a strong correlation between pattern formation, and the affinity of the metal for
silicon; metals forming a MeSi$_2$ phase (high affinity) lead readily to patterns, metals forming a MeSi phase (moderate affinity) less readily, and metals without a silicide phase led to no patterns. Many of these metals have similar masses to each other, which points to the critical role of chemistry in these samples, as opposed to kinetics. Alternatively, in the regime of ion-assisted deposition of binary materials, a growing body of experimental evidence has documented the formation of 3D structures including vertically-organized alternating material layers [26] and laterally-organized nanowires [24]. These structures are consistent with numerical studies of phase separation during film growth [38] or at moving fronts more generally [39]. In addition, the regime of ion-assisted growth is of particular interest because the stoichiometry may be chosen a priori to be within the domain of negative values of $F''$. This removes the need for preferential sputtering to first push the material into an unstable ratio before phase separation can occur.

A notable feature of the generalization in the previous section is that it only changes the definition of the coefficient $B'$ describing diffusion, and adds a regularizing term $-E''\nabla^4\phi$ to Eq.19. In contrast, the constants $\{A, C, D, A', C'\}$ remain unchanged by this process. Hence, the models in references [35, 37] could be generalized in the same way with minimal changes to the respective derivations, resulting in equations with much the same structure as Eqs.(18)-(19).

IV. STABILITY ANALYSIS

We now present a stability analysis of Eqs.(18)-(19). After briefly repeating the qualitative analysis of Section (II), we obtain a full bifurcation criteria for the present model, followed by a simplified criteria in the limit of small preferential redistribution. This limit gives intuitive insight into the cause of instability, and highlights several unique features of the ion-assisted phase separation system relative to thermal phase separation.

A. Qualitative Analysis: the presence of a finite-wavelength bifurcation

The qualitative, intuition-building analysis of Section (II B) may be briefly repeated. As before, inserting the standard ansatz (5) into Eqs.(18)-(19) we again obtain a quadratic
equation for the growth rate, with faster-growing solution given by

\[ \sigma_+ (k) = \frac{1}{2} \left( -\tau + \sqrt{\tau^2 - 4\Delta} \right). \]  

(22)

However, the addition of the term \(-\varepsilon \nabla^4 \phi\) to Eq. (19) leads to new definitions for \(\tau\) and \(\Delta\):

\[ \tau (k) = \alpha + (C + B') k^2 + (D + E') k^4 \]

(23)

\[ \Delta (k) = (CA' - AC') k^2 + (CB' + DA') k^4 + (CE' + DB') k^6 + (DE') k^8. \]

(24)

An investigation of the limit \(k \to \infty\) yields an altered expression for the behavior of the very-smallest wavelengths

\[ \lim_{k \to \infty} \sigma_+ (k) \approx -2E'k^4 - 2(DB') k^2 + \mathcal{O}(1). \]

(25)

This justifies the new term \(-E'\nabla^4 \phi\) that we have added to Eqn.(2), for without it, the smallest wavelengths would all be unstable in the regime of phase separation \((B' < 0)\). In contrast, the limit \(k \to 0\) yields the same result as before:

\[ \lim_{k \to 0} \sigma_+ (k) \approx \frac{1}{A'} (CA' - AC') k^2. \]

(26)

This is important because the coefficients \(\{A, C, A', C'\}\) are associated only with the kinetic effects of the collision cascade, and are unchanged by the generalization of the chemical diffusion process. So, for instance, estimates of the values of these parameters performed with the Bradley-Shipman theory in mind remain valid in the present case.

Despite the new parameter \(\varepsilon\) and the expanded range of possible values for \(B'\), the possibilities for an instability remain extremely limited. We recall that the system is unstable only if one of \(\tau\) or \(\Delta\) is negative in Eqs.(23)-(24), and that \(A', D,\) and \(E'\) are positive by definition. Assuming further, as discussed above, that both \(C\) alone, and also the parameter group \((CA' - AC')\), are positive, the only terms in Eqs.(23)-(24) for this system that are not absolutely positive are those containing \(B'\). We conclude that an instability can only occur for a sufficiently negative value of \(B'\). Furthermore, because the estimated positive value of \((CA' - AC')\) stabilizes the long-wavelength modes near \(k = 0\), the bifurcation would be of a finite-wavelength type, leading to the narrow band of unstable modes typical of well-ordered systems.
B. Full Bifurcation Criteria

To obtain a more quantitative treatment of the instability criteria, we first recall that Equation (22) is stable if both $\tau > 0$ and $\sigma > 0$, but unstable if either one is negative. Hence, a bifurcation from stability to instability occurs when either

$$\min_k \tau(k) = 0$$  \hspace{1cm} (27)

or

$$\min_k \Delta(k) = 0.$$  \hspace{1cm} (28)

It is sufficient to examine these two criteria independently. As described elsewhere, both in general [5] and in the context of ion irradiation [37], these two possibilities produce different kinds of instability: if $\tau(k) > 0$ but $\min_k \Delta(k) \leq 0$, the growth rate is real and the instability is stationary; however, if $\Delta(k) > 0$ but $\min_k \tau(k) \leq 0$, the growth rate is complex and the instability is oscillatory. As there is no experimental evidence of oscillatory instabilities, we will focus exclusively here on the stationary bifurcation criteria (28).

To analyze the condition (28), we first, for simplicity, rename coefficients in Eq.24 to

$$a = (CA' - AC')$$
$$b = (CB' + DA')$$
$$c = (CE' + DB')$$
$$d = (DE')$$

We also define

$$\tilde{\Delta} = \frac{\Delta}{k^2} = a + bk^2 + ck^4 + dk^6.$$  \hspace{1cm} (30)

Now, the most unstable mode $k_{\text{max}}^2$ satisfies

$$\Delta' (k) = \left(k^2 \tilde{\Delta}\right)' = k^2 \tilde{\Delta}' + 2k \tilde{\Delta} = 0,$$

and a bifurcation occurs when

$$\Delta (k_{\text{max}}^2) = k_{\text{max}}^2 \tilde{\Delta} (k_{\text{max}}^2) = 0.$$

Because we are looking for $k_{\text{max}}^2 > 0$, we can therefore assume that at the bifurcation to instability both

$$\tilde{\Delta}' = 0$$  \hspace{1cm} (31)

$$\tilde{\Delta} = 0$$  \hspace{1cm} (32)
From condition (31) we have

\[ 2k \left( b + 2ck^2 + 3dk^4 \right) = 0 \]  
(33)

to which we apply the quadratic formula to obtain the definition of \( k_{\text{max}}^2 \):

\[ k_{\text{max}}^2 = \frac{-c + \sqrt{c^2 - 3bd}}{3d}, \]  
(34)

Here the positive root can be shown to always yield either the only positive value for \( k_{\text{max}}^2 \), or the value representing a minimum of \( \tilde{\Delta} \). Now, before inserting the result (34) into Eq. (32), we simplify the latter by means of the result (33); this gives a simplified version of Eq. (32) in the form

\[ 3\tilde{\Delta} \left( k_{\text{max}}^2 \right) = 3a + 2bk_{\text{max}}^2 + ck_{\text{max}}^4 = 0. \]  
(35)

Finally, inserting Eqn. (34) into the simplified Eq. (35), eliminating the square root, and simplifying the expression as much as possible, we obtain for the stability boundary the final result

\[ 3 \left( ab - cd \right)^2 + 4 \left( c^2 - b^2 \right) \left( ac - bd \right) = 0. \]

Unfortunately, this criteria is not particularly illuminating. It is expressed in terms of the constants in Eq. (29), which are themselves expressed in terms of environmental parameters via Eqs. (3)-(4), which, in turn, depend upon the underlying tunable parameters of ion energy, flux, etc.. In this situation, we therefore look for a relevant limiting case of the general problem.

C. The limit of weak coupling: \( AC' \ll CA' \)

In Ref. [30], we observed that for the highly-studied GaSb system, the parameter group \( AC' \) was much smaller the parameter group \( CA' \) with the same dimensions. In fact, because the only place either \( A \) or \( C' \) appear is in the first term \( (CA' - AC') \) of Eq. (24), the relative insignificance of the \( AC' \) term suggests considering, as a leading order approximation, the simplified equations

\[ \frac{\partial h}{\partial t} = C\nabla^2 h - D\nabla^4 h \]  
(36)

\[ \frac{\partial \phi}{\partial t} = -A'\phi + B'\nabla^2 \phi - E'\nabla^4 \phi, \]  
(37)
in which both the term \(-A\phi\) of Eq.\((18)\), and the term \(C'\nabla^2 h\) of Eq.\((19)\), have been neglected. Critically, we observe that in this approximation, the equations have completely decoupled. Of course, a small correction to the solution of these equations preserves the coupling and so prevents the two fields from evolving completely independently. However, this correction would be expected to have relative magnitude \(\frac{AC'}{CA} \ll 1\), and so we label this limit as the *limit of weak coupling*.

The linear stability of this simplified system is quite simple; inserting the standard ansatz \((5)\) into Eqs.\((36)-(37)\), we find the two solutions for the dispersion relation satisfy

\[ \sigma_1(k) = -Ck^2 - Dk^4 \]  
\[ \sigma_2(k) = -A' - B'k^2 - E'k^4. \]

However, because both \(C\) and \(D\) are assumed positive in our regime, the first growth rate is negative for all wavenumbers, and the stability of the system is entirely determined by the second solution \((39)\) associated with concentration. There, if \(B'\) is negative, the most unstable mode \(k_{\text{max}}\) of this approximate model, defined via \(\sigma'(k_{\text{max}}) = 0\), is

\[ k_{\text{max}} = \left( \frac{-B'}{2E'} \right)^{\frac{1}{2}} = \left( \frac{-F''(c_0)}{2\tilde{\varepsilon}} \right)^{\frac{1}{2}}, \]

which gives a most unstable wavelength of

\[ \lambda_{\text{max}} = 2\pi \sqrt{\frac{2\tilde{\varepsilon}}{-F''(c_0)}}. \]

If one takes a very crude model of the free energy of mixing

\[ F_{\text{mix}} = H_{\text{mix}}(c) - TS_{\text{mix}}(c), \]

with the enthalpy of mixing \(H_{\text{mix}}\) a strongly convex function of concentration near the steady state \(c_0\) (as in Figure \((1)b)\), and the entropy of mixing \(S_{\text{mix}}\) obeying a standard solution model that is more weakly convex,

\[ H''_{\text{mix}}(c_0) < S''_{\text{mix}}(c_0) < 0, \]

then the denominator \(-F''(c_0)\) inside the square root is a decreasing function of the temperature \(T\). Provided the temperature (or its effective equivalent \([40]\)) grows with ion
energy, then the model predicts an increasing wavelength as the ion energy increases, which is at least qualitatively consistent with existing experimental results \[41\].

Turning to the bifurcation criteria, defined via \( \sigma (k_{\text{max}}) > 0 \), we have simply

\[
\frac{(B')^2}{4E'} > A',
\]  

(41)

or in physical parameters,

\[
\frac{\tilde{D} \, \Omega \, \Delta}{4\tilde{\varepsilon} \, \Delta} \left[ F'' (c_0) \right]^2 > P_0 [c_{B,B} A'_A (c_{A,0}) + c_{A,B} A'_B (c_{B,0})].
\]  

(42)

Here, on the left-hand side of the inequality, \( F (c_0) \) and \( \tilde{\varepsilon} \) are associated with the energetics (driving force) of the binary material, and \( \tilde{D} \) with the kinetics (mobility). On the right-hand side, the expanded parameter \( A' \) describes the replenishment of species \( A \) from the bulk, minus the sputter rate of species \( A \) at the interface; it thus represents an ion-energy dependent net replenishment rate, which is proportional to the net sputter rate. Unfortunately, many of the parameters in the inequality \(42\) vary non-trivially with ion energy, and more study is needed to extract precise predictions. However, qualitatively, the instability criteria is clearly a competition between chemical energetics and kinetics on the one hand, and ion erosion on the other. Even more simply, the criteria can be expressed as a comparison of two timescales: instability will occur only if the amorphous layer has enough time to phase separate before it is sputtered away and replaced with fresh material from the bulk.

D. Unique Role of the ion Beam.

It is worth taking special note of three unique contributions of the ion beam to the regime described here, relative to more typical thermally-driven phase separation systems. First, the makes phase separation energetically possible: by preferentially sputtering one component of a common binary material, it drives the system from an energetically-stable stoichiometry to an energetically-unstable one. Second, it makes phase separation possible kinetically. Normally, even in an unstable stoichiometry, the film would not phase separate at room temperature. However, the ion beam supplies a great deal of noise into the film, giving atoms the mobility to travel down gradients of the chemical potential.
Figure 2. An schematic illustration of the connection between ion assisted phase separation and thermal phase separation, revealed in the limit of weak coupling $A \gamma \ll C \alpha$. Here, the effect of material replenishment is subtract a constant from the dispersion relation, which shifts the entire curve downward. This turns the longwave instability typical of thermal phase separation into one with a narrow band of unstable modes.

Finally, and most striking, the ion beam transforms phase separation from a longwave into a finite-wavelength process, as illustrated in Fig. 2. In a standard, thermally-driven phase separation system, one has the Cahn-Hilliard equation \([34]\), for which the linearization yields

$$\frac{\partial \phi}{\partial t} = -B' \nabla^2 \phi - E' \nabla^4 \phi.$$ \hspace{1cm} (43)

This equation is unstable, but the instability is longwave: i.e., the long-wavelength modes near $k = 0$ are unconditionally unstable. Because of this feature of the instability, thermal phase separation generically exhibits disordered structures and coarsening, under the well-known Ostwald Ripening phenomenon \([42]\). In contrast, under ion-irradiation, fresh material, at the bulk concentration, is always entering the film as the old material is sputtered away \([21, 35]\). This process contributes the leading-order damping term $\phi_t \propto -A' \phi$ in Eqn. (37), which stabilizes the long waves and prevents coarsening, enabling the emergence of ordered patterns. Ironically, this term is similar to one conjectured to exist a decade ago by the original observers of ordered dots in GaSb \([8]\), except that it is located
in the equation for the concentration field rather than that of the height field. Indeed, it was obtained even earlier to describe phase separation during deposition [43], in an envisioned limit of surface confined atomic mobility. Ion beams may thus be seen as a tool able to achieve this intriguing theoretical limit.

V. A DISTINGUISHING EXPERIMENTAL SIGNATURE

Any proposed alternative to an existing theory must be testably distinguishable from the original. We therefore provide here an experimental signature that distinguishes between the morphological instability of Bradley and Shipman [21, 22], and the chemically-driven instability just proposed. The signature arises from the structure of the matrix in Eq.(6) describing the linear evolution of perturbations, which we will examine through the lens of each theory in turn. It will be particularly important in what follows to carefully recall the definition of the coefficient $A$ in Eq.(3). This coefficient is often described as representing “preferential sputtering.” However, the phrase “preferentially sputtered” is most naturally interpreted as a statement on the relative values of $\Lambda (c)$: i.e., the material with the greater value of $\Lambda$ is preferentially sputtered, and leads to enrichment of the opposing component. In contrast, the constant $A$ contains the derivatives $\Lambda'(c)$ of the sputter yields. It therefore characterizes the effect of changing concentration on the total erosion rate. It is entirely possible for species $A$ to have a larger yield than species $B$, and hence to be “preferentially sputtered,” but simultaneously to induce less total erosion when its concentration is increased.

This possibility is illustrated in Figure 3 by two potential, idealized yield curves for the system Ar→GaSb (the true curves are unknown), where one observes Sb to be preferentially sputtered during the early stages of irradiation. In the first sketch, we illustrate the possibility that the concentration dependence of the yields of Ga and Sb are assumed to be linearly proportional to concentration. Hence, because Sb is preferentially sputtered from a target at the 50/50 composition, then increasing the total amount of Sb increases the total sputter rate, and we would choose Sb to be species A. An alternative possibility is envisioned in the second sketch, inspired by the observation that GaSb seems to undergo Gibbsian surface segregation [44, 45], in which a very thin surface layer becomes
Figure 3. Comparison of two possible idealized yield curves $\Lambda_A (c)$, $\Lambda_B (c)$. In both figures, Sb is “preferentially sputtered” relative to Ga at the 50 at% concentration. However, the net sputtering has a qualitatively different dependence on concentration. Schematic (a) would be associated with an idealized compound for which the yields are linear in the concentration. Here, increasing antimony concentrations always lead to increased sputter rates. However, schematic (b) would describe a system subject to surface enrichment, which appears as nonlinear dependence of the yield on concentration. Here, despite the fact that antimony is preferentially sputtered at 50 at%, increasing the antimony concentration decreases the overall yield.

rich in Sb due to its lower surface energy relative to Ga. One can easily envision that this would enhance the sputtering of Sb across a wide range of concentrations, which manifests itself as a nonlinearity in the curves. Here, although Sb is “preferentially sputtered” across a wide range of concentrations, increasing the Sb concentration actually decreases the overall sputter rate, and so we would choose Ga to be species A.

With this clarification, we now consider the theory of Bradley and Shipman, to which the second row of the matrix (6) is relevant:

$$C'k^2u_1 + (\sigma (k) + A' + B'k^2) \phi_1 = 0$$

(44)

Here $\sigma > 0$ characterizes any instability, $A' > 0$ by definition (replenishment), and $B' > 0$ by assumption (simple Fickian diffusion). Hence, the relative phases of the height and concentration fields (as determined by the relative signs of $u_1$ and $\phi_1$) are determined by the sign of the coefficient $C'$. Because the Bradley-Shipman instability requires that $C' < 0$, we conclude that $u_1 \phi_1 > 0$, so that the concentration variations of species $A$ are in phase
with the height variations. The physical interpretation of this scenario is that the surface first undergoes undulations due to an erosive instability, after which the preferentially-redistributed species is driven into the valleys [21]. The negative value of the product $AC'$ implies that the species producing a higher net sputter yield is left on the hilltops, which stabilizes the longwaves (see Figure 4a).

We next turn to the chemically-driven instability proposed here, to which the first row of the matrix (6) is relevant (this row is not changed by the generalization we have performed):

$$
(\sigma (k) + Ck^2 + Dk^4) u_1 + A\phi_1 = 0.
$$

Here, again, $\sigma > 0$ characterizes any instability, we are assuming $C > 0$ as discussed above, $D > 0$ by definition, and $A > 0$ by choice of species A. Hence, we conclude that $u_1\phi_1 < 0$, so that the concentration variations are now out of phase with the height variations. A physical interpretation of this scenario, as suggested in the numerical study of Le Roy et al. [28], is that preferential sputtering first induces the material to phase-separate into large regions of 50/50 GaSb containing small islands of the species producing a lower net sputter yield, which then recede more slowly than the bulk of the surface (see Figure 4b).

Because of this notable experimental difference between the two mechanisms, it would be invaluable to determine experimentally both the relative yields of Ga and Sb in terms of the composition of the amorphous film, so as to identify the species leading to greater overall sputtering, and then to identify the relative phase of that species relative to the height field during the early stages of pattern formation. Unfortunately, although it is known that Sb sputters preferentially from a fresh 50/50 target, the relative slopes of the yield curves with respect to concentration are currently unknown, as are the relative concentrations at the peaks and troughs of the structures. Using ex-situ electron energy loss spectroscopy (EELS) applied to a single nanostructure, Le Roy et al. observe very well-defined Ga-rich caps at the top of the structure [25]. However, those observations were performed in the presence of oxygen, which preferentially reacts with Ga, and can therefore produce results that differ significantly from in-situ conditions [45]. Therefore, both sets of data needed to distinguish between the kinetic and chemical routes to instability remain (important) open experimental questions.
Figure 4. Representative illustrations of two finite-wavelength instability regimes. (a) In a kinetically-driven instability, the surface geometry is fundamentally unstable, while the chemistry follows the interface via the preferential redistribution term $C'\nabla^2 u$ in Eqn.(19). To stabilize long waves, it is necessary that the low-yield species B be preferentially pushed into the valleys, which leaves the hilltops saturated with the high-yield species A. (b) In a chemically-driven instability, the surface is fundamentally stable, following the unstable chemistry via the preferential sputtering term $-A\phi$ in Eqn.(18). Hence, the hilltops are left saturated with the low-yield species B. Mass redistribution acts to stabilize against long waves.

VI. CONCLUSIONS

Motivated by a growing body of experimental [24–27] and numerical [24, 28] evidence suggesting that phase separation plays an important role in pattern formation during the irradiation of two-component targets, and molecular dynamics simulations suggesting that existing theories neglecting this phenomenon may not explain the patterns [30], we have presented a generalization of the Bradley-Shipman theory of irradiated binary compounds [21, 22] that admits the phase separation mechanism. We demonstrated that the resulting model readily admits the development of ordered patterns even for parameter values where the BS theory cannot. A special limit suggested by the estimated parameter val-
ues allows a simple, intuitive understanding of the instability criteria, and highlights the potentially unique nature of ion-assisted phase separation relative to thermal phase separation. Finally, we identified a distinct experimental signature that distinguishes between the two instabilities, that highlights the need for specific additional experimental data on this system.

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[1] W. L. Chan and E. Chason. Making waves: kinetic processes controlling surface evolution during low energy ion sputtering. J. Appl. Phys., 101:121301, 2007.
[2] F. Frost, B. Ziberi, A. Schindler, and B. Rauschenbach. Surface engineering with ion beams: From self-organized nanostructures to ultra-smooth surfaces. Appl. Phys. A, 91:551–559, 2008.
[3] S. Facsko, T. Dekorsy, C. Koerdt, C. Trappe, H. Kurz, A. Vogt, and H. L. Hartnagel. Formation of ordered nanoscale semiconductor dots by ion sputtering. Science, 285:1551–1553, 1999.
[4] M. C. Cross and P. C. Hohenberg. Pattern formation outside of equilibrium. Reviews of modern physics, 65:851–1123, 1993.
[5] M. Cross and H. Greenside. Pattern Formation and Dynamics in Nonequilibrium Systems. Cambridge University Press, 2011. ISBN: 0521770505.
[6] B. P. Davidovitch, M. J. Aziz, and M. P. Brenner. On the stabilization of ion sputtered surfaces. Phys. Rev. B, 76:205420, 2007.
[7] C. S. Madi, B. P. Davidovitch, H. B. George, S. A. Norris, M. P. Brenner, and M. J. Aziz. Multiple bifurcation types and the linear dynamics of ion sputtered surfaces. Phys. Rev. Lett., 101:246102, 2008.
[8] S. Facsko, T. Bobek, A. Stahl, and H. Kurz. Dissipative continuum model for self-organized pattern formation during ion-beam erosion. Phys. Rev. B, 69:153412, 2004.
[9] R.M. Bradley. Redeposition of sputtered material is a nonlinear effect. *Physical Review B*, 83:075404, 2011.

[10] S. A. Norris. Stability analysis of a viscoelastic model for ion-irradiated silicon. *Physical Review B*, 85:155325, 2012.

[11] R. Gago, L. Vásquez, O. Plantevin, T. H. Metzger, J. Muñoz-García, R. Cuerno, and M. Castro. Order enhancement and coarsening of self-organized silicon nanodot patterns induced by ion-beam sputtering. *Appl. Phys. Lett.*, 89:233101, 2006.

[12] B. Ziberi, F. Frost, M. Tartz, H. Neumann, and B. Rauschenbach. Ripple rotation, pattern transitions, and long range ordered dots on silicon by ion beam erosion. *Appl. Phys. Lett.*, 92:063102, 2008.

[13] C. S. Madi, H. B. George, and M. J. Aziz. Linear stability and instability patterns in ion-sputtered silicon. *J. Phys. Cond. Matt.*, 21:224010, 2009.

[14] Charbel S. Madi and Michael J. Aziz. Multiple scattering causes the low energy-low angle constant wavelength bifurcation of argon ion bombarded silicon surfaces. *Applied Surface Science*, 258:4112–4115, 2012. (IINM2011 Bhubaneswar Conference Proceedings).

[15] G. Ozaydin, A.S. Ozcan, Y.Y. Wang, K.F. Ludwig, H. Zhou, R.L. Headrick, and D.P. Siddons. Real-time x-ray studies of Mo-seeded Si nanodot formation during ion bombardment. *Applied Physics Letters*, 87:163104, 2005.

[16] G. Ozaydin, Jr. K. F. Ludwig, H. Zhou, and R. L. Headrick. Effects of mo seeding on the formation of si nanodots during low-energy ion bombardment. *J. Vac. Sci. Technol. B*, 26:551, 2008.

[17] G. Ozaydin-Ince and K. F. Ludwig Jr. In situ x-ray studies of native and mo-seeded surface nanostructuring during ion bombardment of si(100). *J. Phys. Cond. Matt.*, 21:224008, 2009.

[18] Kun Zhang, Marc Brötzmann, and Hans Hofsäss. Surfactant-driven self-organized surface patterns by ion beam erosion. *New Journal of Physics*, 13:013033, 2011.

[19] S. Macko, F. Frost, B. Ziberi, D.F. Forster, and T. Michely. Is keV ion-induced pattern formation on Si(001) caused by metal impurities? *Nanotechnology*, 21:085301, 2010.

[20] V. B. Shenoy, W. L. Chan, and E. Chason. Compositionally modulated ripples induced by sputtering of alloy surfaces. *Physical Review Letters*, 98:256101, 2007.
[21] R. Mark Bradley and Patrick D. Shipman. Spontaneous pattern formation induced by ion bombardment of binary compounds. Physical Review Letters, 105:145501, 2010.

[22] P. D. Shipman and R. M. Bradley. Theory of nanoscale pattern formation induced by normal-incidence ion bombardment of binary compounds. Physical Review B, 84:085420, 2011.

[23] R. M. Bradley and J. M.E. Harper. Theory of ripple topography induced by ion bombardment. J. Vac. Sci. Technol., 6:2390–2395, 1988.

[24] Kazuhiko Fukutani, Koichi TANJI, Tatsuya SAITO, and Tohru DEN. Fabrication of well-aligned nanowire array embedded in Si matrix using limited spinodal decomposition. Japanese Journal of Applied Physics, 47:1140–1146, 2008.

[25] S. Le Roy, E. Barthel, N. Brun, A. Lelarge, and E. Søndergård. Self-sustained etch masking: A general concept to initiate the formation of nanopatterns during ion erosion. Journal of Applied Physics, 106:094308, 2009.

[26] Gintautas Abrasonis, Thomas W. H. Oates, Gyorgy J. Kovács, Jorg Grenzer, Per O. Å. Persson, Karl-Heinz H. Heinig, Andrius Martinavičius, Nicole Jeutter, Carsten Baehtz, Mark Tucker, Marcela M. M. Bilek, and Wolfhard Möller. Nanoscale precipitation patterns in carbon-nickel nanocomposite thin films: Period and tilt control via ion energy and deposition angle. J. Appl. Phys., 108:043503, 2010.

[27] H. Hoffmann, K. Zhang, A. Pape, O. Bobes, and M. Brötzmann. The role of phase separation for self-organized surface pattern formation by ion beam erosion and metal atom co-deposition. Appl. Phys. A, 2012.

[28] S. Le Roy, E. Søndergård, I. S. Nerbo, M. Kildemo, and M. Plapp. Diffuse-interface model for nanopatterning induced by self-sustained ion-etch masking. Physical Review B, 81:161401(R), 2010.

[29] C. C. Umbach, R. L. Headrick, and K.-C. Chang. Spontaneous nanoscale corrugation of ion-eroded SiO₂: The role of ion-irradiation-enhanced viscous flow. Phys. Rev. Lett., 87:246104, 2001.

[30] Scott A. Norris, J. Samela, K. Nordlund, M. Vestberg, and M. Aziz. Molecular dynamics estimation of coefficients for irradiated binary alloys: Testing the bradley-shipman theory. arXiv, 2013.
[31] S. A. Norris, M. P. Brenner, and M. J. Aziz. From crater functions to partial differential equations: A new approach to ion bombardment induced nonequilibrium pattern formation. 
*J. Phys. Cond. Matt.*, 21:224017, 2009.

[32] S. A. Norris, J. Samela, L. Bukonte, M. Backman, D. F. K. Nordlund, C.S. Madi, M.P. Brenner, and M.J. Aziz. Molecular dynamics of single-particle impacts predicts phase diagrams for large scale pattern formation. *Nature Communications*, 2:276, 2011.

[33] M. Hansen, K. Anderko, R. P. Elliot, and F. A. Shunk. *Constitution of Binary Alloys*. New York, McGraw-Hill, 1958.

[34] J. W. Cahn and J. E. Hilliard. Free energy of a nonuniform system. I. Interfacial free energy. 
*J. Chem Phys*, 28:258, 1958.

[35] R. Mark Bradley. Theory of nanodot and sputter cone arrays produced by ion sputtering with concurrent deposition of impurities. *Physical Review B*, 83:195410, 2011.

[36] R. M. Bradley. Surface instability of binary compounds caused by sputter yield amplification. 
*Journal of Applied Physics*, 111:114305, 2012.

[37] G. Abrasonis and K. Morawetz. Instability types at ion-assisted alloy deposition: from two-dimensional to three-dimensional nanopattern growth. *Physical Review B*, 86:085452, 2012.

[38] Yong Lu, Cuiping Wang, Yipeng Gao, Rongpei Shi, Xingjun Liu, and Yunzhi Wang. Microstructure map for self-organized phase separation during film deposition. *Phys. Rev. Lett.*, 109:086101, 2012.

[39] E. M. Foard and A. J. Wagner. Survey of morphologies formed in the wake of an enslaved phase-separation front in two dimensions. *Phys. Rev. E*, 85:011501, 2012.

[40] G. Martin. Phase stability under irradiation: Ballistic effects. *Phys. Rev. B*, 30:1424–1436, 1984.

[41] S. Facsko, H. Kurz, and T. Dekorsy. Energy dependence of quantum dot formation by ion sputtering. *Phys. Rev. B*, 63:165329, 2001.

[42] W. Ostwald. Über die vermeintliche isomerie des roten und gelben quecksilberoxyd und die oberflächenspannung fester körper. *Z. Phys. Chem.*, 34:495, 1900.

[43] M. Atzmon, D. A. Kessler, and D. J. Srolovitz. Phase separation during film growth. *Journal of Applied Physics*, 72:442–446, 1992.
[44] W. Yu, J. L. Sullivan, and Saied S. O. Xps and leiss studies of ion bombarded gasb, insb and cdse surfaces. *Surface Science*, 352–354:781–787, 1996.

[45] O. El-Atwani, J. P. Allain, A. Cimaroli, A. Suslova, and S. Ortoleva. The significance of in situ conditions in the characterization of gasb nanopatterned surfaces via ion beam sputtering. *Journal of Applied Physics*, 110:074301, 2011.