

Elastic Relaxations in Ultrathin Epitaxial Alloy Films

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Elastic interactions responsible for the stability of nanometer-scale patterns in ultrathin, bulk-immiscible-alloy films are analyzed within the context of a hybrid atomistic-continuum model. Two apparently different descriptions of alloy film behavior, a continuum elasticity theory describing a deformable substrate and a rigid substrate atomistic scheme, emerge naturally as limiting cases on long and short length scales, respectively. Quantitative first-principles calculations explain the origin of recently observed nanoscale patterns in Co-Ag/Ru(0001), and reveal a surprising failure of the continuum model.

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Recently a growing number of experimental observations have reported the spontaneous formation of nanoscale domain structures on morphologically flat, compositionally inhomogeneous crystalline surfaces. Examples include the hexagonal ordering of “holes” in strained Ag monolayers after exposure to sulfur [1], the formation of monodisperse N-vacancy clusters on $\text{In}_{1-x}\text{Ga}_x\text{N}(0001)$ [2], and lateral composition modulations in thin (1–4 ML) films of size-mismatched, bulk immiscible Co-Ag and Fe-Ag alloys on Mo(110) [3] and Ru(0001) [4,5]. An explanation for the stability of periodic surface structures was given by Marchenko [6] and later by Ng and Vanderbilt [7] who showed, using continuum elasticity models, that the energy of compositionally nonuniform surfaces can be lowered through the formation of periodic stress domains. Within these models it is well understood that nanoscale patterns emerge as a result of the competition between short-range clustering tendencies (e.g., energy cost associated with line interfaces between two immiscible surface alloy phases) and long-range dipolar (e.g., elastic) interactions that favor mixing.

While the continuum theories of Refs. [6,7] successfully explain observed morphologies, few studies have attempted to explore their range of applicability quantitatively. In particular, it is not clear that the continuum elasticity treatment of stress relaxation is accurate when the characteristic length scale of composition modulation is only a few nanometers. At small wavelengths the atomistic structure and the details of surface-substrate bonding likely play a dominant role, while the continuum theory is strictly valid only at large wavelengths. Furthermore, a key question arises from the point of view of controlling self-assembly that is difficult to address quantitatively within the framework of the continuum theory, namely how to predict the preferred wavelength of patterned structures in a specific system from first principles.

In this paper we consider a pseudomorphic monolayer film of an $A_{1-c}B_c$ alloy. The total surface energy can

be thought of as a sum of two contributions: a direct “chemical” interaction energy due to quantum-mechanical bonding effects, and an elastic contribution due to atomic size mismatch. The distribution of alloy species on the surface is described by pseudospin variables S_i assuming values $+1$ (-1) if the lattice site i is occupied by an atom of type A (B). The direct chemical interactions can be conveniently expressed in an Ising-like form [8,9]: $H_{\text{chem}} = \frac{1}{2} \sum_{i,j} V_{ij} S_i S_j + \frac{1}{3!} \sum_{i,j,k} V_{ijk} S_i S_j S_k + \dots$, where V_{ij}, V_{ijk}, \dots are effective pair and multibody interactions. As with the case of bulk alloys [8], the above Hamiltonian can be utilized to examine the ordering tendencies of surface alloys. Such a study of Au-Pd alloys on Ru(0001) was carried out by Sadigh *et al.* [10], who found that, in Au-Pd, the interactions are very short ranged. Standard *ab initio* electronic-structure computations could be used to generate V_{ij} and V_{ijk} . However, for alloys with large size mismatch, long ranged elastic interactions render the inversion procedure used by Sadigh *et al.* impractical, as its application to such systems would require many large unit cell, first principles computations. The model developed here provides a framework for generating an accurate Hamiltonian requiring a limited number of *ab initio* energies and thus establishes an important link between atomistic simulations and continuum theories. Additionally, the atomistic/continuum model presented below provides a clear framework for analyzing the physical origin of the interatomic interactions, i.e., the relative importance of elastic, chemical, and substrate-relaxation terms.

We start from a coarse-grained model of the film+substrate system, shown in Fig. 1. The system is split into two separate, but interacting regions: the top surface alloy layer is treated atomistically, while the energy of the underlying substrate can be treated from discrete (lattice) or continuum theories of elasticity. This subdivision enables us to capture the effects of elastic relaxations on both atomistic and continuum length scales. The total Hamiltonian can be expressed as a sum of three

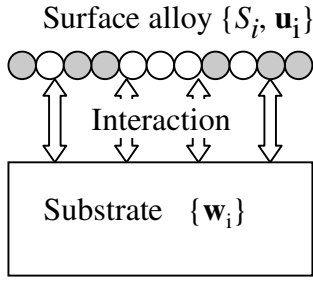


FIG. 1. Partitioning scheme leading to Hamiltonian (1).

terms, $H = H_{\text{surf}} + H_{\text{bulk}} + H_{\text{int}}$, corresponding to the surface energy, substrate elastic energy, and interaction between the substrate and surface atoms, respectively. The surface layer is described using configuration variables S_i and atomic displacements \mathbf{u}_i . The substrate degrees of freedom, \mathbf{w}_i , describe elastic deformations in the subsurface layer. A generic Hamiltonian for the system shown in Fig. 1 can be written as

$$H = \frac{1}{2} \sum_{i,j} \left(J_{ij} S_i S_j + 2 \sum_{\alpha} \Gamma_{ij}^{\alpha} u_{i\alpha} S_j + \sum_{\alpha,\beta} \Phi_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta} \right) + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} T_{ij}^{\alpha\beta} w_{i\alpha} w_{j\beta} + \sum_{i,j} \sum_{\alpha,\beta} A_{ij}^{\alpha\beta} u_{i\alpha} w_{j\beta}, \quad (1)$$

where Latin indices run over lattice sites and Greek indices label Cartesian components. The surface energy H_{surf} is represented by the first term in Eq. (1) in a form that is widely used in studies of bulk alloys [11,12]. The first term in the parentheses is the surface chemical energy, characterized by Ising-like pair interactions J_{ij} , the third term provides the elastic deformation energy of the surface layer, where $\Phi_{ij}^{\alpha\beta}$ is a surface force constant matrix, while the second term, familiar from the theory of Kanzaki forces in bulk alloys [11], leads to composition-induced surface stresses. The elastic energy of the bulk substrate, H_{bulk} , is represented by the second term in Eq. (1), where $T_{ij}^{\alpha\beta}$ is related to the inverse of the substrate Green's function. Finally, the surface-substrate interaction H_{int} is given by the last term in Eq. (1), where the matrix $A_{ij}^{\alpha\beta}$ can be interpreted as a corrugation potential. It determines the force on the substrate below site j due to a surface atom displacement at site i . The Hamiltonian (1) resembles energy functionals commonly used in continuum theories of film structure [13].

Conditions of mechanical equilibrium for the Hamiltonian (1) give a system of equations that determines equilibrium values of the displacements \mathbf{u}_i and \mathbf{w}_i :

$$\sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_{j\beta} = - \sum_j \Gamma_{ij}^{\alpha} S_j - \sum_{j,\beta} A_{ij}^{\alpha\beta} w_{j\beta}, \quad (2)$$

$$\sum_{j,\beta} T_{ij}^{\alpha\beta} w_{j\beta} = - \sum_{j,\beta} A_{ji}^{\beta\alpha} u_{j\beta}. \quad (3)$$

These equations can be solved using a Fourier transform (the general technique is discussed in Ref. [12]). Introduc-

ing the structure factor $S(\mathbf{k}) = \frac{1}{N} \sum_i S_i e^{-i\mathbf{k}\mathbf{R}_i}$, the Hamiltonian (1) can be expressed as

$$H = \frac{1}{2} \sum_{\mathbf{k}} V(\mathbf{k}) |S(\mathbf{k})|^2, \quad (4)$$

where $V(\mathbf{k}) = \sum_j V_{ij} e^{-i\mathbf{k}\mathbf{R}_j}$ is a Fourier transform of effective pair interactions. $V(\mathbf{k})$ includes the effects of all chemical and elastic interactions in the system. As a result, an enormous simplification of the original problem has been achieved, since the effects of surface and substrate relaxations are included exactly in the framework of a discrete lattice model.

The general expression for $V(\mathbf{k})$ is rather complicated, but interesting insights can be gained by considering the limiting case of a very stiff substrate, relevant to Co-Ag/Ru. For this system, first-principles calculations [5] for energetically favored striped superstructures show that $w_{i\alpha} \ll u_{i\alpha}$, i.e., displacements in the surface layer are much larger than the substrate deformation. This result can be rationalized by noting that, due to reduced coordination, it is much easier to slide the surface layer with respect to the substrate than to deform bulk Ru. Neglecting the term with \mathbf{w}_i in Eq. (2), we find that $u_{\alpha}(\mathbf{k}) = -S(\mathbf{k}) \sum_{\beta} [\Phi(\mathbf{k})^{-1}]_{\alpha\beta} \Gamma_{\beta}(\mathbf{k})$, while substrate displacements are found by inverting Eq. (3). In this approximation, the substrate relaxes in response to a force created by surface atom displacements: $F_{\alpha}(\mathbf{k}) = -\sum_{\beta} A_{\alpha\beta}(\mathbf{k}) u_{\beta}(\mathbf{k})$. Notice, however, this "stiff substrate" limit $w_{i\alpha} \ll u_{i\alpha}$ does not imply that the substrate elastic strain energy vanishes completely. The final two terms in Eq. (1) must still be evaluated, yielding the following expression for $V(\mathbf{k})$:

$$V(\mathbf{k}) = \Gamma(\mathbf{k})^{\dagger} [\Phi(\mathbf{k})^{-1} + \Xi(\mathbf{k})^{\dagger} \mathbf{T}(\mathbf{k})^{-1} \Xi(\mathbf{k})] \Gamma(\mathbf{k}), \quad (5)$$

where we have introduced matrix notation for Cartesian components, " \dagger " denotes conjugate transpose, and $\Xi(\mathbf{k}) = \mathbf{A}(\mathbf{k}) \Phi(\mathbf{k})^{-1}$. The more general case, including a distinction between soft and stiff substrate limits, will be described elsewhere.

While it is possible to directly compute most of the matrices entering Eq. (1) for any given system, it is desirable to express them, and therefore $V(\mathbf{k})$, in terms of a few simple physical parameters. To this effect, we consider a model where the surface energy H_{surf} and surface-substrate interaction H_{int} terms are found from the two-dimensional Frenkel-Kontorova scheme [14]. The first (chemical energy) term in the parentheses in Eq. (1) is represented by nearest-neighbor (NN) chemical interactions J . Elastic interactions within the surface layer [the second and third terms in the parentheses in Eq. (1)] are modeled by harmonic springs with stiffnesses K_{ij} and equilibrium bond lengths $a + \Delta_{ij}$, where a is the substrate lattice constant. Expressing the first-order change in interatomic separation as $\delta r_{ij} = (\mathbf{u}_j - \mathbf{u}_i) \cdot \mathbf{e}_{ij}$, where \mathbf{e}_{ij} is a unit vector from surface site i to site j , the surface elastic energy is given by $\frac{1}{4} \sum_{i,j} K_{ij} (\delta r_{ij} - \Delta_{ij})^2$. We neglect all

interactions beyond nearest neighbors and assume that NN spring constants K are independent of atom types. The equilibrium bond length between the atoms of type $A(B)$ is $a + \Delta$ (or $a - \Delta$), and the A - B bondlength is lattice matched to the substrate, i.e., we set $\Delta_{ij} = \Delta \frac{S_i + S_j}{2}$. These choices limit the summation over i and j in Eq. (1) to on-site and NN-pair terms, where $\Gamma_{ij}^\alpha = K\Delta e_{ij}^\alpha$ and $\Phi_{ij}^{\alpha\beta} = K\delta_{ij} \sum_l^{\text{NN}} e_{il}^\alpha e_{il}^\beta - Ke_{ij}^\alpha e_{ij}^\beta$. For the H_{int} term, we assume that all surface atoms experience identical, radially symmetric corrugation potentials linking each surface atom to the substrate deformation directly below. In other words, the interaction energy is given by $H_{\text{int}} = \frac{A}{2} \sum_i (\mathbf{u}_i - \mathbf{w}_i)^2$. Finally, the elastic energy of the substrate, H_{bulk} , is described using the half-space Green's function of the isotropic continuum elasticity theory [15]. The latter depends on $(1 - \nu^2)/E$, where ν is the Poisson ratio and E is the Young's modulus of the bulk substrate.

After straightforward, but somewhat lengthy algebraic manipulations, an explicit form of $V(\mathbf{k})$ for a given surface can be found [16]. As an illustrative example, we give an analytic expression in the one-dimensional case, applicable to [100] stripes on the (0001) surface of a stiff hexagonal substrate:

$$V(k) = -8J' \sin^2(kd/2) - \frac{3K\Delta^2 \sin^2(kd)}{\frac{A}{K} + 6 \sin^2(kd/2)} - \frac{1 - \nu^2}{ES_0 k} |Au(k)|^2, \quad (6)$$

where $d = a\sqrt{3}/2$ is the separation between consecutive rows of atoms and $S_0 = a^2\sqrt{3}/2$ is the surface area per atom. $J' = J + K\Delta^2/4$ represents a renormalized NN interaction. Fourier components of surface atom displacements are given by

$$u(k) = -\frac{i\sqrt{3}\Delta \sin(kd)}{\frac{A}{K} + 6 \sin^2(kd/2)}. \quad (7)$$

The physical meaning of the individual terms in Eq. (6) is as follows. The first term represents the energy, elastic and chemical, stored in a system where all atoms reside on ideal lattice sites. The second term is the energy lowering due to lateral relaxations within the surface layer and it can be shown that this contribution can be described by interactions V_n that decay exponentially with distance similar to those obtained in the widely used Frenkel-Kontorova scheme [14]. The final term is the energy gain due to substrate relaxations. It gives rise to long range elastic interactions which decay in real space as $1/R^3$ and is analogous to the Marchenko [6] and Ng-Vanderbilt [7] continuum results.

Notice that the $V(k)$ derived above depends on just four parameters: (i) $K\Delta^2$ sets the energy scale for elastic relaxations, (ii) $\alpha = 4J/(K\Delta^2)$ gives the relative strength of chemical and elastic energies, (iii) $\kappa = K/A$ determines surface atom relaxations $u(k)$ and, more importantly, the range of elastic interactions associated with these re-

laxations, and (iv) the ratio $\beta = 6Kd(1 - \nu^2)/(ES_0)$ determines the magnitude of the substrate relaxation contribution to $V(k)$. The parameter Δ scales the magnitude of the displacement field $u(k)$, but it affects $V(k)$ only via the combination $K\Delta^2$. In the long-wavelength limit $k \rightarrow 0$, the substrate relaxation term always dominates, since it behaves as $-\frac{K\Delta^2}{2}\beta(kd) + O(k^3)$ while the other terms go as $-\frac{K\Delta^2}{2}(1 + \alpha + 6\kappa)(kd)^2 + O(k^4)$.

The functional form of $V(\mathbf{k})$ allows one to predict the morphology of the equilibrium surface phase. A particularly important quantity is the position of the minimum in $V(\mathbf{k})$, since it determines the wavelength of the energetically most unstable mode in a disordered surface alloy (see Fig. 2). Existence of such a minimum is guaranteed, since with the inclusion of elastic interactions, $V(\mathbf{k}) \propto -k$ as $\mathbf{k} \rightarrow 0$, a property that guarantees a finite periodicity of the energetically preferred composition modulation. In what follows, we assume that J is negative, corresponding to the physically interesting case of chemical tendency to phase separate. Explicit expressions for the minimum in $V(k)$ can be derived from Eq. (6) in the following limits:

(a) The substrate relaxation contribution can be neglected and the minimum wave vector k_{min} is determined by the sum of the interfacial energy and surface relaxation terms in Eq. (6). It is shown below that Co-Ag/Ru(0001) belongs to this class of systems. Then the wave vector of the most unstable mode is given by $k_{\text{min}} = \frac{1}{d}(-\frac{4}{3\alpha\kappa})^{1/4} + \frac{1+3\alpha}{3d}(-\frac{1}{6\alpha\kappa})^{3/4} + O[(\frac{1}{\alpha\kappa})^{5/4}]$, i.e., it decreases with increasing $|\alpha\kappa| = |4J/(A\Delta^2)|$. For reasonable values of α and κ , k_{min} is on the order of a fraction of \AA^{-1} . Therefore, phase separating surface atom interactions and a weak substrate corrugation potential can combine to produce nanoscale composition modulations.

(b) For sufficiently strong clustering tendencies represented by the NN chemical interaction J , the surface relaxation contribution alone cannot overcome the tendency to phase separate. Mathematically, the sum of the first two terms in Eq. (6) produces a minimum at $k = 0$ when

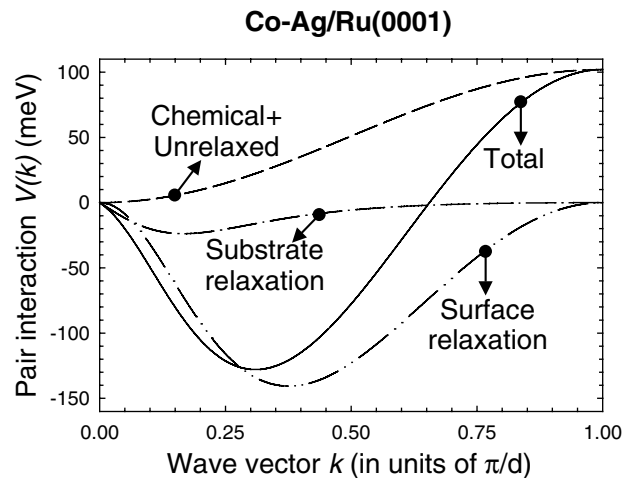


FIG. 2. First-principles pair interactions $V(\mathbf{k})$ for Co-Ag on Ru(0001).

$1 + \alpha + 6\kappa < 0$, which is a hallmark of tendency to phase separate [12]. In this case, the substrate relaxation term plays a major role, since it guarantees the existence of a minimum in $V(k)$ at nonzero $k_{\min} = \frac{-\beta}{2d(1+\alpha+6\kappa)}$. On the length scale of $2\pi/k_{\min}$ the total energy is accurately represented by a sum of interfacial line tension (which includes surface atom relaxation energy) and substrate-mediated dipolar repulsion terms. The continuum theories of Marchenko [6] and Ng and Vanderbilt [7] can be used to study the energetically stable stripe and droplet patterns.

As an illustrative example, Fig. 2 shows $V(\mathbf{k})$ for Co-Ag on Ru(0001), obtained using previously published local spin-density functional (LSDA) results for this system [5]. The values of J , $\kappa = K/A$, and $K\Delta^2$ were determined by fitting the calculated formation energies of periodic stripe structures at 50/50 composition. The ratio β was obtained using the calculated surface stress difference of Co and Ag monolayers on Ru(0001) and calculated elastic constants of hcp Ru for an uniaxial deformation perpendicular to the [0001] direction. This procedure yields values $K\Delta^2 = +185$ meV, $J = -59$ meV, $\kappa = 0.66$, and $\beta = 0.91$. LSDA energies of stripes were reproduced to better than 5 meV/atom. The most striking observation from Fig. 2 is the smallness of the substrate relaxation term. The energy gain due to substrate relaxation is only a few meV/atom in this system. It is thus an excellent approximation to assume that the position of the minimum in $V(\mathbf{k})$ is determined by the first two terms in Eq. (6), i.e., Co-Ag alloys on Ru belong to case (a) considered above. Thus, the unusual disordered alloy structures observed experimentally in Ref. [5] can be attributed to Frenkel-Kontorova-type elastic relaxations within the surface layer and do not arise from substrate relaxation contributions. The predicted minimum wavelength for composition modulation ($2\pi/k_{\min} \approx 1.6$ nm) corresponds well with the feature size observed by scanning tunneling microscopy in Ref. [5] in annealed Co-Ag/Ru(0001) films.

The dominant contribution from relaxations within the surface layer has important consequences for the structure of the alloy film. Specifically, the equilibrium displacement fields associated with this term show an exponential decay, with a decay constant that is a function of $\kappa = K/A$ [which can be deduced from Eq. (7)], whereas the substrate-mediated interactions are associated with slowly decaying dipolar strain fields. This important distinction between the present model and the continuum-dipolar theory should hold generally for surface-alloy systems on stiff substrates, and is amenable to experimental verification through measurements of displacement fields by surface-sensitive microscopy (e.g., STM) or x-ray scattering methods.

In conclusion, we have developed a model of ultra-thin alloy films that captures two physically distinct limit-

ing behaviors: In the long-wavelength limit, our model reproduces the continuum elasticity theory of Ref. [6], while at short wavelengths it is analogous to the atomistic Frenkel-Kontorova scheme [14]. We demonstrate how the parameters of our model can be determined from first-principles electronic-structure calculations to predict the preferred size scale of self-assembled patterns in real systems. Results for the Co-Ag surface alloy on Ru(0001), where nanoscale pattern formation has been recently observed in Refs. [4,5], show that in this case the energetics is dominated by relaxations within the surface layer, while the substrate relaxation contributes a very small amount (less than 10%) to the total formation energies of stable nanostructures. These findings point to limitations of the continuum theory [6,7] in describing structures with nanometer periodicity.

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 - [16] Normal displacements u_{iz} can be decoupled from the lateral components u_{ix} and u_{iy} using the fact that the corresponding off-diagonal elements of \mathbf{A} , $\mathbf{\Phi}$, and $\mathbf{\Gamma}$ vanish for a wide class of substrate orientations and interatomic forces. Indeed, it is easy to show that $A_{ii}^{xz} = A_{ii}^{zx} = A_{ii}^{yz} = A_{ii}^{zy} = 0$ for all surfaces with a C_{2v} symmetry or higher and that $\Gamma_{ij}^z = 0$ and $\Phi_{ij}^{xz} = \Phi_{ij}^{yz} = 0$ for all pairwise radial forces. Normal displacements of surface atoms are given by $u_{iz} = w_{iz}$, and w_{iz} are determined by the substrate Poisson effect.