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Strong effect of substrate symmetry and pre-patterning on self-assembly of compositional patterns

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ABSTRACT

First-principles-based computer simulations are employed to elucidate the effects of substrate symmetry and externally applied “potentials” on directing self-assembly of highly ordered nanoscale patterns. We focus on alloy films as a specific example where the energetics underlying composition modulation can be accurately quantified. We demonstrate that even relatively weak external potentials, with periodicities considerably larger than the intrinsic composition modulation wavelengths, can be highly effective in stabilizing ordered compositional patterns at the nanoscale.

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The spontaneous formation of nanometer-scale stripe and droplet patterns is commonly observed in a wide variety of two-dimensional systems [1], including strained alloy films [2–4], Langmuir–Blodgett monolayers [5], and diblock copolymers [6]. Such pattern-forming systems have received considerable attention for potential applications in nanoelectronics, nanophotonics, high-density magnetic storage, and as templates for hierarchical assembly of complex nanostructures. These applications, however, require highly ordered patterns, and the pronounced disorder intrinsic to many two-dimensional systems represents a fundamental obstacle to their widespread use. Pattern formation in two-dimensional systems is typically understood to reflect a competition between short-range attractive “chemical” interactions, and longer-ranged repulsive interactions arising from elastic strain or electrostatics [1,7,8]. As a result of these competing interactions, the energy may be minimized by the formation of modulated stripe or droplet phases with periodicities in the range of 1–100 nm. In such systems, self-assembly occurs upon annealing at temperatures high enough to allow for appreciable mobility of component species, yet low enough that the patterns are not destroyed by thermal fluctuations.

We consider a particular class of two-dimensional pattern-forming systems, namely ultrathin epitaxial alloy films of size-mis-

matched and bulk-immiscible atomic species. In these materials compositional patterns reflect phase-separation at the nanoscale, allowing for a partial relief of the surface stress at the expense of introducing line boundaries between the two phases. The structure and dynamics of such systems have been extensively studied experimentally [2–4,9–14], and the nature of the patterns that form in them has been the subject of numerous modeling studies based on continuum theories [15–23]. The latter have pointed to interesting possibilities for directing the self-assembly process [19–23]: it has been shown that “pre-patterned” chemical variations on the substrate, and elastic fields induced, e.g., by sub-surface dislocations, can be used to manipulate the scale, symmetry and regularity of the compositional patterns. While these studies suggest very interesting possibilities, outstanding questions remain concerning the strength and periodicity of the external potentials needed to realize highly ordered patterns in the presence of thermal fluctuations that tend to disorder them. The purpose of the present work is to address these questions quantitatively using Monte-Carlo computer simulations, employing a first-principles-based model of the thin-film alloy energetics.

To model self-assembly in epitaxial alloy films, we have developed a first-principles-based hybrid atomistic-continuum model of the configurational energetics [24,25]. The theory makes use of analytical solutions to the elastic fields in the film and substrate induced by lateral composition modulation within the thin film, employing a discrete description of elastic energy in the surface

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layer, and a continuum Green's-function for the substrate response. The mixing energy of a pseudomorphic thin-film alloy is expressed as

$$\Delta E = \sum_{\mathbf{q}} V(\mathbf{q}) |S(\mathbf{q})|^2 \quad (1)$$

where $V(\mathbf{q})$ is an ordering potential describing the contribution to the energy arising from a sinusoidal composition modulation with lateral two-dimensional wave-vector \mathbf{q} and Fourier amplitude $S(\mathbf{q})$. This model can be fit to first-principles calculations, providing a quantitative parameter-free model of ordering energetics. An important feature of the method is that Eq. (1) can be used as the basis for Monte-Carlo simulations, to investigate the nature of the equilibrium patterns that form at finite temperature, and their stability with respect to thermal fluctuations. The ability of the method to predict stable composition wavelengths, and to incorporate thermal fluctuations, with no adjustable parameters, are distinguishing features of the approach relative to continuum models that have

been employed previously to investigate pattern formation in strained binary films.

We consider equiatomic monolayer epitaxial thin films of Fe–Ag alloys on two substrates widely used in experimental investigations, namely Mo(110) and Ru(0001). Fe–Ag is one example of a bulk-immiscible alloy system where nanoscale compositional patterns have been observed to form experimentally [2,12]. From a theoretical point of view it is interesting to consider the relative similarities and differences between pattern-forming tendencies for Fe–Ag on Mo(110) and Ru(0001), since both substrates offer nearly identical nearest-neighbor spacings, implying that the epitaxial-strain contributions to the alloying energetics should be similar for both. As described below, the most relevant difference between the two substrates is their symmetry: while the (110) surface of the body-centered-cubic Mo crystal is two-fold symmetric, the Ru(0001) surface possesses six-fold symmetry.

Details surrounding the first-principles parameterization of $V(\mathbf{q})$ for equiatomic FeAg films on Ru(0001) and Mo(110) substrates

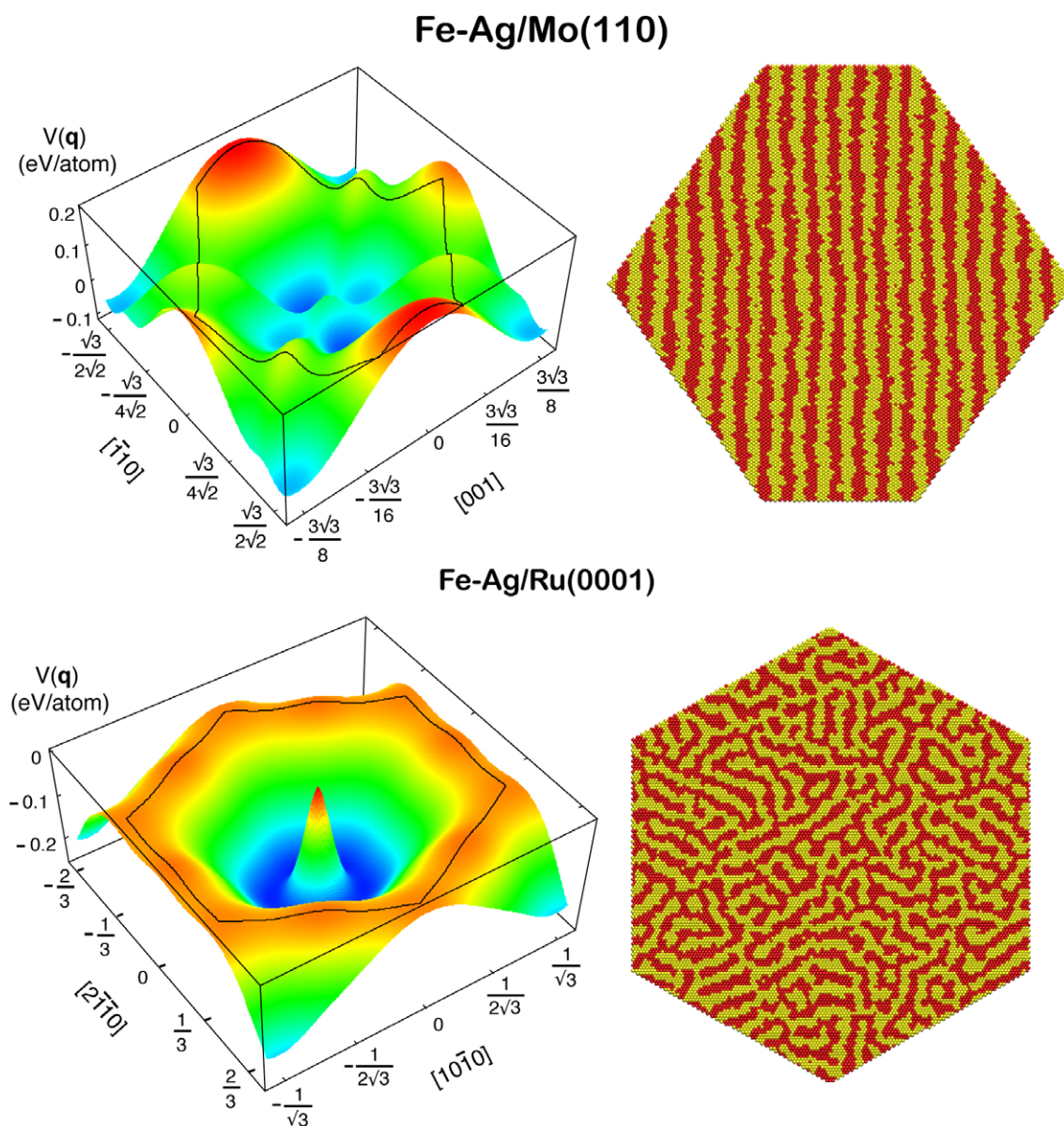


Fig. 1. First-principles calculated ordering potentials $V(\mathbf{q})$ are plotted for FeAg alloys on Mo(110) and Ru(0001) substrates on the upper and lower left, respectively. The equilibrium compositional patterns derived from Monte-Carlo simulations based on these ordering potentials are illustrated by the snapshots on the right, where the stripe periodicities are roughly 2 nm.

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