First-Principles Theory of Elastic Relaxations and Lateral Composition Modulation in Ultrathin Alloy Films

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Recently a growing number of experimental observations have reported the spontaneous formation of nano-scale domain structures on morphologically *flat* crystalline surfaces. Examples include the hexagonal ordering of "holes" in strained Ag monolayers after exposure to sulfur [1], the formation of mono-disperse N-vacancy clusters on $In_{1-x}Ga_xN(0001)$ [2], sputtering-induced formation of two-monolayer-high islands on $CaF_2(111)$ surfaces [3], and lateral composition modulations in thin (1-4 monolayer) films of size-mismatched, bulk immiscible Co-Ag and Fe-Ag alloys on Mo(110) [4]. In each of these cases, structural features have been observed to form spontaneously with length scales in the range of 1-10 nm and characteristically narrow size distributions. The stability of such structures has been explained by Marchenko [5] and Ng and Vanderbilt [6], who showed that the energy of compositionally inhomogeneous surfaces can be lowered through the formation of periodic stress domains.

We will consider the thermodynamic driving force for self-assembly of nano-scale structures in ultrathin alloy films. Specifically, we study a monolayer film of $A_{1-c}B_c$ alloy on a substrate C, assuming that kinetically allowed atom interchanges are confined to the surface layer. In this case, ordering and clustering instabilities in the film are governed by the Fourier transform of the effective pair interactions, $V(\mathbf{k})$. Analytic expressions for $V(\mathbf{k})$ are derived using an *atomistic* model of surface alloy energetics based upon the well-known Frenkel-Kontorova (FK) scheme in the small-displacement (harmonic) limit. In contrast to the standard FK scheme, substrate relaxations are fully incorporated. Applications to first-principles studies of nanoscale laterally composition-modulated structures in $Co_{1-x}Ag_x$ on Ru(0001) are demonstrated.

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