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Systems tasks in nanotechnology via hierarchical multiscale modeling: Nanopattern formation in heteroepitaxy

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Abstract

A kinetic phase diagram for two-dimensional nanopattern formation in heteroepitaxy is generated by symbiotically employing deterministic continuum mesoscopic models and coarse-grained Monte Carlo (CGMC) simulations. The phase diagram at submonolayer film thickness is derived in the absence of thermal fluctuations via linear stability analysis of continuum mesoscopic models. The type of nanoscopic patterns, such as discs and stripes, is deduced from nonlinear analysis. The analysis provides for the first time a physical understanding and scaling laws for pattern feature size, shape, and growth times in terms of the interaction potential parameters, substrate temperature, film thickness and material properties. It is concluded that the long-ranged repulsive interaction determines the pattern wavelength, whereas the short-ranged attractive interactions control the temperature for the onset of patterns. The phase diagram is refined by including thermal fluctuations using CGMC simulations. It is shown that thermal fluctuations are responsible for the non-uniformity in pattern shapes and sizes. CGMC simulations indicate that the phase diagrams from mesoscopic equations are reasonably accurate. The role of temperature on the pattern size distributions and inter-feature distance obtained from CGMC is analyzed. It is found that entropy plays an important role in pattern selection.

Keywords: Kinetic phase diagram; Nanopatterns; Multiscale simulation; Coarse-graining; Model reduction; Systems task analysis; Mesoscopic modeling; Monte Carlo; Diffusion; Entropy

1. Introduction

The recent quest for forming periodic arrays of metal clusters and quantum dots of a material on crystal surfaces of a different metal or semiconductor, i.e., in heteroepitaxy, with a narrow shape and size distribution (Brune et al., 1998; Masumoto and Takagahara, 2002; Gai et al., 2005) has motivated the development of models that provide physical insight and ultimately aid with the design and control of nanotechnology-related processes. The first step in this direction is the development of models that correctly capture the experimentally observed rich variety of pattern shapes, sizes, orientations and densities (Plass et al., 2001). These observables depend on a number of experimentally controllable factors, such as temperature, film thickness and material properties (Vasco, 2004).

Even though phenomenological, equilibrium free-energy-based models (Ng and Vanderbilt, 1995; Daruka and Barabasi, 1998; Shchukin and Bimberg, 1999) can predict the most energetically stable pattern at 0 K by comparing certain pattern shapes, the evolution of the surface morphology is primarily driven by dynamics. For this reason, phenomenological dynamic models, such as phase field, Cahn–Hilliard, and Allen–Cahn models, have extensively been employed for the last fifty years to predict phase diagrams in alloys and polymer matrices (Cahn and Hilliard, 1958; Glotzer et al., 1995; Guyer and Voorhees, 1995; Leonard and Desai, 1998). However, the lack of thermal fluctuations and of microscopic-based free energy functionals renders the kinetic pathway traced by such models questionable.

More recently, molecular scale models, such as the lattice kinetic Monte Carlo (KMC) models, have gained attention for studying epitaxial growth. KMC can incorporate the correct microscopic physics, entropic effects and thermal fluctuations, which are essential for correctly modeling nanoparticle

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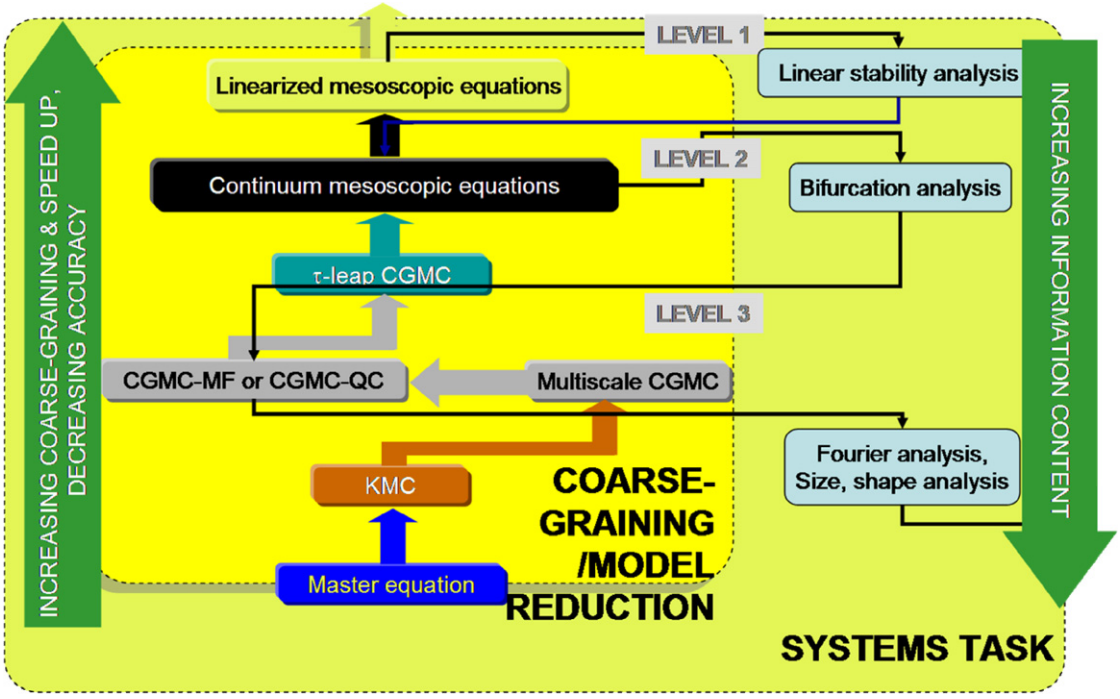

Fig. 1. Systems tasks tools (outer box) are used in conjunction with hierarchical coarse-grained models (inner box) derived from kinetic Monte Carlo models for studying pattern formation and ultimately generating a kinetic phase diagram. In comparison to computationally intensive stochastic simulations, nonlinear analysis of deterministic continuum mesoscopic equations renders prediction of pattern formation over realistic scales easy. The phase diagrams generated from mesoscopic equations are refined by incorporating thermal fluctuations using the computationally more expensive CGMC in the parameter space where nonlinear analysis is invalid.

nucleation and growth. Despite recent advances in the development of efficient KMC algorithms (Gibson and Bruck, 2000; Reese et al., 2001; Chatterjee and Vlachos, 2006b), generation of phase diagrams for patterning of material surfaces via KMC is still a major challenge primarily because of large separation of length (1 nm–0.1 μm) and time scales (1 ps–1 min) in these systems and the associated large computational costs. This challenge is common to all systems tasks (e.g., bifurcation, control, optimization, sensitivity analysis, etc.). Furthermore, standard KMC simulations are extremely inefficient for heteroepitaxial systems where long-range interactions exist. It is clear that while important tools have been exploited, a unifying modeling framework for pattern formation is still lacking.

In the last few years, our group has been developing a bottom-up hierarchy of coarse-grained mesoscopic models, which starts from KMC models. These mesoscopic models include the coarse-grained Monte Carlo (CGMC) method and continuum mesoscopic (partial integro-differential) equations (see Fig. 1, and Sections 3 and 5) (Vlachos and Katsoulakis, 2000; Katsoulakis et al., 2003a; Chatterjee et al., 2004a,b; Chatterjee and Vlachos, 2006a). Continuum mesoscopic equations are reminiscent of the well-known Cahn–Hilliard and Allen–Cahn models but are directly linked with the microscopic KMC processes. They are computationally inexpensive, but lack thermal fluctuations. In contrast to other multiscale techniques, the CGMC method is the only tool that can retain the correct fluctuations and enable access to multiple scales. However, it is still computationally cumbersome to use the CGMC method for systems' tasks, e.g., to generate a phase diagram.

In this paper, we propose a systematic top-down screening approach (Fig. 1) to efficiently study pattern formation by using hierarchically coarse-grained models (namely, mesoscopic equations and CGMC) symbiotically (Chatterjee et al., 2004a; Vlachos, 2005). A phase diagram of nanopatterns is generated via linear and nonlinear analysis of mesoscopic equations. 'Educated' CGMC simulations are subsequently performed, by including thermal fluctuations, at selected regions of the phase diagram to refine it and provide additional information, such as the nanoparticle size, shape, and spacing distributions. This top-down approach is feasible because the coarse-grained models are derived from the same KMC model, and describe the same essential physics at different levels of coarse-graining.

The model system used for demonstration of our approach entails chemisorbed atoms diffusing on a substrate of a different material (closed system with respect to mass). This system is characterized by the interplay of attraction between adsorbates, and long-ranged repulsion interactions typically induced by strain due to lattice mismatch between the deposited atoms and the substrate. Such interplay can lead, under certain conditions, to quantum dots, disks, or wires. Upon heating, the deposit self-organizes into a pattern as a result of the competition between attraction, leading to microphase separation, and repulsion that prevents coalescence of microdomains.

This paper is organized as follows (see Fig. 1). In Section 2, the prototype system is described. In Sections 3 and 4, linear