KINETIC MONTE CARLO SIMULATION OF DYNAMIC PHENOMENA IN THIN FILM GROWTH

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ABSTRACT

In this paper we describe the response of a Kinetic Monte Carlo model to time-varying growth conditions. We vary temperature and partial pressure sinusoidally and identify behavior typical of low-dimensional nonlinear systems. In particular, the frequency content of the roughness response is sensitive to the presence of steps in the surface.

INTRODUCTION

Deposition of a thin film from vapor-phase precursors is an industrially-important process which depends strongly on growth conditions. However, the dynamics associated with growth conditions are not well-understood, and films are typically deposited under constant growth conditions. Recent experiments and simulations indicate that dynamically-varying growth conditions may produce beneficial morphology [4, 5], which motivates our investigation of the time response of a kinetic Monte Carlo simulation.

We consider a crystal surface with steps. When diffusion is high, step flow growth dominates, and the natural response of the system does not possess a natural frequency. The steps do not play an important role when diffusion is low. Instead, the film grows by island nucleation and coalescence, in which the time required to deposit a monolayer of film is the characteristic time.

We will take as actuators the precursor partial pressure, which directly alters the incident flux of precursors, and the substrate temperature, which alters the surface kinetics. Because these macroscopic actuators cannot be varied on fine spatial scales, we focus on temporal variations and search for previously unrecognized dynamics to alter morphology.

MONTE CARLO FILM MODEL

We studied the surface morphology of a growing crystal with a kinetic Monte Carlo model. We consider a single-species material on a cubic lattice, and we increment time as in Fichthorn and Weinberg [1] to achieve a physically-based time. Vacancies in the crystal are prohibited. We define reaction rates for adsorption, desorption, and surface diffusion based on a nearest-neighbor bond-counting model:

$$k_{\text{ads}} = \gamma P_j \sqrt{\frac{1}{2\pi m k_b T}} \tag{1}$$

$$k_{\text{des},i} = \frac{k_b T}{h} \exp\left(-\frac{E_{\text{des},0} + i\Delta E}{k_b T}\right) \tag{2}$$

$$k_{\text{dif},i} = \frac{k_b T}{h} \exp\left(-\frac{E_{\text{dif},0} + i\Delta E}{k_b T}\right), \tag{3}$$

where i, ranging from 0 to 4, is the number of adjacent side neighbors, k_{ads} is the adsorption

rate, $k_{\mathrm{des},i}$ is the desorption rate for a surface site with i nearest neighbors, and $k_{\mathrm{dif},i}$ is the diffusion rate for a surface site with i nearest neighbors. The Boltzmann constant is denoted with k_b, Planck's constant is h, the sticking coefficient is γ, the mass of the particle is m, temperature is T, and the precursor partial pressure is P_j. The chemistry model has four free parameters: three activation energies and a constant in the adsorption rate. The activations energies $E_{\mathrm{des},0}$, $E_{\mathrm{dif},0}$, and ΔE are the depths of the potential energy wells associated with the occurrence of a surface event. Specifically, $E_{\mathrm{des},0}$ is the energy for the desorption of an atom with no side neighbors, $E_{\mathrm{dif},0}$ is the energy for the diffusion of an atom with no side neighbors, and ΔE is the additional energy barrier associated with a single side neighbor.

DISCUSSION

We performed simulations on a 256×256 domain and deposited 20 layers of atoms. Eight steps were inserted into the initialized lattice, and periodic boundary conditions were used to simulate an infinite train of steps. The reaction rate parameters were $\gamma(2\pi m k_b)^{-0.5} = 5\sqrt{\mathrm{K}}\mathrm{Pas}^{-1}$, $E_{\mathrm{des},0} = 2.64 \times 10^{-18} J$, $E_{\mathrm{dif},0} = 3.02 \times 10^{-19} J$, and $\Delta E = 7.59 \times 10^{-20} J$. The activation energy for desorption is sufficiently high such that desorption is negligible in the simulations. We considered a nominal partial pressure $P_{j,o} = 1$ Pa and nominal temperatures T_o of 900 K, 1050 K, and 1150 K. We present here the results of sinusoidal forcing with amplitudes $\Delta T = 25$ K and $\Delta P_j = 0.95$ Pa. The temperature and partial pressure are varied 180^o out of phase, which produces the greatest effect. The simulations are performed for sinusoidal forcing with periods at 1 s intervals, ranging from 1 s to 23 s.

Throughout the simulations we sample the average thickness, surface roughness, number of empty side bonds, adatom density, and island density. In this paper we present the frequency response of the surface roughness W for various forcing frequencies and for the three nominal growth conditions considered. In the frequency response we consider a scaled time which is proportional to the thickness, which produces a more defined peak at the monolayer frequency.

We consider three nominal growth conditions, which represent a wide range of morphologies. At $T_o = 1150$ K, diffusion is high relative to the step width, and step flow growth dominates, as pictured in Figure 1. Conversely, at $T_o = 900$ K, diffusion is low relative to the step width, and the steps do not dominate growth. Islands nucleate instead, producing rough three-dimensional growth as in Figure 2. We present in Figure 3 the frequency response of the surface roughness under sinusoidally-forced growth conditions for the three nominal temperatures. The vertical line denotes the monolayer frequency, and the curved lines mark the forcing frequency and its harmonics. Note that the curved lines pass through the base of each frequency response.

Figure 3(a) contains the frequency content of the surface roughness for $T_o = 900$ K. The response is dominated by the forcing frequency. This peak grows as the forcing period grows because the surface has more time to adjust to slower forcing. In addition to the forcing frequency, a peak is also present at the harmonics of the forcing frequency. This response is excited when the harmonics pass through the monolayer frequency. We do not believe that the harmonics enter the response through algebraic nonlinearities in the actuators. We have conducted simulations in which only the partial pressure is varied, so that the adsorption rate is also forced sinusoidally. The peaks at the harmonics of the forcing frequency still appear in the roughness response, indicating that the film system itself contains nonlinearities.

The response can be understood from a physical point of view by considering the number

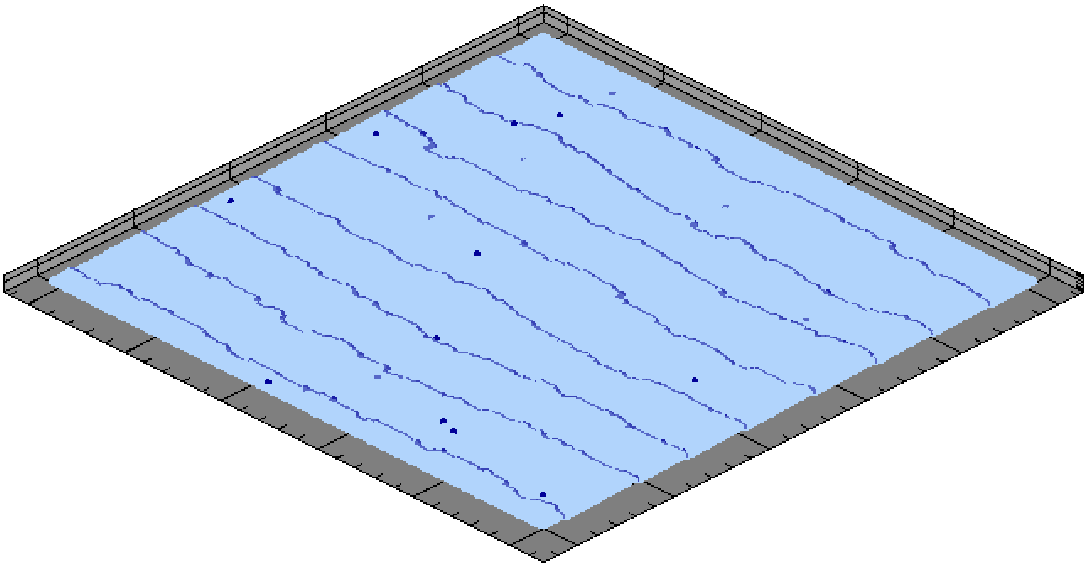

Figure 1: Step flow growth dominates when surface diffusion is high.

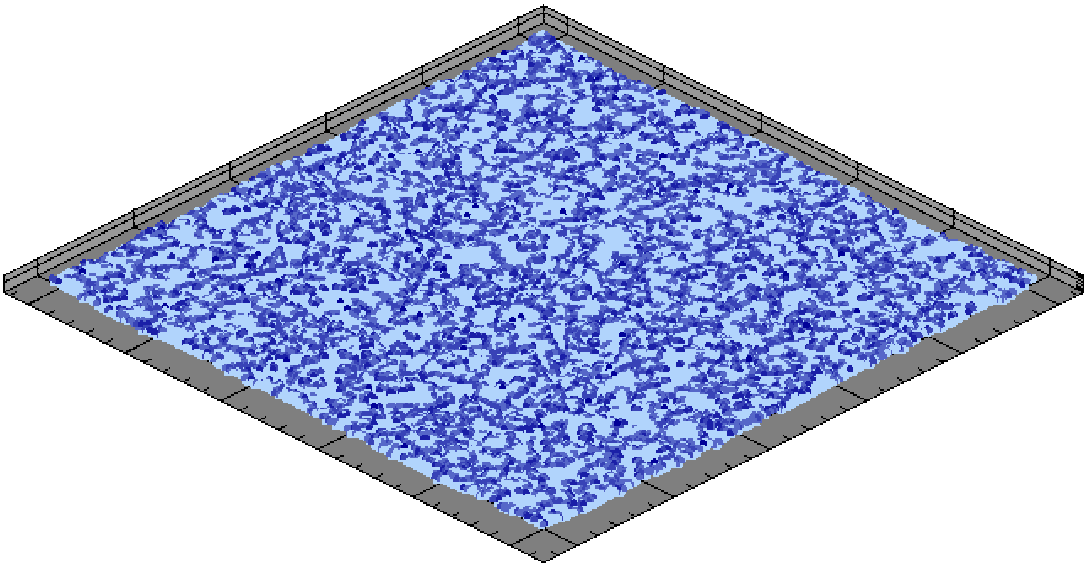

Figure 2: Island growth dominates when surface diffusion is low. Note that the surface contains eight steps.

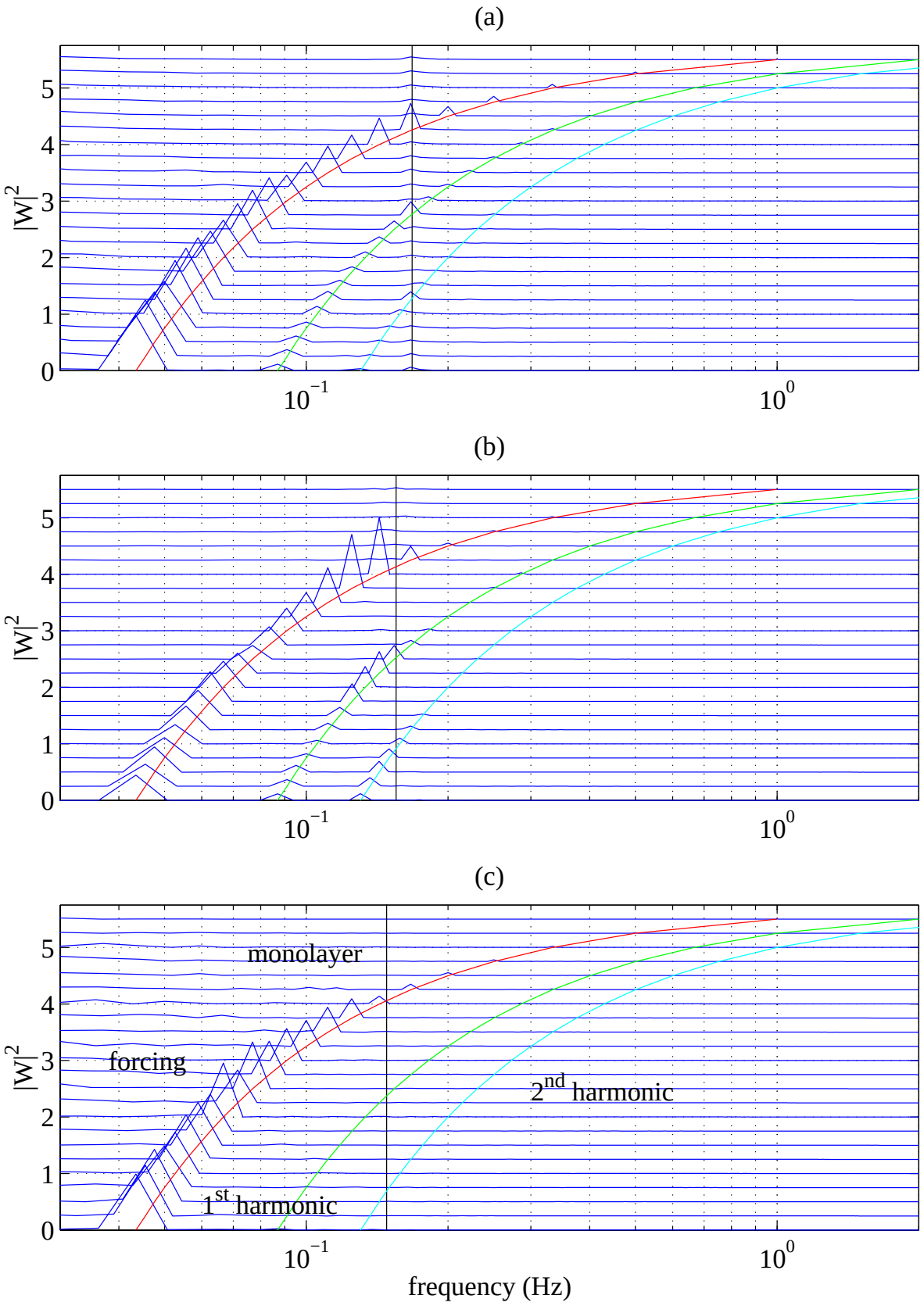

Figure 3: Frequency response of surface roughness for $P_{j,o} = 1$ Pa and $T_o =$ (a) 900 K, (b) 1050 K, (c) 1150 K. Period of forcing ranges from 1 s to 23 s (top to bottom). Vertical scale is arbitrary.

of adatoms deposited during each forcing cycle. When the forcing frequency is equal to the monolayer frequency, the number of adatoms deposited per forcing cycle is equal to the number of atoms in a layer of the crystal. At the end of each forcing cycle, exactly one layer of atoms has been deposited. If we consider the end of each forcing cycle to be the point when temperature is high and adsorption is near zero, the surface approaches a smooth morphology at the end of each cycle. Conversely, if the forcing is slightly slower, a few adatoms will be remain on the terraces at the end of each cycle. At this relatively low temperature, diffusion is low, so the extra adatoms will tend to form islands instead of attaching to the steps. The surface will not approach a smooth surface at the conclusion of each layer of growth, and will primarily respond at the forcing frequency. The monolayer frequency is also excited when any integer layer of adatoms is deposited during a forcing cycle. At the conclusion of each forcing cycle, the surface again approaches a smooth surface. We observe this excitation of the monolayer response in Figure 3(a) when the first and second harmonics of the forcing frequency equal the monolayer frequency.

This type of behavior is seen in low-order nonlinear differential equations and is referred to as superharmonic resonance [3]. Superharmonic resonance specifically refers to a steady-state response in which the forcing frequency induces a response at the natural frequency when the natural frequency is an integer multiple of the forcing frequency. We note that our system is technically not in steady state, because the surface is continually roughening. It is also possible that behavior similar to subharmonic resonance could occur in our system when the forcing frequency is twice or three times the monolayer frequency. However, at frequencies faster than the monolayer frequency, we observe little response at any frequency.

At a higher nominal temperature of 1050 K, the diffusion rate increases, and the steps play a greater role in the frequency response. This frequency response is shown in Figure 3(b). As at 900 K, we see a large response at the forcing frequency, and a smaller response when the forcing harmonics pass through the monolayer frequency. The major difference between the two cases is that at higher temperature, the oscillations induced when the forcing and forcing harmonics pass through the monolayer frequency are excited even when the forcing frequency is slightly less than the monolayer frequency. This change is a result of the increasing importance of the steps at higher temperature. Let us consider again the situation when a single layer of adatoms is deposited during a forcing cycle. The adatoms will tend to form a smooth surface at the end of the cycle. Now consider the case when slightly more than a layer of atoms is deposited during a cycle. These extra adatoms will now be more likely to diffuse to the step edges instead of nucleating islands on the terrace, so at the end of the forcing cycle, the surface will again approach a smooth surface. The growth mode is now a combination of island nucleation and step flow growth, with periods of island growth alternating with periods of step flow growth. The natural frequency of the system is pulled from the monolayer frequency to the forcing frequency, or to a harmonic of the forcing frequency. This is another behavior seen in nonlinear systems and is called synchronization [2].

Synchronization is said to occur when forcing near the natural frequency produces a response at the forcing frequency, but forcing far from the natural frequency yields a response with components at both the natural and forcing frequencies. In our system, we observe synchronization-like behavior associated with the forcing frequency and its harmonics. The synchronization appears to occur when the forcing frequency is slightly less than the monolayer frequency. It also may occur when the forcing frequency is greater than the monolayer frequency, if atoms detach from steps to fill vacancies in a nearly complete layer. However,

detachment from steps will always be less probable than atom diffusion to steps, so we should expect this effect to be less pronounced.

The frequency response associated with the final nominal temperature is simpler than the previous cases. At $T_o = 1150$ K, diffusion is high, and the steps dominate growth. The dominant response occurs at the forcing frequency. The monolayer frequencies ceases to be a natural frequency for the system, because island nucleation and coalescence does not occur. At steady growth conditions, growth occurs by step flow growth as adatoms attach to step edges. When the growth conditions are forced sinusoidally, the roughness is perturbed at the forcing frequency alone.

CONCLUSIONS

Although the surface evolution is defined by a series of reaction rate equations, not differential equations, we have identified system dynamics suggesting that the surface response to temperature and partial pressure might be described by a differential equation. This insight is beneficial in creating low-dimensional models. We are currently developing a set of rate equations, with the goal of capturing the essential dynamics of the Monte Carlo simulation with differential equations for island density and island coverage.

While we have demonstrated that open loop excitation of the system is enough to alter morphology, real-time measurements are possible and may be accomplished with reflective high energy electron diffraction (RHEED). Insight into the surface dynamics would also be beneficial in implementing closed-loop control.

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