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CROSSOVER FROM DIMER NUCLEATION TO ADATOM EXCHANGE DURING SUBMONOLAYER EPITAXY

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ABSTRACT

The nucleation and growth of islands in the early stages of epitaxial growth is studied with kinetic Monte Carlo Simulations and self-consistent mean field rate equations. Specifically, adatom exchange and irreversible dimer formation are allowed to compete equally as the origin of two-dimensional islands. The island size distribution and number density are found to satisfy a dynamic crossover scaling form. The critical island size evolves from one to zero with increasing temperature, decreasing flux, and increasing coverage.

INTRODUCTION

In the early stages of epitaxial growth, atoms deposited onto a crystalline substrate can diffuse freely until they are trapped by defects such as steps and impurities or encounter other diffusing species and nucleate islands. Alternatively, the diffusing atoms can exchange with a substrate atom forming an immobile "island" of only one atom which acts as a trapping site for other diffusing monomers [1, 2, 3]. This process has been observed for numerous metal on metal hetero-epitaxial systems [3]-[7]. An analogous situation occurs if the diffusing species are molecules instead of atoms. Recent work on the chemical vapor deposition of Fe on Si(100) [8], for example, reveal that adsorbed precursor molecules dissociate leaving behind a single Fe atom. This relatively immobile Fe atom acts as a trapping site for preferential dissociation of additional diffusing molecules [8]. Because of their qualitative similarity, in this paper the terms "diffusing monomer" and "exchange" can be used interchangeably with "diffusing molecule" and "dissociation".

A systematic study of the scaling properties of the island number densities in the early stages of growth (submonolayer) may provide important information on the relevant atomistic processes. For example, if islands form from adatom collisions, the total number density of islands N_{ncl} often has a simple power law dependence on the ratio of the surface diffusion rate D and deposition flux F [9, 10],

$$N_{ncl} \sim \left(\frac{D}{F}\right)^{-i/(i+2)} \quad (i > 0) \quad (1)$$

where the critical island size i is one atom less than the size at which an island, on average, grows more rapidly than it decays. Using this equation, it is possible to measure the diffusion constant D and the critical island size by simply counting the number of islands on the substrate [11, 12]. Conversely, if islands form by exchange ($i = 0$) the number density N_{exc} is independent of the deposition flux and predicted by Ref. [3] to obey approximately

$$N_{exc} \sim \sqrt{\frac{\theta h_e}{D}} \quad (2)$$

where h_e is the rate of adatom exchange and θ is the coverage. A systematic study using Eq. 2 can measure the ratio of the energy barrier for exchange to the energy barrier for diffusion. Eqs. 1 is approximately valid for coverages ranging from about 0.05 monolayers to the onset of coalescence. The coverage dependence of Eq. 2 is derived from a simplified rate theory which assumes constant rate coefficients (see below).

The island size distribution function $\langle n_s(\theta) \rangle$ (defined as the number of islands per unit area which contain s atoms) often obeys a simple scaling form [13] given by

$$\langle n_s(\theta) \rangle = \frac{\theta}{\bar{s}^2} g\left(\frac{s}{\bar{s}}\right) \quad (3)$$

where the shape of the scaling function g depends on the critical size i . All of the dependence on D and F (or h_e) is contained in the average island size $\bar{s}(\theta) = \theta/N$. If islands form by exchange, $i = 0$ and the distribution function has a peak at the origin [1, 2, 15]. Otherwise, the peak is near one and the distribution narrows with increasing i [14, 15, 16].

Eqs. 1, 2 and 3 are valid formally for growth on perfectly flat substrates without defects or impurities, fixed and well defined critical island size (independent of temperature, F , and θ), and large values of D/F (exceeding approximately 10^6). Much of the theoretical work on submonolayer scaling has been limited to these restrictions [13, 15, 14, 17]. Understanding the epitaxial growth on a "real", imperfect substrate, however, requires a generalization of these simple scaling ideas. As a practical matter, for example, any real surface has steps which may compete with nucleation and growth of islands for the diffusing monomers on the substrate. It was shown recently that on a vicinal substrate, Eqs. 1 and 3 must be replaced by crossover scaling forms [18]. Also, the so-called critical island size may vary with the growth parameters [3, 16].

In this work, the nucleation and growth on a flat surface is considered in which adatom exchange ($i = 0$) competes equally with irreversible adatom collisions ($i = 1$) as the origin of two-dimensional islands. Meyer and Behm [3] have observed this competition during the growth of Ni on Ag(111). At low temperatures the island density is observed to decrease with temperature as predicted by Eq. 1 with $i = 1$. At higher temperatures the island density increases due to thermally activated adatom exchange with substrate atoms [3]. From Eq. 1, as the ratio D/F increases a monomer must, on average, diffuse further to find another monomer to nucleate a dimer. Exchange will occur, however, when this distance exceeds $x_e = \sqrt{D/h_e}$, the average distance a monomer will travel before exchange with a substrate atom. Hence N_{exc} provides a lower bound for the island density as one increases D/F . It is shown here that the full range of behavior is described by a crossover scaling form similar to that observed for growth on vicinal substrates [18]. Eqs. 1 and 2 are replaced with a single scaling ansatz which includes both limits. A single variable which quantifies the competition specifies uniquely the shape of the distribution function and the value of the total number density. Crossover from $i = 1$ to $i = 0$ occurs with increasing temperature, decreasing flux, and increasing coverage.

SIMULATIONS AND RATE THEORY

Kinetic Monte Carlo (KMC) Simulations are performed on a square lattice. Atoms are deposited randomly at a rate F . Monomers diffuse at a rate $4D = \nu \exp(-\beta E_s)$ until

collision with and irreversible attachment to another monomer, an island, or immobile atom representing an exchanged adatom. E_s is the surface diffusion barrier, $\beta = 1/(k_B T)$, and $\nu = 10^{13}/s$ is the attempt frequency. Alternatively, the diffusing adatoms may undergo place exchange at a rate $h_e = \nu \exp(-\beta E_e)$. Atoms at the edge of the islands diffuse along the edge at a rate $h = \nu \exp(-\beta m E_e)$ where m is the number of lateral nearest neighbors, and E_e is the barrier to edge diffusion [17]. E_e is chosen so that the islands remain essentially square. The effect of varying the edge diffusion barrier is discussed in references [17] and [19].

Note that attachment to an exchanged atom may occur by an additional exchange such that the islands grow within the top layer of the substrate [1]. In this situation the experiment may distinguish between islands formed by exchange and islands formed by monomer collisions. (However, one might also imagine the dimer exchanging as a pair.) Alternatively, the monomer trapped by an exchanged atom may stay in the adsorbed layer [3] such that $i = 0$ and $i = 1$ islands are indistinguishable. In the current simulation all atoms remain in the adsorbed layer. As in Refs. [1]-[3] the displaced atoms have been ignored for simplicity. The current simulations are designed to include the essential physics. The analysis is simplified at the cost of quantitative comparison with experiment. The parameters in the simulations are not chosen to represent a particular experimental system. Instead, they are varied to study the full range of possibilities.

It was shown recently [17] that, for irreversible growth in the absence of exchange, a set of self-consistent mean-field rate equations for the island number densities provide quantitative agreement with KMC for average properties, *e.g.*, the total number density N . The analysis was extended by Zangwill and Kaxiras [2] to study growth where adatom exchange is the only mechanism for nucleating islands. They showed that the qualitative features of the size distribution function were reproduced by the self-consistent theory. In this paper, the methods from Refs. [2] and [17] are combined to study growth with both types of nucleation.

Define $\langle n_0 \rangle$ as the density of mobile monomers, $\langle n_1 \rangle$ as the density of exchanged adatoms, and $\langle n_s \rangle$ as the density of islands containing s atoms. The angular brackets $\langle \rangle$ denote an average over a large area of the substrate. The time derivative of $\langle n_0 \rangle$ is given by

$$\frac{d\langle n_0 \rangle}{dt} = F - 2D\sigma_0\langle n_0 \rangle^2 - D\langle n_0 \rangle \sum_{s=1}^{\infty} \sigma_s \langle n_s \rangle - h_e \langle n_0 \rangle \quad (4)$$

where the first term accounts for the deposition flux, the final three terms account for the loss of mobile monomers to dimer formation, existing islands, and exchange respectively. The capture numbers σ_s measure the rate at which islands (monomers) compete for the diffusing monomers on the substrate (see below). The remaining densities $\langle n_s \rangle$ obey

$$\frac{d\langle n_1 \rangle}{dt} = h_e \langle n_0 \rangle - D\sigma_1 \langle n_0 \rangle \langle n_1 \rangle \quad (5)$$

$$\frac{d\langle n_2 \rangle}{dt} = D\sigma_1 \langle n_0 \rangle \langle n_1 \rangle - D\sigma_2 \langle n_0 \rangle \langle n_2 \rangle + D\sigma_0 \langle n_0 \rangle^2 \quad (6)$$

$$\frac{d\langle n_s \rangle}{dt} = D\sigma_{s-1} \langle n_0 \rangle \langle n_{s-1} \rangle - D\sigma_s \langle n_0 \rangle \langle n_s \rangle \quad (s > 2) \quad (7)$$

The density of exchanged adatoms (Eq. 5) increases with an exchange event and decreases by capture of a diffusing monomer. The density of dimers is increased by collision of diffusing monomers (last term in Eq. 6) or capture of a diffusing monomer by an exchanged adatom (first term on right hand side of Eq. 6) and decreased by capture of a diffusing monomer by a dimer. The form of Eq. 7 is identical to previous work [17]. The contribution of direct capture of the incoming flux by monomers and islands is small for large values of (D/F) and early times. Such terms have been left out for brevity but are included in the numerical solutions below.

All information about island structure and the spatial correlations between islands is contained in the capture numbers σ_s . Following Ref. [17], a quasi-stationary diffusion equation is solved for the local density of monomers $n_0(\mathbf{r}, t)$ in the vicinity of a circular island. The environment surrounding that island is replaced by that of the average system (see Ref. [17] for details). The capture numbers are given by

$$\sigma_s = \frac{2\pi R_s}{\langle n_0 \rangle} \left. \frac{\partial n_0}{\partial r} \right|_{r=R_s} = 2\pi \frac{R_s}{\xi} \frac{K_1(R_s/\xi)}{K_0(R_s/\xi)} \quad (8)$$

where K_j is a modified Bessel function of order j and $R_s = \sqrt{s}$ ($s > 0$) is the effective radius of a square island. ξ is the average distance a monomer will travel before capture given by

$$\xi^{-2} = 2\sigma_0 \langle n_0 \rangle + \sum_{s=1}^{\infty} \sigma_s \langle n_s \rangle + \frac{h_e}{D} \quad (9)$$

A mobile monomer will collide with mobile monomers at twice the *rate* of collision with exchanged adatoms. After corrections for double counting [17], however, the derived capture *number* is the same for both processes, i.e., $\sigma_0 = \sigma_1$ or σ_0 is given by Eq. 8 with $R_0 = 1.0$.

The time derivative for the total number density $N = \sum_{s=1}^{\infty} \langle n_s \rangle$ is derived by adding Eqs. 5-7

$$\frac{dN}{dt} = D\sigma_0 \langle n_0 \rangle^2 + h_e \langle n_0 \rangle \quad (10)$$

Note that the capture numbers depend on the number densities which in turn depend on the capture numbers. Eq. 10 cannot be integrated directly. Instead, Eqs. 4 and Eqs. 5-7 must be solved simultaneously using Eqs. 8 and 9. The total number density is obtained by summing the solution.

RESULTS AND DISCUSSION

Fig. 1 compares the total number density calculated from numerical integration of the self-consistent rate equations (dashed lines) and KMC (solid lines and symbols). The rate equations provide quantitative agreement with KMC. Eqs. 4-7 can readily be written (divide by D) in terms of three parameters (D/F , h_e/D , and the coverage $\theta = Ft$) such that $N = N(D/F, h_e/D, \theta)$. In Fig. 1A the number density is plotted versus h_e/D for

Figure 1: Number density of Islands versus (A) h_e/D at a fixed coverage $\theta = 0.25$ and (B) coverage for $D/F = 10^7$ and h_e/D varying by factors of ten from 10^{-5} (lower curve) to 10^{-2} (upper curve). The dashed lines are solutions to the self-consistent rate equations and the solid lines/symbols are results of the kinetic Monte Carlo Simulations.

$\theta = 0.25$ for four values of D/F . Fig. 1B shows a plot of the number density versus coverage for $D/F = 10^7$ and h_e/D varying by factors of ten from 10^{-5} (lower curve) to 10^{-2} (upper curve).

For small exchange rates the number density is independent of h_e and identical to previous work where exchange is not included [17]. It is convenient to define $N_{ncl}(D/F, \theta)$ as the number density in the absence of exchange, i.e., the solution to the rate equations with $h_e = 0$. When $0.05 \lesssim \theta \lesssim 0.4$ N_{ncl} is described by Eq. 1 with $i = 1$. For larger exchange rates, the number density does not depend on F (consistent with Refs [1]-[3]) and increases as $\sqrt{h_e/D}$ (Fig. 1A). Define $N_{exc}(h_e/D, \theta)$ as the number density in the absence of monomer collisions, i.e., the solution to the rate equations with $\sigma_0 = 0$. The coverage dependence of N_{exc} is not described well by Eq. 2 which was derived by setting $\sigma_s = \text{constant}$ and $\sigma_0 = 0$. Hence, it is necessary to solve the rate equations numerically with self-consistent approximations for the capture numbers to correctly describe the coverage dependence of N_{exc} . Eqs. 4-9 have not been solved analytically.

According to Eq. 3 the island size distribution is completely specified by a "universal" scaling function (for fixed i) and the average island size $\bar{s}$. $\bar{s} = \theta/N$ is simply related to the number density. Hence $N_{ncl}(D/F, \theta)$ and $N_{exc}(h_e/D, \theta)$ provide a natural choice for parameterizing the island growth in the two extreme cases. In the intermediate regime (finite σ_0 and h_e) we postulate that the total number density is a homogeneous function of N_{ncl} and N_{exc} . One can then write N as

$$N = N_{ncl} f\left(\frac{N_{exc}}{N_{ncl}}\right) \quad (11)$$

Figure 2: Kinetic Monte Carlo results from Fig. 1A (symbols) and Fig. 1B (solid lines) rescaled according to Eqs. 12 and 11 respectively.

where the scaling function $f(x) = 1.0$ for $x \ll 1.0$ and $f(x) = x$ for $x \gg 1.0$. At a given coverage, one can include the known dependence on the growth parameters to derive an approximate crossover scaling form given by

$$N \sim \left(\frac{D}{F}\right)^{-1/3} f \left[\left(\frac{h_e}{D}\right)^{1/2} \left(\frac{D}{F}\right)^{1/3} \right]. \quad (12)$$

Eq. 12 replaces Eqs. 1 and 2 as the scaling relation which describes the total number density. Equations of this form arise often in the theory of finite size scaling. Also Eq. 11 is identical to the scaling ansatz shown to apply to growth on vicinal substrates. Indeed, the presence of adatom exchange is similar qualitatively to a finite size effect since $x_e = \sqrt{D/h_e}$ is an upper bound for the average distance between islands (or N_{exc} is a lower bound for N).

Fig. 2 provides a verification of the crossover scaling form predicted by Eq. 11. All of the results from Fig. 1 collapse onto a single curve $f(x)$ when divided by N_{ncl} and plotted versus N_{exc}/N_{ncl} . The approximate form described by Eq. 12 has been used to rescale the number density from Fig. 1A. Proportionality constants have been included, i.e., $N_{ncl} \simeq (.315)(D/F)^{-1/3}$ and $N_{exc}(\theta = .25) \simeq (.229)\sqrt{(h_e/D)}$. The more general form given by Eq. 11 must be used to rescale the data from Fig. 1B since the coverage ranges from 0.001 monolayers to 0.25 monolayers. For this coverage range the values of N_{ncl} and N_{exc} used to produce Fig. 2 are provided by numerical solutions to the rate equations.

The ratio N_{exc}/N_{ncl} quantifies the competition between growth dominated by adatom exchange and growth dominated by island nucleation by monomer collisions. For

Figure 3: Scaled island size distribution for $D/F = 10^7$ and $\theta = 0.25$.

$N_{exc}/N_{ncl} < 1.0$ most of the islands originate from monomer collisions. Conversely, for $N_{exc}/N_{ncl} > 1.0$, adatom exchange is the dominate process for island formation. It is interesting to note that the crossover ($N_{exc}/N_{ncl} = 1.0$) depends on the coverage as well as the other growth parameters. The monomer density decreases with increasing coverage since the growing islands form trapping sites. For small monomer densities, the first order process of adatom exchange (linear in $\langle n_0 \rangle$) will dominate the monomer collision rate which is second order in the monomer density.

The significance of crossover scaling can be appreciated further by examining the properties of the size distribution function. Fig. 3 shows the scaled distribution function for different values of h_e/D . As expected the peak in the distribution moves from one to zero with increasing h_e/D . From above, the ratio N_{exc}/N_{ncl} is the natural variable for describing the importance of adatom exchange and, hence, the change in shape of the distribution function. The scaling *ansatz* for the size distribution is generalized to

$$\langle n_s \rangle = \frac{\theta}{\bar{s}^2} g\left(\frac{s}{\bar{s}}, \frac{N_{exc}}{N_{ncl}}\right). \quad (13)$$

Fig. 4 shows a verification of this scaling *ansatz*. The rescaled distribution produces a single curve for various values of D/F and h_e/D as long as N_{exc}/N_{ncl} is held fixed. Any two systems with the same ratio N_{exc}/N_{ncl} are statistically equivalent apart from an overall change in length scale. A single parameter given by N_{exc}/N_{ncl} uniquely defines the state of the dynamical system.

CONCLUSIONS

In this work, simple scaling rules for the total island number density and island size

Figure 4: Scaled island size distribution for $\theta = 0.25$, $N_{exc}/N_{ncl} \simeq 1.8$ where ($\circ$) $D/F = 10^6$, $h_e/D = 4.7 \times 10^{-4}$, ($\square$) $D/F = 10^7$, $h_e/D = 1.0 \times 10^{-4}$, ($\diamond$) $D/F = 10^8$, $h_e/D = 2.2 \times 10^{-5}$, and ($\triangle$) $D/F = 10^9$, $h_e/D = 4.6 \times 10^{-6}$.

distribution are generalized to account for the competition between adatom exchange and monomer collisions as the origin of island formation during submonolayer epitaxy. Self-consistent rate equations agree quantitatively with KMC and provide a tool for studying the scaling properties. In particular, a single parameter is identified which uniquely quantifies the competition. A dynamic crossover scaling form is shown to apply over a wide range of model parameters.

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