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Island nucleation and growth in epitaxial, amorphous, and nanoparticle thin-films

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A Dissertation
entitled

Island nucleation and growth in epitaxial, amorphous, and
nanoparticle thin-films

by

Yevgen A. Kryukov

Submitted to the Graduate Faculty as partial fulfillment of the
requirements for the Doctor of Philosophy Degree in Physics

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August 2011
The goal of this dissertation is to improve our understanding of two of the key stages in thin-film growth: (a) submonolayer island nucleation and growth and (b) multilayer growth. To explore these phenomena we have used a variety of different methods including the numerical integration of stochastic differential equations, self-consistent rate-equation calculations, and kinetic Monte Carlo simulations, as well as scaling and analytical methods.

In the first part of this thesis we study the roughening process of amorphous silicon thin film grown via low-temperature PECVD (plasma-enhanced chemical vapor deposition). By studying a continuum model which takes into account the effects of shadowing as well as the smoothing effects of surface diffusion, excellent agreement is obtained with experiments. One of our key findings is that surface diffusion plays an important role at short to medium time scales and high H₂ dilution ratio, while shadowing effects are dominant at low H₂ dilution ratio and large time scales. We also find that the initial submonolayer morphology plays a key role in determining the evolution of the surface roughness in the later stages of growth.

Motivated by these results, we have also carried out kinetic Monte Carlo simulations as well as a scaling analysis of the submonolayer growth of 3D islands. In this work we demonstrate that the scaling behavior of the island and monomer densities
for 3D islands is significantly different from that for 2D islands and is also different from previous theoretical predictions. However, despite these differences we find very little or no difference in the scaling behavior of the island-size distribution between 3D and 2D islands. Self-consistent rate-equation calculations for the average island and monomer densities as a function of coverage and deposition flux are also presented and excellent agreement with simulations is obtained.

Finally, the effects of cluster-diffusion on the scaling of the island-density and island-size distribution in submonolayer growth are studied. This work is motivated by recent drop-drying experiments in which a monodisperse solution of Au nanoparticles is “deposited” at the toluene-air interface as a toluene droplet dries in air. In order to obtain a basic understanding, we have carried out extensive kinetic Monte Carlo simulations of a model of irreversible island nucleation and growth in which the cluster diffusion coefficient is assumed to exhibit power-law decay as a function of island-size with exponent $\mu$. Results are presented for a range of possible values of the exponent $\mu$ including $\mu = 1/2$ (corresponding to cluster diffusion via Brownian motion), $\mu = 1$ (corresponding to correlated evaporation-condensation), and $\mu = 3/2$ (corresponding to edge-diffusion), as well as for higher values including $\mu = 2, 3$, and $6$. In general, we find that cluster diffusion leads to a significant broadening of the island-size distribution and also alters the scaling exponent $\chi$ which describes the dependence of the island-density on deposition flux. Results are also presented for the case of reversible growth corresponding to a critical island-size larger than one. In this case, we find that the scaled island-size distribution sharpens with increasing critical island-size and appears to approach the experimentally observed island-size distribution.
Acknowledgments

I am very grateful to my advisor Dr. Jacques G. Amar, for his immense help, guidance and encouragement. I would like to thank Dr. Amar for sharing with me his ideas and great knowledge, and for providing numerous hours of discussions regarding my research.

I want to express my gratitude to my Ph.D advisory committee Dr. Bo Gao, Dr. Robert W. Collins, Dr. Rupali Chandar and Dr. Terry P. Bigioni for their support, advice and valuable suggestions.

I am also very grateful to my former advisor Dr. Victor G. Karpov for all the help and motivation he provided.

My special thanks to the members of our group Dr. Yunsic Shim and Brad Hubartt for their insight and helpful discussions.

It is my pleasure to acknowledge all faculty and staff at the Department of Physics and Astronomy for their support.

Finally, I would like to thank my parents back in Ukraine, my brother and his wife, and of course my wife Erin Kryukova and her family for tremendous support and encouragement to complete my Ph.D degree.
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List of Abbreviations

ISD ................ Island size distribution
KMC ................. Kinetic Monte Carlo
RTSE ............... Real time spectroscopic ellipsometry
MD .................. Molecular dynamics
RE .................. Rate equation
PECVD .............. Plasma-enhanced chemical vapor deposition
KPZ ................. Kardar-Parisi-Zhang
Chapter 1

Introduction

1.1 Thin Film Growth

Because of the usefulness and applicability of thin-films in a wide variety of areas of technology such as the semiconductor industry, photovoltaics, and nanotechnology there is a strong interest in obtaining a better understanding of thin-film growth. In addition, because experimental measurements are often indirect, a theoretical interpretation, as well as comparison with simulations of simplified models, can often be quite useful. One of the advantages of such simulations is that the growth conditions are easily controllable. As a result, the growth process can be studied at an atomic level and additional insight can be obtained regarding the growth conditions needed to achieve a desirable morphology or other specific characteristics of a thin film.

Nucleation and growth play important roles in many physical processes and particularly in thin film growth. For example, it is known that the nucleation of islands in the early stages of film growth corresponding to the “submonolayer” regime before a continuous film is formed, can strongly affect the morphology as well as other properties of a thin-film in the later stages of growth. As a result, much of the theoretical research, as well as the research discussed in this thesis, is focussed on this early stage of growth. However, obtaining an understanding of the later-stage evolution is also
important. Accordingly, simulations of the later stages of growth, corresponding to 
the PECVD growth of amorphous Si, are also discussed in this thesis.

In general, a variety of theoretical and numerical approaches have been used to 
study thin-film growth. The simplest approach, which can be used to study the 
early stages of island nucleation and growth, involves the use of simplified mean-field 
Smoluchowski equations (for which the scaling behavior can in some cases be solved 
analytically) as well as more sophisticated self-consistent rate-equations which are 
typically solved numerically. However, neither of these approaches properly take into 
account correlations as well as fluctuations, and so if more detailed information than 
that corresponding to average quantities is needed (such as the island-size distribu-
tion) then typically kinetic Monte Carlo simulations are used.

The kinetic Monte Carlo approach has the advantage that if the rates for all 
activated processes are known, then it can be used to simulate both the early stages 
of growth (as discussed in Chapters 5 - 7) as well as the later stages of growth. 
However, in many cases (especially in the case of amorphous materials) a detailed 
knowledge of the kinetic atomic processes occurring during growth does not exist. In 
addition, even when such information is available it may be too time-consuming to 
carry out such a simulation. Accordingly in such a case, coarse-grained continuum 
equations (such as described in Chapter 2 and Chapter 4) may be used.

One way to determine the relevant activated processes in thin-film growth is to 
carry out fully atomistic simulations using molecular dynamics (MD). However, the 
time-scales that can be reached using pure MD simulations are typically much shorter 
(e.g. µs) than experimental time-scales which may be of the order of 1 sec -1 min. As a 
result, other methods such as temperature-accelerated dynamics must be used to carry 
out purely atomistic simulations of thin-film growth. Thus, reaching experimentally 
relevant time scales remains one of the biggest challenges in computer simulations of 
thin film growth.
1.2 The scope of this thesis

In this thesis we have used a variety of methods including continuum growth equations, kinetic Monte Carlo simulations, and self-consistent rate-equations as well as analytical approaches to study the early stages of nucleation as well as the later stages of thin-film growth. A brief outline is as follows.

In Chapter 2 we first discuss some of the continuum equations used to model the evolution of the surface morphology in multilayer growth, including the random deposition model, the Edward-Wilkinson model, and the Kardar-Parisi-Zhang (KPZ) equation. We then present a brief discussion of the self-consistent rate equation method used to study submonolayer growth, which is also used in Chapters 5 and 6. In Chapter 3 we then introduce the Monte Carlo method and describe a few types of existing Monte Carlo methods used in thin film growth simulations.

In Chapter 4 we study the evolution of the surface roughness of a-Si:H thin-films grown by low-temperature (200 °C) plasma-enhanced chemical vapor deposition (PECVD) at high process gas pressure (3 mTorr) as a function of of the hydrogen dilution gas flow ratio \( R_H = [H_2]/[SiH_4] \) with \( 15 \leq R_H \leq 60 \). To describe the roughness evolution, we have used a 3D linearized continuum equation which includes a negative surface tension term to take into account the destabilizing effects of short-range attraction and/or shadowing, as well as a smoothing term corresponding to surface diffusion. Using this model we have obtained very good agreement with experimental results for the evolution of the surface roughness in the case of large dilution ratio. However, our results indicate that for small dilution ratios the surface slopes are significantly larger than observed in experiment, and as a result additional nonlinear terms need to be included at large thicknesses. Our results also indicate that surface diffusion plays an important role during PECVD film growth while the diffusion rate increases with increasing hydrogen dilution ratio. We also find that the early stages
of island nucleation play an important role in determining the subsequent roughness evolution. In particular, the assumption of a large wetting angle ($\theta_W \simeq 90^\circ$) for the 3D islands formed in the initial stages leads to significantly better agreement with experiments than a smaller wetting angle ($\theta_W \simeq 45^\circ$). This is consistent with recent experiments on liquid Si droplets on SiO$_2$ substrates [H. Kanai et al., J. Mater Sci. 42, 9529 (2007)] in which a wetting angle of $90^\circ$ was observed. Our simulations also leads to an estimate for the initial length scale corresponding to the island-density just after the nucleation of 3D islands but before a continuous film has been formed.

Motivated by our results in Chapter 4 which indicate that the roughness evolution greatly depends on the initial stages of nucleation, in Chapter 5 we present the results of kinetic Monte Carlo simulations of a simplified model of irreversible 3D island growth, corresponding to a critical island-size $i = 1$. The focus of this Chapter is on the scaling behavior of the island and monomer densities and island size distribution as a function of the deposition flux and coverage. One of our key findings is that for a realistic model, the exponents $y_1$ and $y'_1$ describing the dose- and coverage-dependence of the island density are significantly lower than predicted by previous theories. However, due to the weak dependence on $y_1$ and $y'_1$ this leads to only a small correction to the exponent $\chi_1$ describing the dependence of the peak island-density on flux. Our results also indicate a new kinetic method, applicable to arbitrary critical island-sizes, which may be used to estimate the critical island-size in submonolayer 3D growth. We also found that the scaled island-size distribution for 3D islands is very similar to that for 2D islands, which is consistent with previous experimental work in which 2D island-size distributions were compared with experimental results for 3D islands. The results of self-consistent rate-equation calculations for the average island and monomer densities as a function of coverage and deposition flux are also presented, and excellent agreement with our KMC results is obtained.

In Chapter 6 we present the results of KMC simulations of the irreversible growth
of mobile compact islands on a 2D substrate. This work is motivated by recent drop-drying experiments [1] in which a monodisperse solution of 6 nm diameter Au nanoparticles (coated with dodecanethiol and dissolved in toluene) are “deposited” at the toluene-air interface as a toluene droplet dries in air. During the drying process the monomers in solution are “swept up” by the toluene-air interface and then diffuse and aggregate to form well-ordered nanoparticle clusters which grow and eventually merge to form a highly ordered self-assembled monolayer. One of the major goals of our work is to try to obtain a basic understanding of this process and of how the nanoparticle-nanoparticle interaction as well as the diffusion of nanoparticle clusters affect the island density and island-size distribution.

One major difference between this system and epitaxial thin-film growth is that in contrast to epitaxial growth, nanoparticle clusters diffuse significantly due to Brownian motion, thus significantly broadening the island-size distribution and altering the scaling exponent $\chi$ which describes the dependence of the island-density on deposition flux. However, in both cases the nucleation and growth of islands plays a crucial role. In the model studied in Chapter 6 we have assumed that island growth is irreversible (with no detachment), corresponding to a critical cluster size $i = 1$, while for simplicity the nanoparticle clusters or islands have been assumed to be circular. In addition, we assume instantaneous coalescence of circular islands, while the cluster mobility is assumed to exhibit power-law decay as a function of island-size with exponent $\mu$. We note that in previous work the dependence of the exponent $\chi$ on $\mu$ has been studied for the case of irreversible growth of fractal islands, and a number of theoretical predictions have also been made based on the mean-field Smoluchowski equation approach. However, the island-size distribution, which is the main focus here, has not been studied. Results are presented for a range of possible values of the exponent $\mu$ including $\mu = 1/2$ (corresponding to cluster diffusion via Brownian motion), $\mu = 1$ (corresponding to correlated evaporation-condensation), and $\mu = 3/2$
(corresponding to edge-diffusion), as well as for higher values including \( \mu = 2, 3, \) and 6. For comparison, results for \( \mu = \infty \) (corresponding to no cluster diffusion) are also presented. For the case \( \mu < 1 \) we obtain power-law behavior of the island-size distribution (ISD) \( N_s(\theta) \sim s^{-\tau} \) (where \( N_s(\theta) \) is the number of islands of size \( s \) at coverage \( \theta \)) up to a cross-over island-size \( S_c \). While this power-law behavior is in agreement with the predictions of the Smoluchowski equation, the value of the exponent \( \tau \) obtained in our simulations is higher than the value predicted by mean-field arguments, and some possible alternative explanations for this discrepancy are suggested. A new generalized scaling form for the ISD is also proposed, and it is shown that for \( \mu < 1 \) this form leads to excellent scaling of the ISD as a function of coverage and of the ratio \( D/F \) of monomer diffusion rate to deposition flux. However, for \( \mu > 1 \) due to a competition between cluster diffusion (which tends to broaden the island-size distribution) and island-growth via the diffusion of monomers, a bimodal island-size distribution is found. In addition, our simulation results show that for finite \( \mu > 1 \), there is no single scaling form which can be used to scale the ISD. Instead, over this range of \( \mu \) the ISD becomes sharper with increasing coverage and diffusion to deposition ratio \( D/F \). Results for the dependence of the exponent \( \chi \) describing the flux-dependence of the peak island-density as a function of the exponent \( \mu \) are also presented. At the end of this Chapter, a brief comparison between our KMC simulation results and self-consistent RE results for the scaled island-size distribution for \( \mu < 1 \) is also presented, which explains the discrepancies between the exponent \( \tau \) obtained in our simulations and the Smoluchowski equation predictions.

In **Chapter 7** we then extend these results to the case of reversible growth corresponding to critical island sizes \( i = 2 \) and \( i = 6 \). Our results show that, as expected, with increasing critical island-size \( i \) the ISD peak height becomes significantly higher. However, for finite values of the exponent \( \mu > 1 \), the ISDs still don’t scale using the standard scaling form but instead become sharper with increasing coverage \( \theta \) and as
the ratio $D/F$ of the monomer diffusion rate to deposition rate increases. Results for
the dependence of the exponent $\chi$ on the exponent $\mu$ are also presented for the case
of reversible growth with island-diffusion.

Finally, in Chapter 8 we summarize our work and discuss possible related future
work.
Chapter 2

Continuum equation approaches to modeling thin-film growth

2.1 Continuum equations to study multilayer growth

The evolution of the thin-film morphology during multilayer growth can be studied using continuum stochastic differential equations. These equations are expected to accurately describe interface growth at large length scales, where short length scale details of the system are neglected. In general, these equations can be constructed using so-called symmetry arguments.

We first consider the simplest case of random deposition (RD), in which particles are deposited from a randomly chosen site above the surface. In this model, particle are assumed to fall down vertically until they reach the surface of a film, where they are assumed to stick irreversible without further movement or relaxation. In this model each column grows independently of others resulting in no correlations involved. The evolution of the surface height \( h(\vec{r}, t) \) as a function of position \( \vec{r} \) and time \( t \) can then be described using the following equation,

\[
\frac{\partial h(\vec{r}, t)}{\partial t} = F + \eta(\vec{r}, t),
\]

(2.1)
where $F$ is the constant deposition flux and $\eta(\vec{r}, t)$ is uncorrelated noise, which describes fluctuations in the deposition process and obeys this condition

$$< \eta(\vec{r}, t) > = 0,$$

(2.2)

In addition, the deposition noise is assumed to be uncorrelated, e.g. to satisfy

$$< \eta(\vec{r}, t) \eta(\vec{r}', t') > = 2D\delta^d(\vec{r} - \vec{r}')\delta(t - t'),$$

(2.3)

where $d$ is the dimensionality of the substrate, and the vector $\vec{r}$ is the position along the substrate.

In more complicated models the local growth rate $\frac{\partial h(\vec{r}, t)}{\partial t}$ is assumed to depend on the local height-configuration $h(\vec{r}, t)$ as well as the deposition noise, and requires taking into account basic symmetry arguments [2]:

1) *Invariance under translation in time.*

2) *Translation invariance along the growth direction.*

3) *Translation invariance in the direction perpendicular to the growth direction.*

4) *Rotation and inversion symmetry about the growth direction $\mathbf{n}$.*

5) *Up/down symmetry for $h$.*

The final equation is constructed using combinations of powers of $\nabla^n h$ with elimination of terms that violate symmetry arguments. Thus, the resulting general growth equation has the following form

$$\frac{\partial h(\vec{r}, t)}{\partial t} = (\nabla^2 h) + (\nabla^4 h) + \ldots + (\nabla^{2n} h) + (\nabla^2 h)(\nabla h)^2 + \ldots + (\nabla^{2k} h)(\nabla h)^{2j} + \eta(\vec{r}, t),$$

(2.4)

where $n, k, j$ can take any positive integers. As a next step depending on the particular model many of the terms in Eq. 2.4 can be be neglected as they have only small contribution relatively to other terms. For example, the equation describing the
equilibrium fluctuations of an interface (Edwards-Wilkinson (ED) equation) has the form,

\[ \frac{\partial h(\vec{r}, t)}{\partial t} = F + \nu_2 \nabla^2 h + \eta(\vec{r}, t). \]  \hspace{1cm} (2.5)

Here, \( \nu_2 \) is called surface tension, because the term \( \nu_2 \nabla^2 h \) smoothes the surface and also because this term can be derived in terms of a functional derivative of a free energy which depends on the surface tension. Similarly, an equation taking into account surface diffusion (linearized Mullins equation with noise) can be constructed by adding a diffusion term \( -\nu_4 \nabla^4 h \), thus leading to the equation

\[ \frac{\partial h(\vec{r}, t)}{\partial t} = F - \nu_4 \nabla^4 h + \eta(\vec{r}, t). \] \hspace{1cm} (2.6)

In addition these two equations can be combined into one equation taking into account both surface tension and surface diffusion

\[ \frac{\partial h(\vec{r}, t)}{\partial t} = F + \nu_2 \nabla^2 h - \nu_4 \nabla^4 h + \eta(\vec{r}, t). \] \hspace{1cm} (2.7)

In addition, if the surface tension term is negative (e.g. \( \nu_2 < 0 \)) due to an instability as assumed in Chapter 4, then the competition between smoothing (due to surface diffusion) and roughening due to the instability leads to a critical length scale \( L_c = \sqrt{\nu_4/|\nu_2|} \) such that if \( L \ll L_c \) then surface diffusion dominates, while at larger length-scales \( L > L_c \) the instability dominates.

While linearized equations such as Eq. 2.7 may be applied in many cases, the picture is more complicated for the ballistic deposition (BD) model in which depositing particles stick to the nearest encountered particle (which can be in a neighboring column). This behavior leads to not only vertical growth of the surface but also to lateral growth (i.e. growth in the direction of the local normal to the interface). To take this into account one needs to add an additional nonlinear term \( |\nabla h|^2 \) to the
EW equation, thus leading to the nonlinear Kardar-Parisi-Zhang equation [3]

\[
\frac{\partial h(\vec{r}, t)}{\partial t} = F + \nu_2 \nabla^2 h + \frac{\lambda}{2} |\nabla h|^2 + \eta(\vec{r}, t). \tag{2.8}
\]

2.2 Rate-equation approach to submonolayer growth

One commonly used approach to submonolayer island nucleation and epitaxial growth is the rate-equation approach. This is a mean-field approach which only takes into account average quantities (such as the average number of islands of size \( s \)) but does not take into account the effects of geometry or fluctuations in density or correlations. In the case of irreversible growth the corresponding rate-equations are particularly simple since the growth depends primarily on the ratio \( R = D/F \) of the monomer diffusion rate \( D \) to the deposition flux \( F \). In this case, the rate equations may be written in the following form,

\[
\frac{dN_1}{d\phi} = 1 - 2RN_1^2 - RN_1 \sum_{s=2}^{\infty} \sigma_s N_s - \kappa_1 N_1 - \sum_{s=1}^{\infty} \kappa_s N_s \tag{2.9}
\]

\[
\frac{dN_s}{d\phi} = RN_1 (\sigma_{s-1} N_{s-1} - \sigma_s N_s) - \kappa_{s-1} N_{s-1} - \kappa_s N_s \quad (s \geq 2) \tag{2.10}
\]

where \( N_1(\phi) \) and \( N_s(\phi) \) are average island and monomer densities, \( \phi \) is the deposited dose in monolayers (ML), \( R = D/F \) is the ratio of the monomer diffusion rate \( D \) to the (per site) deposition rate \( F \), the terms with \( \kappa_s \) correspond to direct impingement of atoms deposited on top of islands, area of the island of size \( s \), and the capture numbers \( \sigma_s \) (\( \sigma_1 \)) correspond to the average capture rate of diffusing monomers by
islands of size $s$ (monomers).

In order to numerically integrate the RE’s above we need to know the size- and dose-dependence of the relevant capture numbers $\sigma_s(\phi)$. While various approximations have been attempted (such as $\sigma_s \sim s^{1/2}$ corresponding to a capture number which is proportional to the island perimeter) in general no simple analytic form for $\sigma_s$ leads to an accurate prediction of the evolution of the island and monomer densities $N = \sum_{s \geq 2} N_s$ and $N_1$. However, recently a self-consistent rate equation approach has been developed by Bales and Chrzan [4] (see also [5, 6]) which has been demonstrated to lead to accurate results for the average island and monomer densities, although since correlations are not included, it does not give accurate results for the island-size distribution.

In this approach we consider a quasi-static diffusion equation for the monomer density $n_1(r, \tilde{\phi})$ surrounding an island of size $s$ of the form,

$$\nabla^2 n_1(r, \tilde{\phi}) - \xi^{-2}(n_1 - N_1) = 0 \quad (2.11)$$

where $N_1$ is the average monomer density and $\xi$ is the average capture length. Assuming circular symmetry and solving for $n_1(r)$, using the boundary conditions $n_1(\infty) = N_1$ and $n_1(\tilde{r}_s) = 0$ (where $\tilde{r}_s = r_s + r_1$ is the effective monomer capture radius of an island of size $s$) the following expression for the capture number can be obtained [4],

$$\sigma_s = 2\pi \frac{\tilde{r}_s K_1(\tilde{r}_s/\xi)}{\xi K_0(\tilde{r}_s/\xi)}. \quad (2.12)$$

where the $K_j$ are modified Bessel functions of order $j$. Similarly, the monomer capture radius $\tilde{r}_s$ can be used to calculate the direct impingement term, e.g. $\kappa_s = \pi \tilde{r}_s^2$.

For consistency with the REs (2.9) and (2.10) we require

$$\xi^{-2} = 2\sigma_1 N_1 + \sum_{s=2}^{\infty} \sigma_s N_s. \quad (2.13)$$
Thus, for a given dose $\phi$ and island-size distribution $N_s(\phi)$, the capture-length $\xi$ may be determined self-consistently starting with an initial guess for $\xi$ in Eq. 2.12 and then substituting into Eq. 2.13 and repeating until the process converges. The only unknown quantity remains to be $r_s$, which corresponds to the distance between interacting islands and is defined by their geometry.
Chapter 3

Monte Carlo Methods

3.1 Introduction to Monte Carlo Methods

While stochastic continuum equations are able to describe some aspects of the growth they always involve some approximations and simplifications. More realistic atomic scale models such as deterministic approach of molecular dynamics (MD) and stochastic approach of kinetic Monte Carlo (KMC) allow us to obtain a more complete understanding of the growth process. In MD simulations differential equations of motions of all atoms is the system are solved numerically. However, doing so requires knowledge about interaction potential. This method is most accurate of atomic simulations techniques, but simulation time scale is much smaller (typically from $ps$ to $\mu s$) than demanded by the problem. Thus the scope of MD simulations is limited [7].

One alternative to MD is the Monte Carlo method [7, 8]. Instead of using exact positions and velocities of all atoms (as done in MD) MC simulations is more coarse-grained method which take into account transitions from one energy minimum to another and an atomic configuration depends only on previous configuration. The time scale of this method is much larger than in MD simulations.
3.2 Metropolis Monte Carlo

3.2.1 Markovian Master Equation

MC simulations follow stochastic Markov process to evolve system towards equilibrium state. In this process Markov Master Equation describes time evolution of probability density, which depends on current state but doesn’t depend on history of evolution of the system. If we write $P(\sigma, t)$ as probability that system is at state $\sigma$ at time $t$, and $W(\sigma_i \rightarrow \sigma_f)$ is transition probability per unit time from state $\sigma_i$ to state $\sigma_f$, then we can write Markovian Master equation \cite{7} in the following form

$$\frac{\partial P(\sigma_f, t)}{\partial t} = \sum_{\sigma_i} W(\sigma_i \rightarrow \sigma_f)P(\sigma_i, t) - \sum_{\sigma_f} W(\sigma_f \rightarrow \sigma_i)P(\sigma_f, t), \quad (3.1)$$

We note that in a steady state regime (thermal equilibrium) left-hand side of the Eq. 3.1 is zero and the sum of all transitions into a particular state $\sigma$ equals the sum of all transitions out of the state which is called detailed-balance criterion and can be written as follows

$$W(\sigma_i \rightarrow \sigma_f)P(\sigma_i, t = \infty) = W(\sigma_f \rightarrow \sigma_i)P(\sigma_f, t = \infty), \quad (3.2)$$

in addition, transition probabilities should satisfy Boltzmann distribution

$$P(\sigma, t = \infty) = \frac{e^{-E(\sigma)/k_BT}}{Z}, \quad (3.3)$$

3.2.2 Metropolis Algorithm

In Metropolis algorithm a sequence of random samples is obtained from probability distribution. If we let $\delta E = E(\sigma_f) - E(\sigma_i)$ to be difference in energies between next and previous step and $\tau$ to be MC time step, then transition probability can be
defined as follows

\[ W(\sigma_i \rightarrow x_f)/\tau = \begin{cases} 
  e^{-\delta E/k_BT} & \text{for } \delta E > 0 \\
  1 & \text{for } \delta E \leq 0 
\end{cases} \]  

(3.4)

The details of the Metropolis algorithm are outlined in a few steps below and are repeated until the desired state is reached \([9]\):

1. Randomly choose a number \( \nu \) from a uniform distribution so that \( 0 \leq \nu \leq 1 \) and create new state.

2. Calculate the energy difference \( \delta E \) between the new state and the current state.

3. If \( \delta E \leq 0 \) then to minimize the energy change, use the updated state.

4. If \( \delta E > 0 \), randomly choose from a uniform distribution a number \( \nu' \).
   a. if \( e^{\delta E/k_BT} > \nu' \), then use the updated state.
   b. if \( e^{\delta E/k_BT} \leq \nu' \) then do not use the updated state.

Simulations which incorporate the Monte Carlo method and the Metropolis algorithm are called Metropolis Monte Carlo simulations.

### 3.3 Kinetic Monte Carlo

The dynamical evolution of some materials occurs in a series of “rare events”. These events occur after the system exists for an extended period of time at one potential energy minimum with insignificant localized motion, and cause the system to move into another energy state. Dynamical evolution can then be modeled as the evolution of the system through a series of jumps between the potential energy minima. Kinetic Monte Carlo (KMC) simulations, also called dynamic Monte Carlo \([? \text{ kristen}]\) simulations, model dynamical evolution of this type.
KMC simulations are capable of simulating many stochastic or thermally activated processes for systems with known atomic scale processes. The physical energy barriers in a system are taken into account in the stochastic algorithm that is central to KMC simulations; this allows the system to be dynamically evolved in real time (\textsuperscript{?} bbones). KMC time steps are dependent on the parameters involved in observing the stochastic events and individual time steps will vary with system parameters involving the events occurring during that time step.

Single-processor (serial) KMC simulations have been used to model a variety of dynamical processes ranging from catalysis to thin-film growth. The KMC algorithm used in our models of crystal growth is discussed in the following section.

3.3.1 KMC Algorithm

To evolve a system with known transition rates, the following KMC algorithm called “n-fold-way” \cite{7}/Bortz-Kalos-Lebowitz(BKL)/residence-time algorithm can be used:

1. Set the step time to zero, $t = 0$.

2. Determine all possible events, $i$, with rates $R_i$, and calculate the partial cumulative sums $S_i = \sum_{j=1}^{i} R_j$.

   for $i = 1, \ldots, N$ where $N$ is the total number of events, $R_T = \sum_{i=1}^{N} S_i$ is the total rate.

3. Randomly choose from a uniform distribution a number $\nu_j$ such that $0 \leq \nu_j \leq 1$.

4. Randomly select from all events event $j$ to occur with probability $S_{j-1}/R_T < \nu_j \leq S_j/R_T$

5. Evolve the system after event $j$.  

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6. Evolve the time such that the next time step begins at \( t = t - \ln(\nu')/R_T \) where 
\[ 0 < \nu' < 1 \] is a number randomly chosen from a uniform distribution.

7. Repeat steps 2 to 7.

In general, KMC simulations are more efficient than MC simulations. KMC simulations do not use “rejection” steps as in MC simulations; in both simulations events are randomly selected, but in MC simulations the probability of accepting the event is typically \(< 1\) while the probability of accepting the event in KMC simulations is 1. For this reason, KMC simulations do not spend computing time on rejecting events as MC simulations and generally are more time efficient.

Unfortunately, the KMC algorithm is only usable when all atomic scale processes are known. Both the possible events and the event rates must be known, either through \((\text{ab initio})\) calculations or laboratory experiments. However, for cases in which the atomic scale processes are well understood, KMC is extremely advantageous.

### 3.3.2 Binary-tree Search Algorithm

The search and updating cumulative \( R_T \) scales as \( O(N) \) where \( N \) is the total number of events. These steps can be significantly speed up using a binary-tree search algorithm with \( O(\log_2 N) \) scaling. The resulting binary-tree based algorithm is as follows:

1. Update the list of all possible event types that can occur with corresponding rates for each event type in the system. Let each type \( i \) have event number \( n_i \) with \( R_i \).

2. Construct a binary tree where each node contains the sum of the rates below the node and the lowest level nodes (leaves) contain the sums of the rates for
the events of the same type: \( S^0[i] = n_i R_i \). The root node the tree \( S_{total} = S^k[0] \) has total rate of the entire system at all times, where \( k \) is the number of levels or total depth of the binary tree.

3. Generate a random number \( 0 \leq \psi \leq S_{total} \) and start from the root of the tree \((n = k, \ i = 0)\).

4. Compare the number \( \psi \) with the left branch \( S^{n-1}[2i] \)

5. If \( \psi \leq S^{n-1}[2i] \), descend to the left branch \( n \to n - 1, \ i \to 2i \) and continue to 4.

6. If \( \psi > S^{n-1}[2i] \), update the random number \( \psi \to \psi - S^{n-1}[2i] \) and descend to the right branch \( n \to n - 1, \ i \to 2i + 1 \) and then continue to 4.

7. If the lowest level \( n = 0 \) (leaves of the tree) is reached then \( i \) gives the type of picked event.

8. Another random number is generated \( 0 \leq u \leq n[i] \) and perform the event \( j \) for which \( n^{i-1} < u \leq n^i[i] \).

9. Update the tree.

The binary tree search algorithm is faster not only in selecting events but also in updating the total rate \( R_T \), because after the one of the rates in a tree changes, only corresponding tree branch needs to be updated while the remaining rates do not need to be changed.
Chapter 4

Roughness evolution of a-Si:H thin films

4.1 Introduction

Amorphous silicon (a-Si:H) thin-films grown via chemical vapor deposition (CVD) methods are used in a variety of technologically important areas ranging from large-area microelectronic devices to solar cells. Since the device properties depend on thin-film quality, i.e. near-surface and bulk microstructure and \(H\)-bonding \([11]\), there has been significant interest in developing a greater understanding of the growth process, as well as of the dependence of the properties on growth parameters.

Features in the evolution of the surface roughness of a-Si:H films have been correlated with material and device properties. In particular, it has been found that in a-Si:H based thin film solar cells, the optimum device performances are achieved by incorporating intrinsic a-Si:H layers fabricated under conditions that produce enhanced surface smoothing. Therefore, in addition to modeling the thin-film microstructure and its dependence on hydrogen dilution ratio \([12, 13]\), there is also interest in understanding the dependence of the surface roughness evolution on deposition conditions.

Recently, simplified kinetic Monte Carlo simulations \([12, 13]\) of atomistic models
of a-Si:H grown by plasma-enhanced CVD (PECVD), based on \textit{ab initio} calculations for the relevant activation barriers, have been used to model the dependence of the degree of crystallinity on the hydrogen dilution ratio $R_H = [\text{H}_2]/[\text{SiH}_4]$. However, due to the complexity of the PECVD process [14, 15, 16], these simulations were not able to simulate the evolution of the surface morphology [17]. Therefore, it is of interest to consider somewhat simplified models in order to try to understand the roughness over larger length scales.

Here we present the results of simulations of a simplified coarse-grained continuum model of a-Si:H growth carried out in order to understand the evolution of the surface roughness and its dependence on the hydrogen dilution ratio. Our model takes into account two competing effects - the effect of roughening due to shadowing and/or attraction of depositing species to the film, and a smoothing effect due to surface diffusion. In order to model the initial configuration, we have also used a simplified model of nucleation. For correlation with experiments, we have compared our results with real-time spectroscopic ellipsometry (RTSE) results for low-temperature (200$^\circ$C) PECVD at high process gas pressure (3 mTorr). By varying the parameters in our model, we find good agreement between our simulations and experiments for the case of high dilution ratio. However, our results also indicate that for the case of low dilution ratio, for which the surface is significantly rougher, additional effects (such as nonlinearities) may be important. A comparison of our results for different dilution ratios also indicates that the effects of diffusion are greatly enhanced with increasing $R_H$. Our results also indicate that the early stage of nucleation of 3D islands plays a very important role in determining the subsequent roughness evolution.
4.2 Experiment

The experimental results presented here have been previously discussed in Ref. [18]. However, for completeness here we briefly summarize some of the experimental details. Real-time spectroscopic ellipsometry has been performed in order to study the evolution of the surface roughness thickness for Si:H films fabricated by PECVD on native oxide (SiO$_2$) covered crystalline silicon (c-Si) wafer substrates. In experiments, a rotating-compensator multichannel ellipsometer [19] was affixed to a PECVD chamber at an angle of incidence of 70° from the normal of the substrate, with a spectral range from 1.5 to 5.0 eV and a minimum spectral acquisition time of 80 ms [19]. The substrate temperature $T$, rf (13.56 MHz) plasma power $P$, and total pressure $p$ were fixed at the following values: $T = 200^\circ C$, $P = 0.72$ W/cm$^2$, and $p = 3$ mTorr. The H$_2$ dilution ratio $R_H = [\text{H}_2]/[\text{SiH}_4]$, was set at four different values 15, 20, 40, and 60, leading to deposition rates of 18, 14, 9.5, and 6.6 Å/s respectively. The motivation of the experiment work was to apply a combination of high gas pressure and high hydrogen dilution - the latter up to but not exceeding the amorphous-to-(mixed phase nanocrystalline) transition [a $\rightarrow$ (a+nc)] - in order to increase the deposition rate while retaining high quality a-Si:H films for photovoltaic applications. The elevated process gas pressure of approximately 3 mTorr over the standard value (0.2 mTorr) leads to an almost 15× increase in deposition rate, from about 0.5 to 6.6 Å/s for the highest value of $R_H$ ($R_H = 60$) just before the a $\rightarrow$ (a+nc) transition.

As shown in Fig. 4-1, the surface roughness evolution depends strongly on $R_H$ and exhibits three distinct regimes [11]: (i) smoothing (or coalescence) of initial nucleation-generated clusters (ii) stable surface until a critical thickness and (iii) roughening of the film beyond the critical thickness. For example, for the case of $R_H = 60$, the smoothing regime runs from a film thickness of approximately 8 Å to 200 Å, while the stable regime runs from 200 Å to approximately 1200 Å, and finally
the roughening begins at 1200 Å.

Figure 4-1: Experimental roughness as function of average film thickness for H₂ dilution ratios $R_H = 15, 20, 40, 60$.

The RTSE spectra collected during PECVD of these films were analyzed using a two-layer $\Sigma - \sigma$-minimization procedure [20]. In this approach, an unweighted error function minimization method combining numerical inversion and least squares regression analysis is used to simultaneously obtain the film-specific complex dielectric function spectra and the time evolution of the surface roughness and bulk film thickness [21]. Accurate characterization of the microstructural and optical properties of the substrate is obtained from spectra collected prior to a-Si:H deposition, so that the two layers used in the $\Sigma - \sigma$-minimization procedure consist of only the bulk film of the material and a surface roughness layer represented by a Bruggeman effective medium approximation of 50% volume fraction bulk and 50% volume fraction void [22].
In previous work, the surface roughness $W_{RTSE}$ obtained from RTSE measurements has been compared to the root-mean-square (rms) surface roughness $W_{AFM}$ obtained from AFM measurements [22, 23]. A linear relationship of the form $W_{AFM} = 0.667 W_{RTSE} - 2 \AA$ was observed for $W_{RTSE}$ values up to 100 Å. Therefore, this expression was used to convert the surface roughness obtained from RTSE to the results presented here.

4.3 Model

In order to model the roughness evolution in low-temperature PECVD, we have assumed that the growth takes place in two stages. In particular, we assume that in the first stage 3D islands of a-Si:H nucleate on the native-oxide-covered c-Si substrate and then coalesce to form a bulk layer, while in the second stage the film continues to grow but no new islands are nucleated. For simplicity here we have assumed that at the end of the nucleation stage, the film consists of a random distribution of spherical islands or “caps” with wetting angle $\theta_W$ which have a Gaussian distribution of radii. In equilibrium, one expects that the wetting angle of a “droplet” satisfies Young’s equation, e.g. $\cos(\theta_W) = (\gamma_{12} - \gamma_{13})/\gamma_{23}$ where $\gamma_{12}$, $\gamma_{13}$, and $\gamma_{23}$ correspond to the free energies of the substrate/a-Si:H interface, a-Si:H surface, and the substrate surface respectively. However, since these free energies are not known, and may also depend on the dilution ratio $R_H = [H_2]/[SiH_4]$, for simplicity we have carried out simulations for two different values, e.g. $\theta_W = 45^\circ$ and $\theta_W = 90^\circ$.

To describe the subsequent thin-film evolution, we consider the simplest possible continuum equation which takes into account the effects of roughening due to shadowing and/or or the attraction of depositing species to the film, and smoothing due to surface diffusion and/or evaporation. In particular, we consider the following
nonlinear equation for the surface height \( h(\vec{r}, t) \) at position \( \vec{r} \) and time \( t \),

\[
\frac{\partial h(\vec{r}, t)}{\partial t} = -A_1 M + A_2 \sqrt{gM} - A_3 \sqrt{g} \Delta s M + F + \eta(\vec{r}, t),
\]

(4.1)

where \( g = 1 + |\nabla h|^2 \), \( M = g^{-3/2} \sum_{i,j=x,y} (g \delta_{ij} - h_i h_j) h_{ij} \) is the mean curvature (where \( h_x = \partial h/\partial x \), \( h_{xy} = \partial^2 h/\partial x \partial y \) etc.), \( \Delta s \) is the surface Laplacian, \( F \) is the deposition flux, and \( \eta(\vec{r}, t) \) is a noise term which takes into account the effects of both deposition and diffusion noise. Assuming that \( A_1 = \rho F \), where \( \rho \) is the radius of the depositing species, the first term corresponds to “atomic shadowing” as first proposed by Mazor et al. [24] in the context of columnar growth. However, a similar term has also been derived by Raible et al. [25, 26] due to attractive forces between the surface atoms and the incident particles. Similarly, the second term [27] corresponds to a (positive) “surface tension” due to evaporation/condensation or re-emission (“anti-shadowing”) while the term with \( A_3 \) corresponds to surface diffusion [28]. We note that in the context of a single-species growth model, e.g. only SiH3, one may write \( A_3 = D_s \sigma_s \Omega^2 \epsilon / kT \) where \( D_s, \Omega, \) and \( \epsilon \) are the diffusion constant, atomic volume, and surface density of the diffusing species respectively, \( \sigma_s \) is the surface tension, \( k \) is Boltzmann constant and \( T \) is the film temperature. For amorphous growth we expect that the diffusion constant \( D_s \) is independent of the local slope, and thus it is reasonable to assume that \( A_3 \) is a constant.

Linearizing this equation and dividing by the flux \( F \) - and also ignoring the noise term since it is expected to be small beyond the nucleation regime - we obtain,

\[
\frac{\partial h(\vec{r}, \bar{h})}{\partial \bar{h}} = 1 - \nu_2 \nabla^2 h(\vec{r}, \bar{h}) - \nu_4 \nabla^4 h(\vec{r}, \bar{h}),
\]

(4.2)

where \( h(\vec{r}, \bar{h}) \) is a function of the transverse coordinate \( \vec{r} \) and average height \( \bar{h} = Ft \). Here \( \nu_2 = (A_1 - A_2)/F \) and \( \nu_4 = A_3/F \). As can be seen, this equation contains two competing terms - a 2nd order instability term due to shadowing and/or attraction
modified by the effects of evaporation/condensation, and a 4th order smoothing term due to surface diffusion. As long as the local slope is less than 1, the solution of the linearized equation should give a reasonable approximation to the full nonlinear equation in the absence of deposition noise. In addition, it has the advantage that it can be efficiently integrated using a fast Fourier transform starting from the initial surface profile $h_0(\vec{r}, \bar{h})$. In particular, changing from $\vec{r}$ to $\vec{k}$ space $h(\vec{r}, \bar{h}) \rightarrow \tilde{h}(\vec{k}, \bar{h})$ leads to the solution:

$$
\tilde{h}(\vec{k}, \bar{h}) = \tilde{h}(\vec{k}, \bar{h}_0) \exp \left[ (\nu_2 - \nu_4 k^2) k^2 \bar{h} \right],
$$

(4.3)

As can be seen from Eq. 4.3 there is a critical wavevector $k_c = \sqrt{\nu_2/\nu_4}$ such that short wavelength surface modulations with $k > k_c$ disappear exponentially due to surface diffusion, while those with $k < k_c$ (i.e. long wavelengths) grow exponentially with film thickness. The most unstable mode corresponds to $k_m = k_c/\sqrt{2}$. The surface profile $h(\vec{r}, \bar{h})$ is then obtained from $\tilde{h}(\vec{k}, \bar{h})$ by carrying out an inverse Fourier transform.

As already noted, in order to model the roughness evolution in low-temperature PECVD, we have assumed that the growth takes place in two stages. In particular, we have assumed that at the end of the initial nucleation stage, the film consists of a random distribution of semi-spherical islands or “caps” with wetting angle $\theta_W$ which have a Gaussian distribution of radii with mean value $\bar{R}$ and standard deviation $\sigma$.

Using the relationship $W_{RTSE} = 3\AA + 1.5 W_{AFM}$ (see Sec. 4.2) the initial roughness values in Fig. 4-2 may be converted to a surface roughness layer thickness $d_s = W_{RTSE}$ with a value of approximately 15 Å. Using a geometrical picture, this suggests that the average radius $\bar{R}$ at the end of the nucleation stage is of the order of 15 Å. Accordingly, in our simulations we have used values of $\bar{R}$ close to this value in order to fit the experimental results. In addition, since the initial roughness depends relatively weakly on the dilution ratio $R_H$, in our simulations we have assumed an initial island...
density \( (N_0 = 2.9 \times 10^{-3} \, \text{Å}^{-2}) \) which is the same for all values of \( R_H \). Thus, for a given choice of experimental dilution ratio and assumed wetting angle \( \theta_W \), values of the average island radius \( \bar{R} \) and standard deviation \( \sigma \) were varied in order to obtain an initial configuration for which there is good agreement with the experimental roughness at an average film thickness in the range \( \bar{h} \simeq 10 - 20 \, \text{Å} \). We note that since the initial island distribution was random, this resulted in a significant overlap between different islands - the resulting initial profile was then determined by the maximum height at each point.

In order to determine the subsequent roughness evolution, the resulting initial surface configurations were then numerically integrated using Eq. 4.3 for different values of the parameters \( \nu_2 \) and \( \nu_4 \) to find the best fit. It is worth mentioning that for a given dilution ratio \( R_H \), good fits were only possible for specific values of \( \bar{R} \) and \( \sigma \). For determination of these values an iterative process was used, e.g. values of \( \bar{R} \) and \( \sigma \) matching the initial experimental roughness were first determined, and then \( \nu_2 \) and \( \nu_4 \) were varied to obtain the best match with experiment. If the resulting best fit was not good, then new values of \( \bar{R} \) and \( \sigma \) were selected. This process was continued until reasonable results were obtained up to a film thickness of 500 – 2000 Å depending on the value of \( R_H \). Thus, for a given choice of initial island density the resulting process puts significant constraints not only on the parameters \( \nu_2 \) and \( \nu_4 \) but also on the parameters \( \bar{R} \) and \( \sigma \) describing the initial conditions.

### 4.4 Results

We first consider our simulation results for the case of a large assumed wetting angle \( \theta_W = 90^\circ \). Fig. 4-2 shows the corresponding best-fit simulation results for the surface roughness along with the corresponding experimental results. As can be seen there is very good agreement with experiment for the two largest dilution ratios
$R_H = 40$ and $R_H = 60$. However, for the two smaller values of $R_H$ ($R_H = 15$ and 20) the simulated roughness is significantly higher than the experimentally obtained roughness for thicknesses larger than $\bar{h} \simeq 500 - 1000 \, \text{Å}$. We note that in this case the experimental roughness curve obtained via RTSE also exhibits a bend or inflection point. One possible explanation for this behavior is that a new physical mechanism comes into play for small dilution ratio which suppresses the continued rapid increase in the surface roughness at large thicknesses. Another possibility is that, as pointed out in Ref. [29], for large thicknesses the RTSE measurement tends to underestimate the surface roughness since it does not include the long wavelength contribution. However, one would expect such an effect to occur only for thicknesses significantly larger than 1000 Å. In addition, it is not clear why such an effect should occur for small dilution ratios but not for larger dilution ratios.

Table 4.1: Simulation parameters as a function of hydrogen dilution ratio $R_H$ for different wetting angles. For all cases initial island density $N_0 = 2.9 \times 10^{-3} \, \text{Å}^{-2}$.

<table>
<thead>
<tr>
<th>$R_H(\theta = 90^\circ)$</th>
<th>$\nu_2 (\text{Å})$</th>
<th>$\nu_4 (\text{Å}^4)$</th>
<th>$\sigma (\text{Å})$</th>
<th>$\bar{R} (\text{Å})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.2</td>
<td>6</td>
<td>6</td>
<td>13.5</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>10.5</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>40</td>
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<th>$\nu_4 (\text{Å}^4)$</th>
<th>$\sigma (\text{Å})$</th>
<th>$\bar{R} (\text{Å})$</th>
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<td>60</td>
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</tbody>
</table>

Table 4.1 shows the corresponding values for the average initial island radius $\bar{R}$ and standard deviation $\sigma$ as well as of the parameters $\nu_2$, and $\nu_4$ as a function of the dilution ratio $R_H$ for wetting angles $\theta_W = 90^\circ$ and $\theta_W = 45^\circ$. As can be seen,
Figure 4-2: Experimental roughness (solid lines) and simulation results (dashed lines) using Eq. 4.2 as function of average film thickness for H\textsubscript{2} dilution ratios $R_H = 15, 20, 40, 60$. Simulations correspond to initial surface profile with wetting angle $\theta_W = 90^\circ$.

with our assumption of a dilution-ratio independent initial island density $N_0$, the parameters $\bar{R}$ and $\sigma$ also depend relatively weakly on the dilution ratio. In contrast the surface tension $\nu_2$ increases with increasing $R_H$, while the surface diffusion or smoothing parameter $\nu_4$ increases even more dramatically with the H\textsubscript{2} dilution ratio. These results suggest that increasing the hydrogen dilution leads to increased surface diffusion of mobile species on the surface of the growing a-Si:H film. We note that this is reasonable since we expect that increasing the H\textsubscript{2} dilution leads to a decrease in the number of unsaturated bonds and/or defect sites at the surface, thus increasing the distance that mobile species can diffuse before being trapped or incorporated in the film.
Figure 4-3: Experimental roughness (solid lines) and simulation results using Eq. 2 (dashed lines) as function of average film thickness for H₂ dilution ratios $R_H = 15, 20, 40, 60$. Simulations correspond to initial profile with wetting angle $\theta_W = 45^\circ$.

Similar results are shown in Fig. 4-3 and Table 4.1 for the case of smaller wetting angle ($\theta_W = 45^\circ$). In this case, there is again reasonable agreement up to the largest film thicknesses for the two largest dilution ratios. However, the fit is not quite as good as for $\theta_W = 90^\circ$. Similarly, while there is good agreement for $\bar{h} < 500 - 1000 \text{ Å}$ for $R_H = 15$ and 20, there is poor agreement for larger thicknesses. As for the case of $\theta_W = 90^\circ$, we find that the surface tension $\nu_2$ increases weakly with increasing dilution ratio, while the surface diffusion parameter $\nu_4$ increases much more rapidly with $R_H$. Also, the values of the parameter $\nu_2$ and $\nu_4$ are significantly larger for the case of small wetting angle. We note that while the average initial island radius $\bar{R} \simeq 10 \text{ Å}$ is approximately the same as for higher wetting angle ($\theta_W = 90^\circ$), the width $\sigma$ of the island-radius distribution is several times larger than the average.
radius. Fig. 4-4 shows a summary of our results for the dependence of $\nu_2$ and $\nu_4$ on hydrogen dilution ratio $R_H$ for both wetting angles. As can be seen, for both values of $\theta_W$, the parameter $\nu_4$ exhibits a power-law dependence on the dilution ratio, e.g. $\nu_4 \sim (R_H)^\alpha$ where $\alpha \simeq 2.6$ (1.7) for $\theta_W = 90^\circ$ (45$^\circ$) respectively.

Figure 4-4: Dependence of parameters $\nu_2$ and $\nu_4$ on hydrogen dilution ratio $R_H$ for $\theta_W = 90^\circ$ and $\theta_W = 45^\circ$

Figure 4-5 shows typical plots of the morphology obtained in our simulations at different thicknesses for the case $R_H = 40$ and both wetting angles, e.g. $\theta_W = 90^\circ$ ((a)-(c)) and $\theta = 45^\circ$ ((d)-(f)). As can be seen, the lateral length-scale tends to increase with increasing film thickness due to the elimination of small wavelength fluctuations. However, it appears to saturate at large thicknesses $h > 1000 \text{ Å}$.

To study this behavior more quantitatively, we have fit the circularly-averaged height-difference correlation function $G_2(r) = \langle [h(r) - h(0)]^2 \rangle$ to the form $G_2(r) = w^2 \left(1 - e^{-r^2/\xi^2}\right)$ where $w$ is the surface roughness and $\xi$ is the lateral correlation length. Fig. 4-6 shows the corresponding results for the dependence of $\xi$ on film
thickness $\bar{h}$ for all four values of the dilution ratio for $\theta_W = 90^\circ$. Similar results (not shown) have been obtained for $\theta_W = 45^\circ$. As can be seen, while the correlation length $\xi$ tends to increase with thickness at small thicknesses, it tends to saturate to a value proportional to the maximally unstable wavelength $\lambda_m \simeq \sqrt{2\nu_1/\nu_2}$ at larger thicknesses. We also note that, except for the case $R_H = 15$ for which the initial lateral length scale is larger than the selected wavelength $\lambda_m$, the film thickness at which the correlation length saturates corresponds approximately to that at which the surface roughness begins to increase rapidly as shown in Fig. 4-2.

4.5 Discussion

We modeled the evolution of the surface roughness of a-Si:H film grown via PECVD for values of the hydrogen dilution ratio ranging from $R_H = 15$ to $R_H = 60$ and compared with results obtained using RTSE. In general, we find that the surface roughness decreases with increasing $R_H$ for a given bulk layer thickness. In addi-
Figure 4-6: Lateral length scale parameter $\xi^2$ as function of average film thickness for $R_H = 15, 20, 40, 60$ and $\theta_W = 90^\circ$. Saturation value of $\xi$ corresponds to most unstable mode $k_m = k_c/\sqrt{2} = \sqrt{\nu_2/2\nu_4}$.

tion, the RTSE results indicate that the growth process may be divided into four distinct regimes: (i) an initial island nucleation regime (ii) the formation of a bulk layer via island coalescence (iii) growth at approximately constant roughness (iv) a rapid increase in roughness for large thicknesses.

To get a better understanding of the processes determining the evolution of the surface roughness after the initial stages of island nucleation and coalescence, we have carried out simulations using a simplified linear equation which includes two competing terms describing the local growth rate - a negative surface tension term ($\nu_2 \nabla^2 h$) which takes into account the combined effects of atomic shadowing [30] and evaporation/condensation, and a surface diffusion term [28] ($\nu_4 \nabla^4 h$) which tends to smooth the surface on short length-scales. As an initial configuration in our simulations we have assumed a random distribution of 3D spherical “caps”, with a dilution-ratio
independent initial island density while the average island radius and standard deviation were chosen to match the initial experimental roughness at small film thickness ($\bar{h} \simeq 10 - 20 \text{ Å}$). Since the experimental wetting angle $\theta_W$ was unknown, we have carried out simulations with two different possible values, e.g. $\theta_W = 45^\circ$ and $90^\circ$. The values of the parameters $\nu_2$ and $\nu_4$ were then varied to obtain the best possible agreement with experiment.

For the case of large dilution ratio ($R_H = 40$ and 60), we find very good agreement between our simulation results and experimental results for the surface roughness for all thicknesses up to 3000 Å. We note that better agreement is obtained for the case of a large wetting angle ($\theta_W = 90^\circ$) than for a small wetting angle ($\theta_W = 45^\circ$). It is worth noting that this is consistent with experiments on liquid Si droplets on SiO$_2$ substrates [31] in which a wetting angle of $90^\circ$ was observed.

Figure 4-7: Distribution $F(m)$ of surface slopes $m$ ($\theta_W = 90^\circ$) for $R_H = 60$ (solid lines) and $R_H = 15$ (dashed lines).
Our results also suggest that, at least for large dilution ratios, the dominant processes determining the evolution of the surface roughness may be described by two main effects - an instability due to atomic shadowing (modified by attachment/detachment) and smoothing due to surface diffusion. In this connection, we note that the value of the parameter $\nu_4$ found in our simulations increases rapidly with increasing $R_H$. This is consistent with the expectation that increasing the dilution ratio will lead to a decreased density of trapping sites and an increased diffusion length. Similarly, we find that $\nu_2$ depends relatively weakly on the dilution ratio. In addition, at least for the case of large wetting angle, the magnitude of $\nu_2$, e.g. $0.2 - 0.6$ Å, is significantly less than expected using the Mazor-Srolovitz prediction $\nu_2 = -\delta$ where $\delta$ is the radius of the SiH$_3$ adsorbate. This is consistent with our expectation that the destabilizing effects of atomic shadowing are compensated by the effects of detachment, evaporation, or re-emission [32] thus reducing the magnitude of $\nu_2$.

It is also worth noting that the short-range attraction of depositing particles to the substrate may also play a role in enhancing this instability [25, 33], although we would expect the effects of attraction to be relatively weak, given the relatively high kinetic energies of depositing particles in PECVD. In this connection, we note that the slope on a log-log plot of the experimental surface roughness as a function of film thickness (not shown) is significantly larger than 1 for large film thickness and high dilution ratio ($R_H = 40$ and 60). While this is consistent with our model (since the negative surface tension term is expected to lead to exponential growth of the surface roughness at large thicknesses) it is not consistent with a model which only includes global shadowing since this leads to a roughening exponent $\beta = 1$ at late times [32].

As already noted, the good agreement between our simulation results and experiments for high dilution ratio indicates that surface diffusion plays an important role in the evolution of the surface roughness in low-temperature PECVD. This behavior is consistent with the results of Sperling and Abelson [29] who measured the struc-
ture factor $S(q)$ for a-Si:H films grown via hot-wire CVD (HWCVD) and found a $q^{-4}$ dependence which is typical of surface diffusion. However, this raises the question of what is diffusing, or perhaps more precisely what is the dominant diffusing species? In this connection, we note that recent atomistic kinetic Monte Carlo models based on first-principles calculations [13, 12] which have been able to account for the dependence of the degree of crystallinity on temperature and dilution ratio do not include the effects of diffusion. This suggests that while diffusion may play an important role in determining the surface roughness, it may be less important for the nucleation and growth of nanocrystals.

We also find relatively good agreement between our simulations and experiments for low hydrogen dilution ratio ($R_H = 15$ and 20) for thicknesses which are not too large, e.g. up to the point (e.g. ‘amorphous-to-amorphous transition’ [18]) where the roughness starts increasing rapidly. However, in this case the rate of increase of the experimentally measured roughness decreases at large thicknesses. One possibility is that some new physical mechanism comes into play at large thicknesses for small dilution ratios which suppresses the rapid increase in roughness. However, another possibility is that the development of large slopes at large film thicknesses implies that the linearized Eq. 4.2 cannot be used, but instead the fully nonlinear Eq. 4.1 should be used.

In order to determine if this is the case, we have examined the distribution of surface slopes $F(m)$ (where $m$ is slope magnitude) at large thicknesses for both small and large dilution ratios. As can be seen in Fig. 4-7, for large dilution ratio the slopes are typically significantly less than 1 even at large film thicknesses. In contrast, for small dilution ratio significantly larger slopes of the order of 1 or larger are observed in our simulations. This suggests that for small dilution ratios and large film thicknesses, it may be necessary to use the nonlinear form of Eq. 4.1. In this connection, we note that the strength of the instability term ($-A_1M$) in Eq. 4.1 decreases with increasing
slope $|\nabla h|$ and $g = 1 + (\nabla h)^2$, thus possibly explaining this effect. On the other hand, the nonlinear surface diffusion term $-A_3 g \Delta_s M$ also decreases with increasing $g$, while the stabilizing attachment/detachment term $A_2 \sqrt{g} M$ is also reduced, but less significantly. Therefore, numerical integration of the fully nonlinear Eq. 4.1 will be needed to determine if the differences for small dilution ratio and large film thicknesses can be explained by these nonlinear effects.

Besides the nonlinearities inherent in Eq. 4.1, which may be important for small dilution ratios and large film thicknesses, another important issue is the initial configuration. Since in our simulations it was found that the surface roughness evolution is quite sensitive to the initial configuration, it is desirable to directly model the early stages of island nucleation and coalescence. While a full atomistic simulation of a-Si growth is difficult because of the complexity of the PECVD process, in Chapter 5 we carried out simulations of a simplified atomistic model that allows us to obtain a better understanding of the thin-film morphology during the nucleation regime.

We now consider some possible extensions or modifications to the simplified continuum model presented here. In particular, we note that Raible et al. [26, 34] have suggested a number of additional terms to describe amorphous thin-film growth. These include a Kardar-Parisi-Zhang (KPZ)-like term [3] proportional to $|\nabla h|^2$ which may be related to the dependence of the film density on slope, as well as a “conserved KPZ term” (proportional to $\nabla^2 |\nabla h|^2$) due to the slope dependence of the local density of diffusing species [35]. By adding terms of this form, and also including the effects of finite scanning-tunneling microscopy (STM) tip size, Raible et al. [25] were able to quantitatively explain the experimentally observed saturation of the surface roughness in amorphous ZrAlCu thin films grown by physical vapor deposition. In the future, it may be of interest to consider the addition of similar nonlinear terms to Eq. 1 since these may become important at large thicknesses and for low $R_H$.

Another effect which has not been directly considered in our simulations is the
effect of global shadowing, which may occur when atoms are deposited at an angle with respect to the substrate. Such an effect may be expected in PECVD due to the fact that deposition takes place in a plasma in which the radicals are traveling in random directions before hitting the surface, thus leading to shadowing of valleys by hills. While this provides another possible explanation for the instability term $-\nu_2 \nabla^2 h$ in Eq. 4.2, shadowing is a non-local effect and therefore cannot be fully described simply by including this term. Therefore, it may also be of interest to carry out simulations in which shadowing and/or re-emission are directly taken into account.

In conclusion, to model the experimentally observed roughness evolution we have used a simplified linearized continuum equation which takes into account the destabilizing effects of atomic shadowing and/or attraction as well as the smoothing effects of surface diffusion. By varying the initial configuration as well as the parameters $\nu_2$ and $\nu_4$, we have found good agreement with experiment in the case of large dilution ratios ($R_H = 40$ and $R_H = 60$). The good agreement between our simulations and experiments at high dilution ratio indicates that surface diffusion plays an important role. However, there is disagreement at large thicknesses for small dilution ratios ($R_H = 15$ and $R_H = 20$) when surface slopes $m$ become larger than 1. Further work will be needed to take into account a variety of nonlinear effects which may affect the surface roughness in this case, as well as to understand the atomistic mechanisms of a-Si:H surface growth.
Chapter 5

Scaling of the island density and island-size distribution in irreversible submonolayer growth of 3D islands

5.1 Introduction

In Chapter 4 we observed that evolution of the surface roughness greatly depends on early nucleation stages when submonolayer of 3D islands is formed. These results and earlier studies [37, 38, 39, 40, 41] showed that the ordering and size-distribution of islands in submonolayer growth plays an important role in determining the later stages of thin-film growth. Accordingly, during the past few years considerable experimental and theoretical effort [42] has been devoted to studying the dependence of the submonolayer scaling behavior on deposition conditions. Of particular interest is the dependence of the (per-site) island-density $N$ and island-size distribution $N_s(\theta)$ (where $N_s$ is the number density of islands of size $s$ at coverage $\theta$) on such deposition parameters as the deposition flux $F$ and growth temperature $T$. 
One concept that has proven especially useful is that of a critical island size, corresponding to one less than the size of the smallest “stable” cluster. For example, in the case of submonolayer growth of 2D islands on a 2D substrate, standard nucleation theory\cite{38, 39} predicts that the peak island density satisfies,

\[ N_{pk} \sim (D/F)^{-\chi_i} e^{E_b/(i+2)k_B T} \]  

\[ (5.1) \]

where \( D = D_0 e^{-E_a/k_B T} \) is the monomer hopping rate, \( E_a \) is the activation energy for monomer diffusion, \( E_b \) is the binding energy of the critical nucleus, \( i \) is the critical island size, and \( \chi_i = \frac{i}{i+2} \). In addition, it has been shown that in the pre-coalescence regime the island-size distribution (ISD) satisfies the scaling form \cite{43, 44},

\[ N_s(\theta) = \frac{\theta}{S^2} f_i \left( \frac{s}{S} \right), \]

\[ (5.2) \]

where \( S \) is the average island size, and the scaling function \( f_i(u) \) depends on the critical island size \cite{45}.

While much of the theoretical work has focused on an analysis of the scaling behavior in the case of homoepitaxial 2D island growth or on quantum dot formation in the case of heteroepitaxial growth \cite{46}, in some cases 3D islands may also be formed in the submonolayer regime, e.g. before a complete layer is formed. For example, sputter deposition of Al, Cu, and Cr \cite{47, 48} on amorphous SiO\(_2\) and TiO\(_2\) as well as plasma-enhanced chemical vapor deposition (PECVD) of hydrogenated amorphous Si on SiO\(_2\) \cite{49, 50} can lead to non-wetting 3D island growth. Therefore, understanding the scaling behavior of the island-density and size-distribution in the case of 3D island growth is of great interest.

We note that in the case of 3D island growth a distinction should be made between the coverage \( \theta \) corresponding to the substrate area fraction covered by islands, and the dose \( \phi \) corresponding to the number of particles per unit area (or equivalent
monolayers) deposited. In particular, since the onset of island-coalescence is related to the coverage $\theta$ we expect that the scaling of the peak island-density is equivalent to that of the island density at fixed coverage. Based on this assumption, standard nucleation theory [38, 39] predicts that for 3D island growth, the effective value of the exponent describing the flux-dependence of the peak island density is given by $\chi'_i = \frac{i}{i+2.5}$ rather than $\chi_i = \frac{i}{i+2}$ as for 2D islands. This relation has been used to analyze the dependence of the peak 3D island density on temperature and flux in a number of experimental papers [51, 52]. However, while there have been many studies of 2D island growth, there have been few theoretical [53] studies of the scaling behavior of the island-density and ISD for 3D islands.

Here we present the results of simulations of a simple model of 3D irreversible island growth, carried out in order to better understand the relevant scaling behavior in this case. We have also compared our results for the scaled island-size distribution with those obtained for 2D islands. In addition to our simulations, we also present a general theoretical relation (valid for any critical island-size) connecting the exponent $\chi_i$ corresponding to the flux-dependence of the island-density at fixed dose $\phi$, and the exponent $\chi'_i$ corresponding to the flux-dependence of the peak island density. For comparison with our simulation results we also present self-consistent rate-equation results for the island and monomer densities as a function of coverage.

In qualitative agreement with the standard RE prediction, we find that (in contrast to the case of 2D islands) for 3D islands the island density does not saturate with increasing coverage in the pre-coalescence regime. Accordingly, the effective value of $\chi'_i$ is indeed somewhat smaller than the value ($\chi_1 = 1/3$) for 2D irreversible island growth. However, due to the fact that the average capture number for 3D islands increases with coverage, some deviations are also observed. For example, the effective values of the exponents $y_1$ and $y'_1$ describing the dependence of the island density on dose $\phi$ and coverage $\theta$ in the pre-coalescence regime are significantly
smaller than the standard RE prediction. As a result, the value of $\chi'_1$ obtained in our simulations ($\chi'_1 \approx 0.30$) is somewhat larger than the standard RE theory prediction ($\chi'_1 = 2/7 \approx 0.286$). We also find good agreement between the results of a self-consistent RE calculation and our simulation results for the island and monomer densities as a function of coverage/dose and $D/F$. However, despite these differences we find very little difference between the scaled ISD for 3D islands and that for 2D islands. In addition to these results, we also discuss the dependence of the exponent $\chi'_i$ on the critical-island size $i$. However, since $\chi'_i$ depends only weakly on $y'_i$, this only leads to small deviations from the standard RE predictions for $\chi'_i$. Finally, we discuss the suitability of measuring the exponents $y_i$ (or $y'_i$) rather than $\chi'_i$ in order to estimate the critical island size.

5.2 Model

Our simulations are motivated by recent experiments on amorphous Si grown via PECVD for which it was found in Chapter 4 that there is a large wetting angle. Accordingly, here we assume that the 3D islands are hemispherical, while a substrate consisting of a square lattice of deposition sites with lattice constant $a$ is also assumed for simplicity. In particular, each island of size $s$ is represented by a hemisphere with volume $v_s = 2\pi r^3_s/3$ and radius $r_s = r_1 s^{1/3}$ where $r_1 = a/2$. While such an assumption is not entirely realistic for small islands, we do not expect that inclusion of a more realistic size-dependence for small islands will affect the results presented here since the asymptotic scaling behavior is determined by the large islands.

In order to take deposition into account, in our model atoms are randomly deposited onto the substrate with rate $F$ per unit time per lattice site, while monomers are assumed to hop in each of the 4 nearest-neighbor directions with hopping rate $D_h = D/4$, where $D$ is the total hopping rate. Since we are assuming irreversible
growth, when two monomers are nearest-neighbors they are assumed to form a stable dimer, while any monomers which overlap with an island either via direct impingement or via diffusion are assumed to aggregate irreversibly to the island. In particular, we assume that when two monomers become nearest-neighbors they form a hemisphere with radius $r_2$ whose center is located at the center-of mass of the two monomers. Similarly, if a monomer overlaps with an island, then the monomer is “absorbed” and the radius of the island is increased accordingly. Although the focus here is on the pre-coalescence regime in which there is a low probability of island coalescence, we also assume that if two islands overlap then a third island is formed by the “union” of the two initial islands. In this case, the radii of the islands is also adjusted to ensure mass conservation.

For comparison, we have also carried out similar simulations for the case of 2D circular islands. In this case, everything is the same as for the 3D case except that the island area and radius are given by the expressions $a_s = \pi r_s^2$ and radius $r_s = r_1 s^{1/2}$ with $r_1 = a/2$ as before. In order to avoid finite-size effects, in our kinetic Monte Carlo (KMC) simulations we have used a large system size of $1024 \times 1024$ lattice sites, while averages over 100 runs were taken to obtain good statistics. In order to determine the asymptotic dependence of the island density on coverage and $D/F$ our simulations were carried out using values of $D/F$ ranging from $10^9 - 10^{11}$ up to a maximum coverage of 0.2 monolayers (ML).

5.3 Results

5.3.1 Scaling approach to 3D island growth

Before presenting our simulation results, we first consider the standard RE approach for the flux-dependence and dose-dependence of the island density for a given critical island-size $i$. In particular, assuming size- and coverage-independent capture
numbers $\sigma$ one may write the following truncated rate-equations for the densities $N$ ($N_1$) of stable islands (monomers),

\[
\frac{dN}{d\phi} = \sigma R N_1 N_i, \tag{5.3}
\]

\[
\frac{dN_1}{d\phi} = 1 - 2\sigma R N_1^2 - 2\kappa_1 N_1 - \sum_{s \geq 2} \kappa_s N_s - (\sigma R N_1 - \frac{\delta_s}{F}) \sum_{s=2}^{i} N_s - \sigma R N_1 N \tag{5.4}
\]

where $N = \sum_{s \geq i+1} N_s$ and $\delta_s$ corresponds to the monomer detachment rate for an island of size $s$. In the limit of large $D/F$ and beyond the nucleation regime the first and last terms in Eq. 5.4 dominate and $dN_1/d\phi \simeq 0$ which implies

\[
N_1 \sim (RN)^{-1} \tag{5.5}
\]

Assuming the Walton relation \cite{k46} $N_i \sim N_i^i e^{E_b/k_B T}$ (where $E_b$ is the binding energy of the critical nucleus), and substituting Eq. 5.5 into Eq. 5.3 and solving for $N$ we obtain,

\[
N \sim R^{-i/(i+2)} \phi^{1/(i+2)} e^{E_b/(i+2)k_B T} \tag{5.6}
\]

which implies that $N \sim F^{\chi_i} \phi^{y_i}$ where

\[
\chi_i = i/(i+2), \quad y_i = 1/(i+2) \tag{5.7}
\]

We note that this expression for $\chi_i$ has been verified in many simulations of 2D submonolayer island growth \cite{a14, a16, a17, a15, a18}. However, the result for $y_i$ has only been found to be valid for point-islands \cite{a16, a17}. In contrast - due to the fact that the average capture number and impingement terms increase with increasing coverage - for 2D islands the island-density saturates with increasing coverage and one has
\( y_i = 0 \).

We now consider the standard RE prediction for the exponents \( y_i' \) and \( \chi_i' \) describing the coverage-dependence and flux-dependence (at constant coverage) respectively of the island density for 3D islands. In particular one may write,

\[
\theta \sim NS^{2/3} \sim N(\phi/N)^{2/3} \sim N^{1/3} \phi^{2/3}
\]

(5.8)

where \( S = \phi/N \) is the average island size. Substituting into Eq. 5.6 we obtain,

\[
N \sim F^{2\chi_i/(y_i+2)}\theta^{3y_i/(y_i+2)} \sim F^{\chi_i'}\theta^{y_i'}
\]

(5.9)

which implies that,

\[
\chi_i' = 2\chi_i/(y_i + 2) \quad , \quad y_i' = 3y_i/(y_i + 2)
\]

(5.10)

Substituting the expressions for \( \chi_i \) and \( y_i \) in Eq. 5.7 this result leads to the standard RE prediction for the flux-dependence of the peak island density for 3D islands [57],

\[
\chi_i' = \frac{i}{i+2.5}
\]

(5.11)

as well as the result,

\[
y_i' = \frac{3}{5+2i}
\]

(5.12)

Substituting Eq. 5.6 into Eq. 5.8 and inverting to obtain \( \theta(\phi) \) we also obtain the following expression for the coverage \( \theta \) as a function of dose \( \phi \) in the case of 3D islands,

\[
\theta \sim R^{-\chi_i/3} \phi^{\gamma_i}
\]

(5.13)

where \( \gamma_i = (y_i+2)/3 \). We note that in the case of irreversible growth, Eq. 5.13 implies
θ \sim \phi^{7/9} \simeq \phi^{0.778}. Table 5.1 shows a summary of the exponents $\gamma_i, y_i, y'_i, \chi_i, \text{ and } \chi'_i$ as a function of critical island size $i$ for $i = 1 \ldots 8$. As can be seen, except for the exponent $\gamma_i$ all of the other exponents depend sensitively on the critical island-size.

Table 5.1: Standard RE predictions for exponents as function of critical island-size.

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<th>$i$</th>
<th>$\gamma_i$</th>
<th>$y_i$</th>
<th>$y'_i$</th>
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<td>7</td>
<td>0.704</td>
<td>0.111</td>
<td>0.158</td>
<td>0.778</td>
<td>0.737</td>
</tr>
<tr>
<td>8</td>
<td>0.700</td>
<td>0.100</td>
<td>0.143</td>
<td>0.800</td>
<td>0.762</td>
</tr>
</tbody>
</table>

5.3.2 Simulation results

We first consider the dependence of the island and monomer densities on dose $\phi$ for the case of irreversible growth of 3D (hemispherical) islands. As can be seen in Fig. 5-1, in contrast to the case of 2D islands (see Fig. 5-6) for which the island-density saturates at doses less than 1 ML, for 3D islands the saturation dose is much higher than 1 ML since the effective coverage is reduced. Also shown in Fig. 5-1 are our self-consistent RE results (solid curve). We note that these results were obtained using the methods discussed in section 2.2, with the assumption (appropriate for hemispherical islands) that \( r_s = 1/2 s^{1/3} \). As can be seen, there is very good agreement with our simulation results. However, a power-law fit to the dependence of the island density on dose in the pre-coalescence regime (see Fig. 5-2) gives an effective value \( (y_1 \simeq 0.24) \) which is significantly lower than the standard RE prediction given by Eq. 5.7 \( (y_1 = 1/3) \). In contrast, fits for the island density at constant dose as a function of $D/F$ (not shown) give a value $\chi_1 \simeq 0.32$ in good agreement with the standard prediction of $1/3$.
Figure 5-1: Island-density \( N \) and monomer density \( N_1 \) as function of dose \( \phi \) obtained from KMC simulations (symbols) and self-consistent RE calculations (solid curves) for \( D/F = 10^9 - 10^{11} \).

We now consider the dependence of the island density on coverage. As can be seen in Fig. 5-3, the island density (solid curves) saturates at a coverage slightly above 0.1 ML. As indicated by the continued increase of the total density of nucleated islands (dashed curve) this saturation is due to coalescence. In addition, fits to the coverage-dependence in the pre-coalescence regime (see Fig. 5-4) give a value of \( y_1' \) (\( y_1' \approx 0.32 \)) which is significantly lower than the standard RE prediction (\( y_1' = 3/7 \approx 0.43 \)) although in good agreement with the value obtained using Eq. 5.10 if we assume the measured value of \( y_1 \) (\( y_1 \approx 0.24 \)) rather than the predicted value (\( y_1 = 1/3 \)). Also shown in Fig. 5-3 (inset) is a plot of the island-density at fixed coverage (\( \theta = 0.07 \)) in the pre-coalescence regime as a function of \( D/F \). As can be seen the effective value of the island-density scaling exponent obtained in our simulations (\( \chi_1' \approx 0.30 \)) is slightly higher than the standard RE prediction (\( \chi_1' = 2/7 \approx 0.286 \)) but still somewhat lower
than the value \(1/3\) expected for 2D islands.

In order to further understand the difference between the coverage- and dose-dependence of the island-density for 3D islands, in Fig. 5-5 we show the dependence of the coverage \(\theta\) on dose \(\phi\) obtained in our simulations. As can be seen, the dependence of coverage on dose exhibits power-law behavior, e.g. \(\theta \sim \phi^{\gamma_1}\) over the entire range of dose, with an exponent \(\gamma_1 \simeq 0.76\) which is somewhat smaller than the standard RE prediction \(\gamma_1 = 7/9 \simeq 0.78\) but in good agreement with the expression \(\gamma_1 = (y_1 + 2)/3\) given in Eq. 5.13 if we assume \(y_1 = 0.24\). For comparison, simulation results for the island density as a function of coverage for 2D circular islands are shown in Fig. 3(b) up to a coverage \(\theta = 0.5\) ML. As can be seen, the saturation coverage is close to that for 3D islands. In addition, we again find excellent agreement in the pre-coalescence regime \((\theta < 0.1\) ML\) between our self-consistent RE results (curved
Finally, we compare the submonolayer morphology and scaled island-size distribution for 2D and 3D islands. Fig. 5-7 shows typical pictures for 3D ((a) -(c)) and 2D ((d)-(f)) islands at \( \theta = 0.07 \) ML and \( D/F = 10^9 - 10^{11} \). As expected, with increasing \( D/F \) the island-density decreases while the average island-size increases. However, due to the fact that the capture number for 2D islands is larger than that for 3D islands, the island-density is much lower for 2D islands than for 3D islands.

Fig. 5 shows the corresponding results for the scaled ISD for 2D and 3D islands. As can be seen, there is very good scaling behavior as a function of \( D/F \), while there is very little difference between the scaled ISD for 2D and 3D islands. We also note that the scaled ISD obtained in our simulations in the pre-coalescence
Figure 5-4: Island density as function of coverage showing power-law behavior beyond the nucleation regime.

regime \((\theta = 0.07 \text{ ML})\) is very similar to that obtained in previous simulations of the irreversible growth of compact (square) 2D islands [56]. In particular, in the pre-coalescence regime the peak of the ISD is slightly shifted to the right from \(s/S = 1\), while the value of \(f(0) \ (f(0) \simeq 0.4)\) is somewhat larger than the standard point-island prediction \((f(0) \simeq 1/3)\). In contrast, if we consider the scaled ISD at fixed dose (not shown) and increasing values of \(D/F\), poor scaling behavior is found since the coverage decreases with increasing \(D/F\).

5.4 Discussion

In order to understand the scaling behavior of the island density and island-size distribution in irreversible 3D island growth, we have carried out kinetic Monte
Carlo simulations of a simplified model. For comparison we have also derived general expressions based on a mean-field RE analysis, for the exponents $y_i$ describing the dose-dependence, $y'_i$ describing the coverage dependence, and $\chi'_i$ describing the $D/F$-dependence (at fixed coverage) of the island density as a function of critical island size $i$. We note that, since the onset of coalescence is determined by the coverage, the exponent $\chi'_i$ also describes the dependence of the peak island-density on $D/F$. A general expression for the exponent $\gamma_i$ describing the dependence of coverage on dose has also been derived.

In contrast to the standard RE predictions ($y_1 = 1/3, y'_1 = 3/7 \simeq 0.43$) for 3D irreversible growth [38], we find significantly lower values ($y_1 \simeq 0.24, y'_1 \simeq 0.32$) for the effective exponents describing the dose- and coverage-dependence of the island density for 3D islands. This may be explained by the fact that, in contrast to the standard RE assumption of size-independent capture-numbers, for 3D islands the
island-radius increases with the number of atoms in an island. Accordingly, the average capture-number also increases with coverage, thus leading to a decrease in the rate of nucleation as well as the effective exponents $y_1$ and $y'_1$ describing the increase in the island-density in the pre-coalescence regime. We note that a similar effect occurs in 2D island growth \cite{44, 55}. However, in this case the strong increase in the average capture number with island-size leads to saturation of the island-density. As a result, the coverage-dependence of the island-density for 3D islands is intermediate between that for 2D islands (for which $y_1 = 0$) and the standard RE prediction based on the assumption of size-independent capture-numbers. This behavior should be contrasted with that obtained for point-islands (for which the
Figure 5-7: Comparison of morphology at coverage $\theta = 0.07$ for 3D islands ((a)-(c)) and 2D islands ((d)-(f)). System-size $L = 1024$ while from left-to-right, $D/F = 10^9$, $10^{10}$, and $10^{11}$.

ratio $\bar{r}/l$ of the average island radius $\bar{r}$ to the average island distance $l$ is small and approaches 0 with increasing $D/F$ for which the value of $y_1$ obtained in simulations [56] ($y_1 \simeq 0.33$) is in good agreement with the standard RE prediction.

Our results also indicate that the value of $\chi'_1$ ($\chi'_1 \simeq 0.30$) for 3D islands lies in between the value for 2D islands ($\chi_1 = \chi'_1 = 1/3$) and the standard RE prediction ($\chi'_1 = 1/3.5 \simeq 0.29$). This value of $\chi'_1$ is also consistent with Eq. 5.10 and the value of $y_1$ obtained in our simulations. However, since the exponent $\gamma_1$ depends only weakly on $y_1$ (e.g. $\gamma_1 = (y_1 + 2)/3$), and $y_1$ is significantly less than 1, the resulting “correction” to $y_1$ leads to only a very small change in the exponent $\gamma_1$ (e.g. $\gamma_1 \simeq 0.76$ rather than the expected value $\gamma_1 = 7/9 \simeq 0.78$).

For comparison, we have also carried out self-consistent RE calculations and good agreement was found between our RE results for the island and monomer densities and our KMC results. It is worth noting that, in contrast to previous work [4, 56] on square and fractal islands in which an adjustable “fudge-factor” which scales the overall island radius was needed to take into account geometrical factors, in this case good agreement was obtained without any adjustable parameters. This is most
likely due to the fact that the circular island geometry assumed in our simulations is consistent with that assumed in the self-consistent RE approach.

We have also presented a comparison of results for the island-density and scaled island-size distribution (ISD) for 2D and 3D irreversible island growth. Since the average capture number is smaller for 3D islands, the island density is significantly larger (for the same value of $D/F$) than for 2D islands. However, somewhat surprisingly, we find that there is very little difference between the scaled ISD for 3D islands and that for 2D islands (see Fig. 5-8). This indicates that, as previously found in simulations of 2D submonolayer island growth [45], the scaled ISD is primarily determined by the critical island-size rather than the island morphology. We note that this result is also consistent with a previous analysis [58] of experimental results for InGaAs/GaAs growth [59], which indicates a small critical island size for the formation of 2D platelets.
While our simulation results clearly indicate that for typical values of $D/F$ the scaling behavior deviates from the standard RE predictions, it is also of interest to consider the asymptotic limit of infinite $D/F$. In this connection, we note that for point-islands (for which the ratio $\bar{r}/l$ of the average island radius $\bar{r}$ to the average island distance $l$ is small) the value of $y_1$ obtained in simulations [56] ($y_1 \simeq 0.33$) is in good agreement with the standard RE prediction. We therefore expect that if $\bar{r}/l$ goes to zero in the limit of large $D/F$, then the asymptotic scaling behavior will be the same as for point-islands. However, in general one may write $\bar{r} \sim (\theta/N)^{1/2}$ (where $\theta/N$ is the average area per island) and $l \sim N^{-1/2}$ which implies $\bar{r}/l \sim \theta^{1/2}$. This implies that in the asymptotic limit of large $D/F$, the ratio $\bar{r}/l$ remains independent of $D/F$ and only depends on the coverage. As a result, we expect that the deviations from standard RE theory found in our simulations for $D/F = 10^9 - 10^{12}$ will also occur for higher values of $D/F$. This is consistent with our observation that with increasing $D/F$ the exponents $y_1$ and $y'_1$ do not approach the standard RE values.

Finally, we consider the general problem of experimentally determining the critical island-size in 3D island growth. As already noted, except for the exponent $\gamma_i$ describing the dependence of the coverage on dose (or time) all of the other exponents depend sensitively on the critical island-size. In addition, since the exponent $\chi'_i$ depends only weakly on the dynamic exponent $y_i$ (see Eq. 5.10) deviations from the standard RE theory for 3D islands are likely to be relatively small compared to the dependence on $i$ (see Table 5.1). This is consistent with the fact that our measured value of $\chi'_1$ (0.30) is close to the standard RE prediction $\chi'_1 \simeq 0.286$. As a result, a direct determination of $\chi'_i$, by measuring the peak island-density as function of deposition flux, is still the most accurate method to determine the critical island-size. However, such a measurement requires carrying out several growth experiments with different fluxes, and in some cases it may be difficult to control the deposition flux. In this case, our results indicate (see Table 5.1) that in contrast to the case of 2D
islands (for which \( y_i = 0 \)) for 3D islands an upper bound to the critical island-size may be determined from a single experiment by measuring the exponent \( y_i \) describing the time-dependence of the island-density.
Chapter 6

Effects of cluster diffusion on the island density and size distribution in irreversible submonolayer island growth ($i = 1$)

6.1 Introduction

The work described is this chapter is motivated by recent drop-drying experiments of Au nanoparticles (decorated with dodecanethiol) in a toluene solution [1]. A schematic of the experiment is shown in Fig. 6-1. After droplet of toluene solution containing a monodisperse solution of 6 nm diameter Au nanoparticles is placed on the substrate, it starts drying, causing nanoparticles to flow to the surface of the droplet where they can diffuse. As the concentration (coverage) of nanoparticles on the surface increases they form islands with various sizes $s$ (where $s$ is number of nanoparticles in the island). At the finale stage when the drop is completely dried nanoparticles form a perfectly ordered monolayer with triangular packing shown on Fig. 6-2.
Island growth in drop-drying experiments is similar to epitaxial growth with reversed deposition flux. However, one of the key differences is that usually in epitaxial growth after islands have been formed, they have very limited diffusion ability (because of strong island binding to the substrate), while islands on the surface of the liquid can easily diffuse. Our goal in this chapter is to understand how ability of larger islands of size $s > 1$ to diffuse affects scaling behavior in submonolayer island nucleation and growth.

Figure 6-1: Schematics of different time stages of drop drying experiment. As drying progresses, coverage of the nanoparticles increases (from left to right on picture).

Of particular interest is the dependence of the total island-density $N$ and island-size distribution $N_s(\theta)$ (where $N_s$ is the density of islands of size $s$ at coverage $\theta$ and $s$ is the number of monomers in an island) on deposition parameters such as the deposition flux $F$ and growth temperature $T$. As we discussed in Chapter 5 the concept of critical island size [38], corresponding to one less than the size of the smallest “stable” cluster has proven to be useful in studies of submonolayer epitaxial growth. For example, if we assume that only monomers can diffuse, then in the case of submonolayer growth of 2D islands on a solid 2D substrate, standard nucleation theory [38, 39] predicts that the peak island density $N_{pk}$ and the monomer density $N_1$ at fixed coverage satisfy,

$$N_{pk} \sim (D_{1,h}/F)^{-\chi_i} \quad N_1 \sim (D_{1,h}/F)^{-\chi'_i} \quad (6.1)$$

where $D_{1,h}$ is the monomer hopping rate, $i$ is the critical island size, $\chi_i = \frac{i}{i+2}$ and
\( \chi'_i = 1 - \chi_i \). We note that in the case of irreversible island growth \((i = 1)\) this implies that \( \chi_1 = 1/3 \) and \( \chi'_1 = 2/3 \). In addition, it has been shown that in the absence of cluster-diffusion and in the pre-coalescence regime the island-size distribution (ISD) satisfies the scaling form \([43, 44]\),

\[
N_s(\theta) = \frac{\theta}{S^2} f_i \left( \frac{s}{S} \right),
\tag{6.2}
\]

where \( S \) is the average island size, and the scaling function \( f_i(u) \) depends on the critical island size \([45]\).

Figure 6-2: STM image of formed monolayer of nanoparticles after the drop completely dried out. Insets show schematics of individual nanoparticles and image of fast Fourier transform of the nanoparticle monolayer.

However, we note that the possibility of cluster diffusion during growth has already been considered theoretically for the case of epitaxial growth, since in some cases (such as in growth on metal(111) surfaces) it is also possible for significant small cluster diffusion to occur \([60, 61, 62]\). In addition, several mechanisms for the diffusion of large clusters on solid surfaces have also been proposed \([63, 64, 65, 66, 67, 68, 69]\). In
each case, scaling arguments predict that the cluster diffusion coefficient $D_s$ decays as a power-law with island-size $s$ (where $s$ is the number of particles in a cluster), i.e. $D_s \sim s^{-\mu}$. In particular, three different limiting cases have been considered [63, 64, 65, 66, 67, 68, 69] - cluster diffusion due to uncorrelated evaporation-condensation ($\mu = 1/2$), cluster diffusion due to correlated evaporation/condensation ($\mu = 1$), and cluster diffusion due to periphery diffusion ($\mu = 3/2$). We note that the case $\mu = 1/2$ also corresponds to the Brownian (Stokes-Einstein) diffusion of compact 2D clusters in two-dimensions.

In order to understand the effects of island diffusion on the submonolayer scaling behavior a number of simulations have previously been carried out. For example, Jensen et al [70] have studied the effects of island-diffusion with $\mu = 1$ on the percolation coverage for the case of irreversible growth without relaxation, corresponding to islands with fractal dimension $d_f \simeq 1.5$. More recently, Mulheran and Robbie [71] have used a similar model to study the dependence of the exponent $\chi$ on the cluster-diffusion exponent $\mu$ for values of $\mu$ ranging from 0 to 9. They found that for small values of $\mu$ the value of the exponent ($\chi \simeq 0.45$) is significantly larger than the value ($\chi \simeq 1/3$) expected in the absence of cluster diffusion, although it decreases with increasing $\mu$. However, the scaling of the ISD was not studied [72].

Motivated in part by these simulations, Krapivsky et al [73, 74] have carried out an analysis of the scaling behavior for the case of point-islands, based on the corresponding mean-field Smoluchowski equations [75]. Their analysis suggests that due to the large amount of diffusion and coalescence in this case, for $\mu < 1$ the total island density saturates (corresponding to “steady-state” behavior) while the ISD exhibits power-law behavior of the form, $N_s \sim s^{-\tau}$, where $\tau = (3 - \mu)/2$ and the prefactor does not depend on coverage.$^1$. This power-law dependence for the ISD is predicted to hold up to a critical island-size $S_c$, where $S_c \sim S^\zeta$ and $\zeta = 2/(\mu + 1)$.

---

$^1$The expression $\tau = (3 - \mu)/2$ has also been derived by Cueille and Sire [76] and Camacho [77]
In contrast, for $\mu \geq 1$ continuous island evolution is predicted, e.g. the total island density does not saturate, and as a result no simple power-law behavior is predicted for the ISD. Their analysis also indicates that for all values of $\mu$, one has $\chi_1 = \chi'_1 = 1/2$ with logarithmic corrections. However, it should be noted that the point-island approximation is typically only valid at extremely low coverages.

Here we present the results of kinetic Monte Carlo simulations of irreversible island growth with cluster diffusion for the case of compact islands with fractal dimension $d_f = 2$. Accordingly, in contrast to much of the previous work [70, 71, 78] our model is an off-lattice model. However, our main goal here is not to explain these experiments but rather to obtain results which may be used as a reference for future work. As already noted, if cluster diffusion is due to 2D Brownian motion (as might be expected at a fluid-interface) then the value of the exponent $\mu$ ($\mu = 1/2$) is the same as that expected for uncorrelated evaporation-condensation. However, we also present results for $\mu = 1$ (corresponding to cluster-diffusion due to correlated evaporation-condensation), $\mu = 3/2$ (corresponding to cluster-diffusion due to periphery diffusion) as well as for higher values of $\mu$ ($\mu = 2, 3, 6$ and $\infty$).

### 6.2 Model and Simulations

For simplicity we have studied a model of irreversible aggregation in which all islands are assumed to be circular and rapid island relaxation (perhaps due to periphery diffusion) is assumed. In particular, in our model each island or cluster of size $s$ (where $s$ is the number of monomers in a cluster) is represented by a circle with area $A_s = \pi d_s^2/4$ and diameter $d_s = d_1 s^{1/2}$, where $d_1$ is the monomer diameter. In addition, each cluster of size $s$ may diffuse with diffusion rate $D_s = D_1 s^{-\mu}$ where $D_1 = D_{1,h} \delta^2/4$ is the monomer diffusion rate, $D_{1,h}$ is the monomer “hopping rate”, and $\delta$ is the hopping length. Similarly, we may write $D_s = D_{s,h} \delta^2/4$ where $D_{s,h}$ is
the hopping rate for a cluster of size $s$.

In order to take into account deposition, monomers are also randomly deposited onto the substrate with rate $F/d_1^2$ per unit time per unit area. Since instantaneous coalesce and relaxation is assumed, whenever two clusters touch or overlap, a new island is formed whose area is equal to the sum of the areas of the original clusters, and whose center corresponds to the center-of-mass of both islands. We note that in some cases a coalescence event may lead to overlap of the resulting cluster with additional clusters. In this case, coalescence is allowed to proceed until there are no more overlaps. In addition, if a monomer lands on an existing cluster, then that monomer is automatically ‘absorbed’ by the cluster.

Thus, at each step of our simulation either a monomer is deposited (followed by a check for overlap with any clusters) or a cluster is selected for diffusion. If a cluster is selected for diffusion, then the center of the cluster is displaced by a distance $\delta$ in a randomly selected direction. For computational efficiency, and also because it is the smallest length-scale in the problem, in most of the results presented here we have assumed $\delta = d_1$. However, we have also carried out some simulations with smaller values ($\delta = 0.5 \, d_1$ and $\delta = 0.25 \, d_1$) in order to approach the continuum limit. As discussed in more detail in Sec. 6.6, our results indicate that the dependence of the island and monomer densities on the hopping distance $\delta$ is relatively weak.

We note that besides the exponent $\mu$ describing the dependence of the cluster diffusion rate on cluster-size, the other key parameter in our simulations is the ratio $R_h$ of the monomer hopping rate to the monomer deposition rate (scaled by the ratio of the hopping length to the monomer diameter) e.g.,

$$R_h = \frac{D_{1,h}}{F} \left( \frac{\delta}{d_1} \right)^2$$  \hspace{1cm} (6.3)

We note that this definition implies that the dimensionless ratio $R = D_1/Fd_1^2$ of the
monomer diffusion coefficient $D_1$ to the deposition flux satisfies,

$$R = R_h/4$$  \hspace{1cm} (6.4)

Our simulations were carried out assuming a 2D square substrate of size $L$ (in units of the monomer diameter $d_1$) and periodic boundary conditions. In order to avoid finite-size effects, the value of $L$ used ($L = 4096$) was relatively large, while our results were averaged over 100 runs in order to obtain good statistics. In order to determine the asymptotic dependence of the island density on coverage and $R_h$ our simulations were carried out using values of $R'_h = 4R_h/\pi$ ranging from $10^7 - 10^9$ up to a maximum coverage of 0.3 monolayers (ML). In order to study the dependence on $\mu$, simulations were carried out for $\mu = 1/2$ (corresponding to Brownian diffusion or uncorrelated evaporation-condensation), $\mu = 1$ (corresponding to correlated evaporation-condensation), and $\mu = 3/2$ (corresponding to periphery diffusion) as well as for higher values ($\mu = 2, 3, \text{ and } 6$) as well as the case $\mu = \infty$ corresponding to only monomer diffusion.

In order to obtain a quantitative understanding of the submonolayer growth behavior, we have measured a variety of quantities including the monomer density $N_1 = (\pi/4) n_1/L^2$ (where $n_1$ is the number of monomers in the system) as a function of coverage $\theta$, and the total island density $N = (\pi/4) n/L^2$ (where $n$ is the total number of islands including monomers in the system). In addition, we have also measured the island-size distribution $N_s(\theta)$ where $N_s = (\pi/4) n_s/L^2$ corresponds to the density of islands of size $s$. We note that the factors of $\pi/4$ in the definitions above take into account the fact that the area of a monomer is $(\pi/4) d_1^2$, and as a result the densities defined above all correspond to area fractions. Similarly, the coverage $\theta = \sum_{s \geq 1} sN_s$ corresponds to the fraction of the total area covered by islands (including monomers).
6.3 Simulation Methods

While a simple Monte Carlo approach can be used [79] to simulate the processes of monomer deposition and cluster diffusion such a method can be very inefficient for large values of $R_h$ and small values of $\mu$, since the large range of island-sizes and diffusion rates can lead to a low acceptance ratio. Accordingly, here we use a kinetic Monte Carlo approach. In particular, if we set the deposition rate $F$ per unit area $d^2_1$ equal to 1, then the total deposition rate in the system is $L^2$ while the hopping rate for a cluster of size $s$ is given by $R_{s,h} = R_hs^{-\mu}$. As a result, the total diffusion rate for all clusters is given by $R_T = \sum_{s=1}^{\infty} n_s R_{s,h}$ (where $n_s$ is the number of clusters of size $s$) while the total rate of deposition onto the substrate is $L^2$. The probability $P_{dep}$ of depositing a monomer is then given by,

$$P_{dep} = \frac{L^2}{R_T + L^2} \quad (6.5)$$

while the probability of cluster diffusion is $P_{diff} = 1 - P_{dep}$. If cluster diffusion is selected, then a binary tree [80] (whose bottom leaves correspond to the total hopping rate $n_s R_{s,h}$ for each size $s$) may be used to efficiently select with the correct probability which cluster will move as well as to efficiently update $R_T$. However, for large $R_h$ and small $\mu$ the maximum cluster-size can be larger than $10^4$ and as a result the computational overhead associated with the binary tree can still be significant.

Accordingly, we have implemented a variation [81] of the binary tree approach in which a range of cluster-sizes are clustered together into a single ‘leaf’ or bin. In particular, to minimize the size of the binary tree, starting with island-size $s > 3$ we have used variable bin-sizes such that each bin contains several different cluster sizes ranging from a starting value $i$ to a value approximately equal to $1.2i$. Using this scheme allows us to use a binary tree with a maximum of 64 leaves and a rejection probability of only 10%. To further decrease the computational overhead, our binary
tree grows dynamically from 4 leaves to as many as needed.

By properly selecting the rates in the binary tree and the corresponding acceptance probabilities, one can ensure that each diffusion event is selected with the proper rate. In particular, if we define the rate of bin \( i \) as \( \mathcal{R}_{b_i} = n_{b_i} \mathcal{R}_{\text{max}, b_i} \), where \( \mathcal{R}_{\text{max}, b_i} \) is the maximum cluster-diffusion rate in bin \( b_i \) (corresponding to the smallest cluster-size in the bin) and \( n_{b_i} \) is the number of islands in the bin, then the sum over all leaves may be written,

\[
\mathcal{R}^T_b = \sum_{i=1}^{n} \mathcal{R}_{b_i},
\]

(6.6)

The probability of attempting a diffusion event is then given by,

\[
P_{\text{diff}} = \frac{\mathcal{R}^T_b}{\mathcal{R}^T_b + L^2}
\]

(6.7)

while the probability of selecting bin \( i \) is given by \( P_i = \mathcal{R}_{b_i}/\mathcal{R}^T_b \). Once a bin is selected using the binary tree, a specific cluster is then selected randomly from the list of all the clusters in that bin. This implies that a cluster of size \( s \) will be selected with probability \( P_s = n_s/n_{b_i} \). Thus, by assuming an acceptance probability for the selected cluster-diffusion event given by

\[
P_{\text{acc}} = \frac{R_s}{\mathcal{R}_{b_i}},
\]

(6.8)

each diffusion event will be selected with the proper rate.

Since our simulations are carried out off-lattice, one of the most time-consuming processes is the search for overlaps every time a cluster is moved. While the simplest way to carry out such a search is to check for overlaps with all other islands in the system, the search time scales as \( L^2 \), and as a result it becomes very time-consuming for large systems. Accordingly, we have used a neighbor look-up table [82] which contains a list of all other islands within a buffer-distance of each island. The search for overlaps is then carried out only among the neighbors on this list rather than
over all the islands in the system. The neighbor list is updated whenever the total displacement of any island since the last update is larger than half the buffer-distance.

To speed-up the updates of the neighbor table, we have also used a “grid” method [82] in which our system is divided into an $n_g$ by $n_g$ grid of boxes of size $l_g = L/n_g$ and each cluster can be rapidly assigned to a given box. Using this method the search for neighbors only includes clusters within an island’s box as well as the 8 adjacent boxes. As a result, the table update time is reduced to $9L^2/n_g^2$ instead of $L^2$. To further optimize the speed of our simulations, the grid size is varied as the average island-size increases.

### 6.4 Generalized Scaling Form for the Island-size Distribution

As discussed in Sec. I, in both simulations and experiments on submonolayer epitaxial growth, the island-size distribution (ISD) is typically assumed to satisfy the scaling form given in Eq. 6.2. However, this scaling form has been derived [43, 44, 45] on the assumption that there is only one characteristic size-scale $S$ corresponding to the average island-size, and that the ISD does not diverge for small $s/S$. However, in our simulations of monomer deposition and cluster diffusion and aggregation with $\mu < 1$, we find that the ISD exhibits a well-defined power-law behavior for small $s/S$. In addition, the existence of a shoulder in the ISD for large $s = S_c$ implies the existence of a second characteristic length-scale which scales as $S_c \sim S^\xi$. We note that this corresponds to an island size-scale such that steady-state behavior breaks down, due to the existence of mass-conservation and a finite diffusion length.

In general one would expect this to lead to a more complicated two-variable scaling of the form $N_s(\theta) = A \ g(s/S, s/S_c)$. However, if the power-law behavior for small $s/S$ is well-defined (and $\tau > 1$) then it is possible to derive a generalized scaling
form involving only one variable. In particular, we assume that a scaling form for the island-size distribution may be written,

\[ N_s(\theta) = A(S, \theta) f(s/S^\zeta) \]  

(6.9)

In order to determine \( A(S, \theta) \) note that \( N = \sum_{s \geq 1} N_s = \theta/S = A(S, \theta) \sum_{s \geq 1} f(s/S) \Delta s \).

Converting to an integral this may be rewritten as \( \theta/S = A(S, \theta) S^\zeta \int_{1/S^\zeta}^{\infty} f(u) u \, du \)

where \( u = s/S^\zeta \). If we now assume that \( f(u) \sim u^{-\tau} \) for small \( u \) and \( \tau > 1 \), then the small-\( u \) part of the integral dominates and we obtain, \( A = \theta/S^{1+\tau\zeta} \). This leads to the generalized scaling form,

\[ N_s(\theta) = \frac{\theta}{S^{1+\tau\zeta}} f\left(\frac{s}{S^\zeta}\right) \]  

(6.10)

We note that a similar scaling form (corresponding to the special case \( \zeta = 1 \)) has previously been derived in Ref. [83] for the case of the deposition of spherical droplets with dimension \( D > d \) on a \( d \)-dimensional substrate. We also note that for \( \zeta = 1 \) and \( \tau = 1 \) (corresponding to the critical value of \( \tau \)) the standard scaling form Eq. 6.2 is obtained.

### 6.5 Results

#### 6.5.1 Stokes-Einstein diffusion (\( \mu = 1/2 \))

We first consider the case \( \mu = 1/2 \) corresponding to Stokes-Einstein diffusion. Fig. 6-3 shows our results for the total cluster density \( N \) (including monomers) as well as for the monomer density \( N_1 \) as a function of coverage for three different values of \( R'_h \) ranging from \( 10^7 \) to \( 10^9 \). In good agreement with the theoretical prediction in Refs. [73] and [74] of “steady-state” behavior for \( \mu < 1 \), we find that both the monomer density \( N_1 \) and total island density \( N \) reach an approximately constant value beyond
a critical coverage $\theta_m$. We note that this coverage decreases with increasing $R_h$, while the peak island and monomer densities also decrease with increasing $R_h$.

The inset in Fig. 6-4 shows our results for the exponents $\chi$ ($\chi \simeq 0.46$) and $\omega$ ($\omega \simeq 0.38$) corresponding to the dependence of the peak island density $N_m$ and coverage $\theta_m$ on $R_h$. In qualitative agreement with the results of Mulheran et al [71] for fractal islands, the value of $\chi$ obtained in our simulations is slightly lower but close to 1/2. This is also consistent with the prediction [73, 74] that for point-islands $\chi$ should be equal to 1/2 with logarithmic corrections. Fig. 6-4 shows the corresponding scaled island density $NR_h^{\chi}$ as a function of the scaled coverage $\theta R_h^{\chi}$. As can be seen there is good scaling up to and even somewhat beyond the value ($\theta R_h^{\chi} \simeq 1$) corresponding to the peak in the island-density. In contrast, replacing the scaled coverage by $\theta R_h^{\omega}$ as in Ref. [71], leads to good scaling at $\theta = \theta_m$, but the scaling is significantly worse for $\theta \neq \theta_m$. Also shown is the scaled monomer density $N R_h^{\gamma}$ (where the peak monomer density scales as $N_{1, pk} \sim R_h^{-\gamma}$ and the coverage corresponding to the peak monomer density scales as $\theta_{1, m} \sim R_h^{-\omega'}$ and $\gamma \simeq \omega' \simeq 1/2$) as a function of the scaled coverage $\theta R_h^{\gamma}$. As for the case of the island density, there is good scaling up to and even beyond the scaled coverage corresponding to the peak of the monomer density. We note that in contrast to the exponents $\chi$ and $\omega$, the exponent $\gamma$ does not appear to depend on $\mu$. In particular, we find that for all the values of $\mu$ that we have studied, the value of $\gamma$ ($\gamma \simeq 0.45 - 0.47$) is close to the value ($\gamma = 1/2$) expected in the absence of cluster-diffusion.

We now consider the scaled island-size distribution (ISD). In Refs. [73] and [74] a mean-field (MF) Smoluchowski approach was used to predict "steady-state" power-law behavior of the form,

$$N_s(\theta) \sim s^{-\tau} R_h^{-\chi}$$

(6.11)

for $\mu < 1$ (where $\tau = (3 - \mu)/2$ and $\chi = 1/2$) for island-sizes $s << S_c$ where
$S_c$ corresponds to the shoulder in the ISD for large $s$. Similarly, the exponent $\zeta$ characterizing the scaling of $S_c$ as a function of $S$ (e.g. $S_c \sim S^\zeta$) was predicted to satisfy the MF expression $\zeta = 2/(\mu + 1)$. For $\mu = 1/2$ these expressions imply that $\tau = 5/4$ and $\zeta = 4/3$. Since $N \sim R_h^{-\chi}$ and $S = \theta/N$, one has $\theta/S \sim R_h^{-\chi}$ and Eq. 6.11 may be rewritten as,

$$N_s(\theta) \sim s^{-\tau} \theta/S$$  \hspace{1cm} (6.12)

Fig. 6-5 shows the ISD scaled using this form. As can be seen there is reasonably good scaling for $s < S_c$, although the tail of the distribution does not scale. However, the measured value of the exponent $\tau$ ($\tau \approx 4/3$) is significantly higher than the MF prediction ($\tau_{MF} = 5/4$) while the measured value of $\zeta$ ($\zeta \approx 3/2$) is also significantly higher than the MF prediction ($\zeta_{MF} = 4/3$). Fig. 6-6 shows the corresponding scal-
Figure 6-4: Scaled densities $N R'_h^{\chi}$ and $N_1 R'_h^{\gamma}$ as a function of scaled coverage ($\theta R'_h^{\chi}$ and $\theta R'_h^{\gamma}$, respectively). Inset shows dependence of peak island density $N_m$ and coverage $\theta_m$ on $R'_h$.

ing results obtained using our generalized scaling form Eq. 6.10 with the measured exponent values $\zeta = 3/2$ and $\tau = 4/3$ corresponding to $N_s(\theta) \sim S^{-3} \theta f(s/S^{3/2})$. As can be seen, both the power-law region for small $s/S$ as well as the ‘bump’ for large $s/S$ scale well using this form. However, for the smallest clusters (e.g. monomers and dimers) there is poor scaling due to deviations from power-law behavior.

6.5.2 Correlated attachment-detachment ($\mu = 1$)

We now consider the case $\mu = 1$ which corresponds to cluster diffusion via correlated attachment-detachment and also corresponds to Brownian motion of a cluster confined at a liquid-air interface in the absence of additional hydrodynamic correlations. We note that this is the critical value for power-law behavior of the ISD (which
Figure 6-5: Scaled ISD for $\mu = 1/2$ obtained using steady-state scaling form Eq. 6.12.

is expected to occur for $0 \leq \mu < 1$) and as a result Krapivsky et al [73, 74] have predicted “nested” logarithmic behavior for the island-density.

Since the simulations are not as computationally demanding as for $\mu = 1/2$, in this case we have carried out simulations up to $\theta = 0.3$. Fig. 6-7 shows our results for the total island density $N$ and monomer density $N_1$ as a function of coverage for $R'_h = 10^7 - 10^9$. As can be seen, while there is a plateau in the island-density which appears to broaden and flatten somewhat with increasing $R'_h$, the plateau is not as flat as for the case $\mu = 1/2$, thus indicating deviations from steady-state behavior. As for the case $\mu = 1/2$, a plot of the scaled densities $NR'_h^\chi (N_1 R'_h^{\gamma})$ as a function of scaled coverage $\theta R'_h^\chi (\theta R'_h^{\gamma})$ shows relatively good scaling up to the coverage corresponding to the peak island-density, although the value of $\chi (\chi \simeq 0.45)$ is slightly lower than that obtained for $\mu = 1/2$.

We now consider the island-size distribution. As shown in Fig. 6-8, in this case the
Figure 6-6: Scaled ISD obtained using generalized scaling form Eq. 6.10 with \( \tau = 4/3 \) and \( \zeta = 3/2 \).

ISD does not exhibit a well-defined power-law behavior. In particular, on a log-log plot the ISD is curved with a slope \( \tau \simeq 2 \) for small \( s \) and a smaller effective slope \( (\tau \simeq 1) \) for large \( s \). Similarly, while \( \zeta \simeq 1 \) its effective value ranges from 1.03 to 1.1 depending on the value of \( R'_h \) and coverage. As a result, neither the standard scaling form Eq. 6.2 nor the generalized scaling form Eq. 6.10 can be used to scale the entire island-size distribution. However, using the generalized scaling form (6.10) with \( \zeta \simeq 1 \) and \( \tau = 2 \), we find good scaling for small \( s/S \) (see Fig. 6-8), although the ISD does not scale for large \( s/S \). On the other hand, if we use the standard scaling form (6.2) (which corresponds to the generalized scaling form with \( \zeta = 1 \) and \( \tau = 1 \), see inset of Fig. 6-8) then the ISD scales for \( s > S_c \) but not for small \( s \). We note that this lack of scaling is perhaps not surprising since for \( \mu \geq 1 \) there are two characteristic size-scales \( S \) and \( S_c \), but no well-defined power-law behavior.
6.5.3 Periphery diffusion ($\mu = 3/2$)

We now consider the case $\mu = 3/2$ which corresponds to cluster diffusion via edge-diffusion. In this case, the dependence of the total island density $N$ and monomer density $N_1$ on coverage and $R'_h$ is similar to that found for $\mu = 1$. In particular, there is a plateau in the island-density which appears to broaden with increasing $R'_h$, although it is not as flat as for the case $\mu = 1$, thus indicating deviations from steady-state behavior. In addition, the peak island-density for $\mu = 3/2$ is somewhat larger than for $\mu = 1$. As for the case $\mu = 1$, a plot of the scaled densities $NR'_h^\chi (N_1R'_h^\gamma)$ (with $\chi \simeq 0.46$ and $\gamma \simeq 0.45$) as a function of scaled coverage $\theta R'_h^\chi (\theta R'_h^\gamma)$ shows relatively good scaling up to the coverage corresponding to the peak island-density.

We note that for $\mu > 1$, Krapivsky et al [73, 74] have predicted that for point-islands there is a continuous logarithmic increase in the total island density of the
Figure 6-8: Scaled ISD for $\mu = 1$ using generalized scaling form (6.10) with $\zeta = 1$ and $\tau = 2$. Results correspond to coverages $\theta = 0.025, 0.05, 0.1, R'_h = 10^7 - 10^9$ and $\mu = 1$. Inset shows corresponding scaling results obtained using the standard scaling form (6.2).

form,

$$N \approx R^{-1/2} \left[ \frac{\sin(\pi/\mu)}{\pi} \ln(\theta R^{1/2}) \right]^{\mu/2}$$

(6.13)

However, we find that for $\mu = 3/2$ and higher (not shown) scaling plots using this form (e.g. $NR^{1/2}$ as a function of $|\ln(\theta R^{1/2})|^{\mu/2}$) provide very poor scaling. In particular, since $\chi \simeq 0.45$, the scaled peak island-density increases with $R$ while the peak position also shifts significantly to smaller values.

We now consider the scaled ISD for $\mu = 3/2$. Again in this case, it is not possible to scale the entire ISD using the average island-size $S$ since there are two characteristic size-scales but no well-defined power-law behavior. In particular, if we use the generalized scaling form Eq. 6.10 with $\tau = 2$ and $\zeta = 1$, then reasonable scaling is only obtained for the small-$s$ “tail” corresponding to $s/S < 0.1$ (not shown). In
addition, as shown in Fig. 6-9, using the standard scaling form Eq. 6.2 neither the tail nor the peak scale. Instead we find that the height and width of the “power-law” portion of the ISD corresponding to small $s/S$ decreases with increasing $R_h'$ and coverage, while the peak near $s/S = 1$ becomes higher and sharper. As a result, the power-law portion of the ISD is significantly less important than for smaller values of $\mu$. In particular, for $R_h' = 10^9$ and $\theta = 0.1$, it corresponds to only approximately 10% of the area under the curve.

![Figure 6-9: Scaled ISD for $\mu = 3/2$ using standard scaling form (6.10).](image)

Fig. 6-11 shows pictures of the submonolayer morphology for $R_h' = 10^9$ and $\theta = 0.1$ for $\mu = 1/2, 1, 3/2, \text{and} 2$. We note that the size-scale $M$ of each picture decreases with increasing $\mu$ so that approximately the same number of islands is visible. As can be seen, in qualitative agreement with our results, there is a very broad distribution of island-sizes for $\mu = 1/2$ while the distribution becomes narrower with increasing $\mu$. 

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6.5.4 Scaling of ISD and densities for $\mu \geq 2$

In order to obtain a better understanding of the dependence of the island density and ISD on the mobility exponent $\mu$, we have carried out additional simulations for larger values of $\mu$ ($\mu = 2, 3$ and 6) as well as in the limit $\mu = \infty$ in which only monomers can diffuse. While the ISD shows excellent scaling for the case $\mu = \infty$ as a function of coverage and $R'_h$ (see Fig. 4(b)), in general we find that (just as for the case $\mu = 3/2$) for all finite $\mu \geq 2$, the ISD does not scale but instead exhibits a peak near $s/S = 1$ which becomes higher and sharper with increasing $R'_h$ and coverage. In addition, the width and height of the small-$s$ “tail” of the ISD decreases significantly with increasing $\mu$, as well as with increasing $R'_h$ and coverage.

![Scaled ISD](image)

Figure 6-10: Scaled ISD for $\mu = \infty$.

Fig. 6-12 shows a summary of our results for the scaled ISD at coverage $\theta = 0.1$ and $R'_h = 10^9$ for $\mu = 1, 3/2, 2, 3, 6$, and $\infty$. As already discussed, for $\mu > 1$ a peak develops at $s/S = 1$ whose height increases with $R'_h$ and coverage $\theta$, although some-
what surprisingly for $R_h' = 10^9$ the ISD peak-height $f_{pk}$ depends non-monotonically on $\mu$. Accordingly, we have carried out power-law fits at fixed coverage using the form $f_{pk} \sim (R_h')^\eta$ (with $R_h'$ ranging from $10^7$ to $10^9$ and at $\theta = 0.025$ and $\theta = 0.1$) in order to get an estimate of the asymptotic dependence of the ISD peak-height on $R_h'$ and $\mu$. As shown by the inset of Fig. 6-12, while the effective value of $\eta$ appears to depend somewhat on coverage, in general, we find that $\eta(\mu)$ decreases with increasing $\mu$ from a value of approximately 0.11 for $\mu = 3/2$ to 0.05 for $\mu = 6$. Thus, while the scaled ISD for $\mu > 1$ appears to diverge with increasing $R_h'$ the rate of divergence decreases with increasing $\mu$.

Figure 6-11: Pictures (size $M \times M$) of the submonolayer morphology at coverage $\theta = 0.1$ and $R_h' = 10^9$ for (a) $\mu = 1/2$ ($M = 4096$) (b) $\mu = 1$ ($M = 709$) (c) $\mu = 3/2$ ($M = 624$) (d) $\mu = 2$ ($M = 485$).

Fig. 6-13 shows a summary of our results for the monomer density $N_1$ and total island density $N$ as a function of coverage for $\mu = 1/2, 1, 3/2, 2, 6,$ and $\infty$ for the case $R_h' = 10^9$. As can be seen, up to the coverage $\theta_{1,m}$ corresponding to the peak
Figure 6-12: Scaled ISDs (corresponding to $R'_h = 10^9$ and $\theta = 0.1$) for $\mu = 1, 3/2, 2, 3, 6, \text{ and } \infty$. Inset shows dependence of effective exponent $\eta(\mu)$ on $\mu$.

Monomer density both the island and monomer density are essentially independent of $\mu$. Fig. 6-13 also shows clearly that both the island-density and the coverage $\theta_m$ corresponding to the peak island-density increase with increasing $\mu$, while the monomer density decreases with increasing $\mu$.

Fig. 6-14 shows a summary of our results for the dependence of the exponents $\chi$, $\chi'$, and $\gamma$ on $\mu$. As can be seen, the exponent $\chi$ depends continuously on $\mu$, decreasing from a value close to $1/2$ for small $\mu$ ($\mu = 1/2$) and approaching a value close to $1/3$ for large $\mu$. We note that these results are similar to previous results obtained for fractal islands with $d_f = 1.5$ by Mulheran and Robbie [71]. Similarly, we find that the exponent $\chi'$ describing the dependence of the monomer density at fixed coverage on $R'_h$ also shows a continuous variation with increasing $\mu$, starting at a value close to $1/2$ for $\mu = 1/2$ and increasing to a value close to $2/3$ for large $\mu$. In contrast, the
exponent $\gamma$ describing the flux-dependence of the peak monomer density is close to $1/2$ for all $\mu$.

6.6 Discussion

We have carried out simulations of a simplified model of irreversible growth of compact islands in the presence of monomer deposition and a power-law dependence ($D_s \sim s^{-\mu}$) of the island mobility $D_s$ on island-size $s$. In particular, we have considered the cases $\mu = 1/2$ (corresponding to cluster-diffusion via Brownian motion), $\mu = 1$ (corresponding to cluster-diffusion via correlated evaporation-condensation), and $\mu = 3/2$ (corresponding to cluster-diffusion via periphery diffusion). For comparison, we have also carried out simulations for higher values of $\mu$ including $\mu = 2, 3$ and $6$ as well as $\mu = \infty$.

In agreement with the predictions of Ref. [73] and Ref. [74] for point-islands, we find that for small values of $\mu$ the value of the exponent $\chi$ characterizing the dependence of the peak-island density on $R'_{h}$ is close to but slightly lower than $1/2$. However, we also find that $\chi$ decreases continuously with increasing $\mu$, approaching the value $1/3$ for large $\mu$. As already noted, these results are in good agreement with previous results obtained for fractal islands [71]. Similarly, the exponent $\chi'$ characterizing the dependence of the peak monomer density on $R'_{h}$ is also close to $1/2$ for small $\mu$, but increases with increasing $\mu$, approaching the value $2/3$ in the limit $\mu \to \infty$. In contrast, the exponent $\omega$ describing the dependence of the coverage $\theta_m$ (corresponding to the peak-island density) on $R'_{h}$ is significantly smaller than $1/2$ for small $\mu$ and also decreases with $\mu$, approaching zero in the limit of infinite $\mu$. This is consistent with the fact that when only monomers are mobile ($\mu = \infty$) the peak island-density occurs at a coverage which is independent of $R'_{h}$ in the asymptotic limit of large $R'_{h}$. For comparison, we note that while the monomer density $N_1(\theta)$
depends on $R'_h$, it only depends on $\mu$ for coverages beyond the peak monomer density (see Fig. 6-13). As a result, the exponents $\gamma$ and $\omega'$ corresponding to the dependence of the peak monomer density (and corresponding coverage $\theta_{1,m}$) on $R'_h$ are close to $1/2$ for all $\mu$.

The similarity of our results for $\chi$ and $\omega$ to previous results [71] for fractal islands suggests that these exponents (along with the exponent $\chi'$) depend primarily on the cluster-mobility exponent $\mu$ and substrate-dimension $d$ but not on the shape or fractal dimension of the islands. We note that such a result is not entirely surprising, since for the case in which only monomers can diffuse ($\mu = \infty$) it has been found that the exponent $\chi$ depends only weakly on the island fractal dimension [42]. In addition, we have found that the scaled island and monomer densities ($NR^\chi$ and $N_1R^\chi$) lead to reasonably good scaling as a function of $\theta R^\chi$, up to and somewhat beyond the peak island-density. We note that this scaling form is somewhat different from that used in Ref. [71] in which the coverage is scaled by $\theta R^\omega$ so that only the peak scales.

In addition to the scaling of the island and monomer densities, we have also studied the dependence of the island-size distribution (ISD) on the cluster-mobility exponent $\mu$. In agreement with the prediction [73, 74, 76, 77] that for point-islands well-defined power-law behavior should be observed for $\mu < 1$, for the case $\mu = 1/2$ we find a broad distribution of island-sizes with a well-defined power-law. However, in contrast to the point-island prediction that $\tau = (3 - \mu)/2$ (which implies $\tau = 5/4$ for $\mu = 1/2$) the value of $\tau$ obtained in our simulations ($\tau \simeq 4/3$) is somewhat larger. Similarly, the value of the exponent ($\zeta \simeq 3/2$) describing the dependence of the crossover island-size $S_c$ on $S$ for $\mu = 1/2$ is also significantly larger than the point-island prediction $\zeta = 2/(\mu + 1) = 4/3$. One explanation for this is that for compact islands the coalescence rate decreases more slowly with increasing island-size than for point-islands due to the increase in “capture number” with increasing island-radius. However, another possible explanation is that the existence of correlations which are
Figure 6-13: Island density $N$ and monomer density $N_1$ as function of coverage for $R'_h = 10^9$ and $\mu = 1/2, 2, 3, 6, \text{ and } \infty$.

not included in the mean-field Smoluchowski equations leads to a higher value of $\tau$.

To address this question we have carried out additional rate-equation calculations using a newly-developed self-consistent RE method [84] which takes into account the effects of cluster-diffusion as well as additional KMC simulations for circular islands. As shown in Fig. 6-15, rate-equation calculations were carried out for both point-islands (corresponding to island-dimension $d_f = \infty$) and circular islands (corresponding to $d_f = 2$) for several values of $\mu < 1$. As can be seen, for a fixed value of $\mu < 1$, changing from circular islands to point islands leads to a significant decrease in the measured value of the exponent $\tau$. In addition, the measured values of $\tau$ for point-islands are in good agreement with the theoretical prediction $\tau = (3 - \mu)/2$.

The good agreement between self-consistent RE results for point-islands and the Smoluchowski theory (combined with the good agreement with simulations for circular islands) demonstrates that the discrepancies between our simulation results and
the Smoluchowski predictions are not due to correlations (which are not included in the self-consistent RE approach) but are indeed due to the fact that for realistic islands, the capture-number increases with the island-size.

We now discuss our results for the scaling of the island-size distribution. In contrast to previously studied growth models with only limited cluster-diffusion [42, 43, 44, 45], in which there is a single well-defined peak in the ISD corresponding to the average island-size $S$, in the presence of significant cluster mobility there are typically two different size-scales $S$ and $S_c$. As a result, in general it is not possible to scale the ISD using just the average island-size $S$. However, for the case $\mu < 1$ (corresponding to well-defined power-law behavior up to a critical island-size $S_c$) our results confirm that for compact islands the ISD exhibits steady-state behavior. As a result, the power-law region corresponding to $s < S_c$ can be scaled using the steady-state Eq. 6.12, although the large-$s$ “tail” does not scale. Accordingly, we have proposed...
Figure 6-15: Dependence of exponent $\tau$ on diffusion exponent $\mu$ for compact and point islands. Shown results are obtained using KMC (compact islands) and RE (compact and point islands) simulations.

A generalized scaling form for the ISD, $N_s(\theta) = \theta / S^{1+\tau\zeta} f(s/S^\zeta)$ for the case $\mu < 1$. Using this form, we have obtained excellent scaling for the case $\mu = 1/2$.

In contrast for $\mu = 1$, there are still two competing size-scales $S$ and $S_c$, but there is no well-defined power-law behavior. As a result, no single scaling form can be used to scale the entire ISD. However, we find that the value of the exponent $\zeta$ ($\zeta \simeq 1$) is close to that obtained using the point-island expression $\zeta = 2/(\mu + 1)$. In addition, for small $s/S$ the ISD satisfies $N_s(\theta) \sim s^{-\tau_{\text{eff}}}$ where $\tau_{\text{eff}} \simeq 2$. As a result, we find that the small $s/S$ “tail” of the ISD can be scaled using the generalized scaling form Eq. 6.10 with $\tau = 2$ and $\zeta = 1$, while the standard scaling form Eq. 6.2 leads to reasonably good scaling of the ISD for $s > S_c$.

However, for $\mu > 1$ there is no effective power-law behavior even for small $s/S$ and as a result, neither the general scaling form Eq. 6.10 nor the standard scaling form
Eq. 6.2 lead to good scaling of the ISD for finite $R'_h$. Instead we find that using the standard scaling form (2), the fraction of islands corresponding to small $s/S$ decreases with increasing $R'_h$ and coverage, while the peak of the scaled ISD increases in height and becomes sharper. As a result, the peak position shifts to the left with increasing $R'_h$ and coverage and appears to approach 1 for large $R'_h$. Interestingly, this implies, as shown in Fig. 6-9 and Fig. 6-12, that for $\mu > 1$ the peak of the scaled ISD is even higher than for the case of irreversible growth without cluster diffusion ($\mu = \infty$). In addition, our analysis of the $R'_h$-dependence of the peak height suggests that while the scaled ISD for $\mu > 1$ appears to diverge with increasing $R'_h$ the rate of divergence decreases with increasing $\mu$.

It is also interesting to compare our results for $\mu > 1$ with those obtained by
Kuipers and Palmer [78] who studied the scaled ISD for the case of fractal islands, assuming an exponential dependence of the cluster mobility, e.g. $D_s \sim D_1 \xi^s$ where $\xi < 1$. Because of the rapid decay of the mobility with increasing cluster-size assumed in their model, the resulting scaled island-size distributions (using the standard scaling form Eq. 6.2) were much closer to those obtained for the case of irreversible growth with no cluster mobility (e.g. $\mu = \infty$) than the results presented here. However, for values of $\xi$ which were not too small, they also found some evidence of a small island-size “tail”, although it was much weaker than found here.

Finally, we consider the continuum limit of our simulations. In all of the results presented so far we have assumed a hopping length $\delta$ equal to the monomer diameter $d_1$. This makes our simulations similar to previous simulations [42, 43, 44, 45, 70, 71, 74] with and without cluster mobility in which a lattice was assumed. However, it is also interesting to consider the continuum limit $\delta \to 0$. In order to do so, we have carried out additional simulations with smaller values of $\delta$ ($\delta = d_1/2$ and $d_1/4$). In general, we find that both the monomer density $N_1$, as well as the density $N'$ of all clusters not including monomers exhibit a weak but linear dependence on the hopping length $\delta$ (see inset of Fig. 6-16) e.g.,

$$X(\delta) = X(0)[1 + \alpha(\mu) (\delta/d_1)]$$

(6.14)

(where $X$ corresponds either to the monomer or island density and $X(0)$ corresponds to the continuum limit). Thus, by performing a linear extrapolation we may obtain the corresponding densities in the continuum limit. As shown in Fig. 6-16, for $\mu = 1/2$ and $\mu = 3/2$ the island-density $N'$ depends relatively weakly on the hopping length, and as a result there is very little difference between our results for $\delta = d_1$ and the continuum limit. In contrast, the monomer density exhibits a somewhat stronger dependence on the hopping length $d_1$. However, in general we find $\alpha(\mu) < 0.1$ while
the value of $\alpha(\mu)$ decreases with increasing $\mu$. In particular, in the limit $\mu = \infty$ in which only monomers can diffuse, we find $\alpha(\infty) = 0.01 (0.07)$ for the island and monomer density respectively. These results indicate that in the continuum limit the island and monomer densities are only slightly lower than in our simulations. We thus expect that in the continuum limit the scaling behavior will not be significantly different from the results presented here.
Chapter 7

Effects of cluster diffusion on the island density and size distribution in reversible submonolayer island growth ($i > 1$)

One of the logical extensions of the work described in Chapter 6 is to study reversible growth, e.g. $i > 1$. This is of particular interest because we expect that, due to the triangular lattice geometry of nanoparticle islands in the Au nanoparticle drop-drying experiments, clusters of size three (corresponding to a trimer) and size seven (corresponding to a septamer) are particularly stable (since all nanoparticles in these clusters have at least two bonds). Accordingly, in order to understand the effects of critical island-size on the scaling behavior we have carried out additional simulations for the case of reversible growth corresponding to a critical island size $i = 2$ (corresponding to the case in which all islands larger than dimers are stable) and $i = 6$ (corresponding to the case in which all islands larger than a hexamer are stable). For the case $i = 2$, we assume that dimers can break-up (with a single-bond detachment rate $R_{1d} = r_{1d}R'_h$) while all larger islands are assumed to be stable. For
the case $i = 6$, the detachment rate for dimers is assumed to be the same. However, we also allow monomers to detach from all islands with sizes $3 \leq s \leq 6$ with a two-bond detachment rate $R_{2d} = r_{1d}^2 R_h'$, while all islands larger than 6 are assumed to be stable. The value of the detachment parameter $r_{1d}$ was chosen to be sufficiently large that for the case $\mu = \infty$ (corresponding to no cluster diffusion) we recovered the corresponding theoretical values $\chi_i = i/(i + 2)$.

### 7.1 Results

Fig. 7-1 shows our results for the scaling exponent $\chi_2(\mu)$ for the case $i = 2$, as well as for the exponents $\chi_6(\mu)$ and $\chi'_6(\mu)$ for the case $i = 6$, as a function of the cluster-diffusion exponent $\mu$. As can be seen, for the case $i = 6$, the exponent $\chi$ varies continuously from the theoretical value $\chi = 3/4$ for the case $\mu = \infty$ (no cluster diffusion) to the value $\chi = 1/2$ for small $\mu$. While no theoretical analysis has been carried out for the case of small $\mu$, we note that this value of $\chi$ is the same as predicted in Ref. [73] using the Smoluchowski equation for the case $i = 1$. Similar behavior is obtained for the case $i = 2$, although in this case the corresponding theoretical predictions for both limits are the same (e.g. $\chi = 1/2$). As a result the exponent $\chi_2$ does not appear to depend significantly on $\mu$.

We now briefly discuss our simulation results for the scaled island size distributions. As can be seen in Figs. 7-2 and Fig. 7-3 the scaled ISD becomes sharper with increasing critical island-size as well as with increasing values of $\mu$. However, in both cases, the ISD does not scale but instead the peak-height increases with increasing coverage and $R_h'$. 

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Figure 7-1: Dependence of scaling exponents $\chi$ and $\chi'$ on cluster-diffusion exponent $\mu$ for the case of critical island size $i = 6$ and $i = 2$. 
Figure 7-2: ISD for critical island size $i = 1$ and $i = 2$ for two values of diffusion exponent $\mu = 1$ and $\mu = 3/2$. Data taken at coverage $\theta = 0.01$ and dimer detachment parameter $r_2 = 0.01$ (in the case of $i = 2$).
Figure 7-3: ISDs for critical island size $i = 6$ corresponding to two values of cluster-diffusion exponent $\mu = 1$ and $\mu = 3/2$, $R'_h = 10^8$ and $R'_h = 10^9$. Data taken at coverage $\theta = 0.01$ and dimer detachment parameter $r_2 = 0.01$ and $r_6 = 2 \times 10^{-4}$. 
Chapter 8

Conclusions and Future Outlook

The work presented in this dissertation involves computer simulations of thin film growth, in which various techniques such as continuum stochastic differential equations and kinetic Monte Carlo methods were used to study PECVD growth of amorphous silicon (Chapter 4), submonolayer nucleation and growth of 3D islands (Chapter 5) and effects of island diffusion during submonolayer growth (Chapter 6, and 7).

In each of these studies we successfully explained some of the key phenomena and found new interesting behavior of the studied systems, e.g.:

- We modeled the experimentally observed roughness evolution using a simplified linearized continuum equation which takes into account the destabilizing effects of atomic shadowing and/or attraction as well as the smoothing effects of surface diffusion. By varying the initial configuration as well as the negative surface tension parameter $\nu_2$ and surface diffusion parameter $\nu_4$, we have found good agreement with experiment in the case of large dilution ratios ($R_H = 40$ and $R_H = 60$). The good agreement between our simulations and experiments at high dilution ratio indicates that surface diffusion plays an important role.

- We have carried out kinetic Monte Carlo simulations of a simplified model of 3D irreversible 3D island growth. One of our key findings is that for a realistic
model, the exponents $y_1$ and $y'_1$ describing the dose- and coverage-dependence of the island density are significantly lower than predicted by previous theories. However, due to the weak dependence on $y_1$ and $y'_1$ this leads to only a small correction to the exponent $\chi_1$ describing the dependence of the peak island-density on flux. Our results also suggest a new kinetic method, applicable to arbitrary critical island-sizes, which may be used to estimate the critical island-size in submonolayer 3D growth. In addition we carried out self-consistent RE calculations and compared with our KMC simulation results. Excellent agreement was obtained for the island and monomer densities as function of coverage. However, we found very little difference between the scaled ISD for 3D islands and that for 2D islands.

- We have also presented the results of KMC simulations of irreversible (and preliminary results of reversible) growth of mobile compact islands which on a 2D substrate. In our model, we assumed instantaneous coalescence of circular islands, while the cluster mobility was assumed to exhibit power-law decay as a function of island-size with exponent $\mu$. Results were presented for several cases of $\mu = 1/2, 1, 3/2$ corresponding to cluster diffusion via Brownian motion, correlated evaporation-condensation, and edge-diffusion respectively, as well as for higher values including $\mu = 2, 3,$ and $6$.

For the case $\mu < 1$ we obtained power-law behavior of the ISD $N_s(\theta) \sim s^{-\tau}$ (where $N_s(\theta)$ is the number of islands of size $s$ at coverage $\theta$) up to a cross-over island-size $S_c$. While power-law behavior is in agreement with theoretical predictions, the value of the exponent $\tau$ obtained in our simulations is higher than value predicted by the mean-field equations. A new generalized scaling form for the ISD for $\mu < 1$ were also proposed. In addition our simulations results show that there is no single scaling form can be found for finite values
of $\mu$ in a range $1 < \mu < \infty$. In this range ISD becomes sharper with increasing coverage and diffusion to deposition ratio $D/F$.

While each of these projects has provided significant insight into the dynamics of island nucleation and thin-film growth, in the future it would be of interest to pursue a number of different extensions of this work. For example, in the case of the PECVD of amorphous silicon, it would be interesting to carry out molecular dynamics and energetics calculations of the diffusion of Si and related radicals on the a-SiO$_2$ surface, in order to determine with more accuracy the relevant diffusion length for 3D nucleation. Similarly, since it is possible that in PECVD growth of amorphous silicon, the critical island-size is larger than 1, it would be of interest to extend the simulations of irreversible 3D island growth carried out in Chapter 5, to the case of higher critical island-size. Finally, we note that the drop-drying experiments discussed in Chapter 6, provide a number of intriguing aspects which are worthy of further investigation. For example, one interesting extension for which we have already presented some results in Chapter 7 is to study reversible growth ($i > 1$) as well as the effects of higher critical island-sizes on the scaling behavior of the island-size distribution. By considering similar extensions to the model studied here it should also be possible to study the effects of monomer desorption and/or evaporation during island nucleation, as well as the effects of anomalous diffusion (due for example to turbulence) on the nucleation and growth process. In addition, by considering lattice-based models, it should also be possible to study more realistically the effects of island-relaxation mechanisms on the island geometry and nucleation process. Finally, while such a simulation is likely to be quite challenging, it would also be of interest to carry out molecular dynamics simulations of nanocluster islands at the toluene/air interface in order to better understand the processes of island relaxation as well as the dependence of the cluster diffusion coefficient on island-size.
References


[17] We note that in the atomistic simulations of Refs. [12] and [13] only a minimal amount of roughness was observed.


[35] We note that an additional nonlinear term proportional to the Gaussian curvature $K_G = ((h_{xx}h_{yy} - h_{xy}^2) / (1 + (\nabla h)^2)$ has been suggested in Ref. [25] due to the effects of attraction of incoming particles to the film, and has also recently been suggested on more general grounds by Escudero [36]. However, the coefficient of this term is expected to be relatively small [25].


[72] Kuipers and Palmer [78] have considered the scaling of the ISD in a similar model. However, in their model the cluster diffusivity was assumed to decay exponentially with cluster-size.


