Island Nucleation in Silicon on Si(111) Growth under Chemical Vapor Deposition

K. E. Khor and S. Das Sarma

Condensed Matter Theory Center, Department of Physics, University of Maryland, College Park, Maryland 20742-4111

(January 13, 2022)

Abstract

Recent experiments show that the islanding behavior during chemical vapor deposition (CVD) of Si on Si(111) using disilane (Si$_2$H$_6$) is quite different from that due to molecular beam epitaxy (MBE). While the latter can be understood using rate equation theories (RET), the islanding exponent (connecting the power law growth of island density with growth rate) obtained for the CVD growth is a puzzle, with the CVD exponent being almost twice the MBE exponent. We carry out (2+1) dimensional kinetic Monte Carlo (MC) simulations to study this CVD growth. Hydrogen plays a critical role during growth. Disilane breaks up into hydrides on the Si surface. We use MC simulations to explore a number of cases involving one or two migrating species and show that the large islanding exponent is probably due to the presence of two hydrides, one of which has a much shorter lifetime than the other. We modify RET taking this possibility into account in order to shed light on the experimental observation. We calculate the scaling properties of the island distributions using MC simulations and the modified RET, and conclude that the large effective CVD exponents arise from the failure of the simple island number scaling scenario which no longer applies to the two-component
situation prevailing under CVD growth conditions.

68.55Ac, 68.55.-a, 81.15Kk
I. INTRODUCTION

Molecular beam epitaxy (MBE) growth of semiconductors has been studied extensively by means of rate equation theories; in particular, island nucleation and growth of homoepitaxial silicon on silicon is known to be well described by these theories. On the other hand chemical vapor deposition (CVD) growth has been much less well studied theoretically, even though it is widely used in semiconductor technology. CVD homoepitaxy introduces atoms of one or more species other than that of the substrate, which may alter substantially the physical and chemical properties of the surface, such as the surface free energy and the diffusion of atoms. Clearly island nucleation behavior will also be affected under CVD conditions. In silicon homoepitaxy using disilane Si₂H₆, the surface is hydrogenated as Si is deposited - the ratio (of Si to H) cannot be varied. It is known that the hydrogen atoms passivate the Si surface by saturating surface dangling bonds. In this study we look at the experimental work of Andersohn et al. on the CVD growth of Si on Si(111) using disilane gas. They obtained results for both MBE and CVD growth of Si/Si(111). From the perspective of kinetic Monte Carlo (MC) simulations, as we shall see later, this CVD process is a straightforward extension of MBE; we can therefore, look for understanding of mechanisms which contribute to the differences between the two growth processes. Andersohn et al. obtained exponents for the island density N versus growth rate R’ of 0.7 for MBE growth and a substantially larger value of 1.25 for CVD - in the latter case rate equation theories were applied naively. We study this system by means of MC simulations and also generalize and extend standard rate equation theories to systems when more than one mobile species is involved as is appropriate for CVD growth. Our goal is to understand the substantial difference in growth rate exponents between MBE and CVD by carefully incorporating in the growth model the different adatom dynamics in the two cases. The growth experiments of Andersohn et al. were carried out in the temperature range of 480°C to 540°C. Experimental work on disilane decomposition on Si(111)7X7 surfaces suggests that incident disilane molecules interact with bare (dangling bond) Si sites and deposit various hydrides such as
SiH₂ and SiH on the surface, with the latter being the only long-lived hydride⁵. The dihydride decomposes to the monohydride and hydrogen; the hydrogen atoms may be left on the substrate to passivate dangling bonds. At the lower end of the above temperature growth range, the monohydride breaks down very slowly through H evaporation or desorption. Once a site is passivated by hydrogen or a hydride, no further adsorption of disilane can happen at this site. STM images show that as a result of hydrogen passivation, the 7x7 surface reconstructions are replaced by the 1x1 H-stabilised surface¹⁶. Kulkarni et al suggest that for temperatures above 490°C, the H desorption channel opens up rather substantially through removal by disilane molecules and also through the recombination of hydrogen atoms from two nearest neighbor monohydrides, although this latter process occurs at a much lower rate than the former. In the experiments of Andersohn et al Si is deposited on Si(111) at the rate of 1/10 to 10 bilayers(BL) per minute. The CVD experiments are carried out in the submonolayer regime with Si coverages θ ≤ 0.3 monolayers(ML). At 480°C, the low end of the growth temperature range used, the hydrogen desorption rate is so small that no significant amount of hydrogen has been removed during deposition. This is important for CVD experiments, since the high growth exponents seem to apply to the entire temperature range. This suggests that the large CVD growth exponents may be essentially independent of hydrogen desorption.

Andersohn et al plotted island density N against growth rate R for MBE growth for the two temperatures, 410°C and 500°C for a coverage of θ ~ 0.3 bilayers(BL); they fitted their results to the relationship given by rate equation theories² (RET),

\[ N = \left( \frac{R}{D_o} \right)^\eta \exp \left( - \frac{E}{kT} \right), \] (1)

where \( D_o \) is the diffusion preexponential and E an activation energy parameter, with the growth or the islanding exponent \( \eta(= i^*/(i^* + 2)) \) for two dimensional (2D) islanding for steady state nucleation in the complete condensation regime². In Eq. 1 \( i^* \) is the critical cluster size for 2D islanding. They obtained \( \eta = 0.7 \) for Si/Si MBE which corresponds to \( i^* \sim 5–7 \text{atoms} \). For Si MBE where there is little or no evaporation, the deposition rate \( R \) is
equal to the growth rate $R'$. Andersohn et al also applied Eq. 1 to their CVD experiments. Mean growth rates $R'$ are calculated from the deposition times needed to attain a fixed coverage of about a third of a bilayer $\theta(\sim 0.3 \text{ BL})$, which is determined from STM images so that material which has diffused to step edges outside the imaged area is excluded from $\theta$. For CVD growth they obtained exponents in the range $\eta \sim 1.1 - 1.25$, clearly substantially larger than the MBE exponent $\eta \sim 0.7$. This is manifestly inconsistent with the above RET expression for $i^*$ which asserts that $\eta$ must necessarily lie between 0 and 1. The failure of the simple rate equation theory for CVD growth suggests that the presence of two or more adatom species may alter nucleation behavior qualitatively, necessitating some new insight into the RET formulation for CVD. These species comprise adatoms of Si and its various hydrides, SiH and SiH$_2$. Of the hydrides, only SiH is long-lived. The dihydride may decompose into a monohydride with the extra hydrogen going to saturate a neighboring dangling bond on the Si(111) surface. The monohydride should diffuse as a complex, since the Si-H bond is very strong $\sim 3.1\text{eV}$, compared to typical diffusion barriers of the order of $1\text{eV}$ or less. It is known that the mobility of the monohydride is much less than that of Si adatom in the experimental temperature range. It is reasonable to expect the mobility of the dihydride to be even less than that of SiH. We should also be able to assume that SiH$_2$ moves as a complex, again based on the Si-H bonding energies being much larger than surface diffusion activation energies. Kandel has suggested a different mechanism involving island edge barriers, which we shall discuss later.

Andersohn et al discuss the possible causes for the anomalously high CVD exponents. They consider various physical possibilities which may affect CVD islanding such as a strong growth rate dependent diffusion parameter $D_o$, the transformation of the surface reconstruction from (7x7) to (1x1), possible release of additional Si atoms from the substrate to form extra islands, and hydrogen etching of the surface, introducing the possibility of incomplete condensation to the nucleation process. In the current work we study the CVD problem by using kinetic Monte Carlo simulations and also by rate equation analysis. The MC simulation will be done in (2+1) dimensions on a square lattice (the particular lattice should not
matter since our goal is to understand qualitatively the origin of the large exponents and not to obtain quantitative agreement with experiment). Activation barriers for diffusion in our simulation are chosen using previous MC simulations for Si MBE growth as a guide and also so as to obtain a maximum attainable (in terms of reasonable simulation times and problem sizes) stable critical island size of $i^* = 3$ (for the cubic lattice) for no-evaporation MBE growth. Then larger exponents, if they do arise, say, in the CVD case cannot be attributed to regular causes. Standard rate equation theories assume a single migrating species, usually lone adatoms. In our simulations for CVD we will consider one or more diffusing species composed of Si adatoms and the silicon hydride complexes. We will modify rate equation theories to handle the situation with two species.

We carry out MC simulations for the following cases:

(1)Si MBE without evaporation,

and several distinct situations for CVD growth as given below:

(2)migrating species of SiH, with H allowed to evaporate and the resulting lone Si atom allowed to migrate rapidly to a step edge;

(3)two migrating species of Si and SiH, with H evaporation allowed;

(4)deposition of SiH at a site is accompanied with an extra H saturating a neighboring dangling bond; this represents the decomposition of SiH$_2$ discussed above, and finally;

(5)two migrating species, comprising SiH$_2$ and SiH, with the former being much slower and short-lived.

The details for the MC simulation model for these cases are presented in section II. In section III we present and discuss the simulation results and provide a critical comparison between the MBE and the CVD case. We conclude in section IV summarising our results and discussing the extended RET model applied to this problem. In appendix A we give the details for the generalized rate equation theory appropriate to the two species system. Appendix B gives the standard RET in terms of the actual growth rate rate $R'$ (rather than the deposition rate $R$).
II. KINETIC MONTE CARLO SIMULATION

MC simulations are carried out in (2+1) dimensions on a square lattice. An adatom or adatom complex moves under the solid-on-solid restriction (overhangs and/or bulk vacancies are not allowed). These simplifications are not expected to be important for the study of growth exponents. An adatom moves to a neighboring site by randomly hopping at a rate that depends on its bonding configuration; this rate is given by

\[ R_n = R_0 e^{\frac{-E}{kT}} , \]  

where \( R_0 = d'kT/h \) is a characteristic vibrational frequency and \( d' (=2, \text{ in our case}) \) is the substrate dimension. \( E = E_o + nE_b \) is the activation energy, where \( n \) is the number of nearest neighbors and \( E_b \) is the energy (actually the activation barrier) associated with the bond between nearest neighbors. Since we are dealing with up to two different species comprising adatom complexes from Si, SiH and SiH\(_2\), the parameter \( E_o \) will be different for different species. Although this will mean that each species will diffuse at different rates, we will assume that when two adatom complexes are next to one another, the nearest neighbor bonding remains the same irrespective of their species. This seems to be a reasonable assumption since the bonding is between the Si atoms of the hydrides, and the hydrogen atom is not expected to affect this much. Even if there is some species dependence of this nearest neighbor bonding or activation energy, this should not affect our qualitative conclusion. We will also assume that the hydride SiH (and SiH\(_2\)) will hop as a complex since the bond between Si and H atoms is extremely strong \( \sim 3.1\text{eV}^{,5,6} \) compared to the hopping activation barriers \( \sim 1\text{eV} \). These assumptions are supported by the experiments\(^5\) of Kulkarni et al on the decomposition of disilane on Si(111). In our simulations we allow for the evaporation of hydrogen through a single evaporation rate for the sake of simplicity. Kulkarni et al\(^6\) describe two possible mechanisms for H removal, but only one is significant in our context. We do not expect the simplification of using just one H-evaporation rate to affect our conclusions. In accordance with experimental observations\(^1,5\) once a site is passivated
by a silicon hydride complex, no further deposition on that site is possible; correspondingly an adatom complex can only jump to a H free site.

Our simulation parameters, together with the deposition and evaporation rates, have been chosen so that a critical island size of \( i^* = 3 \) is obtained for MBE growth in the temperature ranges of interest. Results from standard nucleation theory\(^1\) suggest that, for a square lattice as the stable critical island size increases from \( i^* = 1 \) to 3 (and then to 10), the deposition rate decreases by two orders of magnitude for each step in the increase of \( i^* \) (i.e. \( R \) has to decrease by a factor of \( 10^4 \) if \( i^* \) increases from 1 to 10). We use deposition rates in the range \( 0.3 \leq R \leq 32 \) monolayers(ML)/s. For MBE we obtain straight line plots of \( \ln N \) versus \( \ln R \), indicating a power law island density growth as a function of the deposition rate, in agreement with Eq. 1. At the lower limit of \( R \sim 0.3 \), simulation times become so large that it is unlikely that calculations can be extended much below this limit. Exponents larger than \( \eta = 0.6 \), (i.e. \( i^* = 3 \)) for MBE are therefore beyond reasonable simulation times, which is the usual finite time problem in kinetic simulation of very slow dynamics. Note that \( \eta < 1 \), satisfying the theoretical RET bound of \( 0 < \eta < 1 \) corresponding to \( 0 < i^* < \infty \) for the island size. Larger exponents (in the CVD simulations) have to be attributed to mechanisms not operational in MBE growth.

We explore a variety of growth models. Simple MBE of Si on Si(111) provides a starting reference point. Next, since H plays a critical role in CVD growth and the monohydride is the only long-lived species on the substrate, we study a model where SiH is deposited but that the hydrogen is allowed to evaporate at certain rates; if this results in a lone Si adatom, it moves instantaneously to the step edge and is lost to the island nucleation process, as seen in the experiments of Andersohn \textit{et al.} Si adatoms are much more mobile than the hydrides\(^1,6\). Kulkarni \textit{et al} discuss a deposition process where a dihydride breaks up into a monohydride and a hydrogen which passivates a neighboring dangling bond. We explore the effect of this process on nucleation to see if it would lead to an effective deposition rate dependent diffusion of SiH. Finally, we look at the situation with two active migrating species. We assume that of the hydrides the dihydride moves much more slowly than the
monohydride. Another example of growth under two migrating species is to consider the combination of Si and SiH complexes, with the former being much faster than the latter. However, we do not find exponents markedly different from the MBE case until almost all the H has evaporated from the hydride, which is experimentally not the case. For this reason we will not discuss this case further. In the next section we present and discuss our numerical results based on the kinetic MC simulations of Si/Si MBE and CVD process.

III. RESULTS

To model MBE of Si on Si(111) we choose the set of parameters, $E_o = 1.0 \text{eV}$ and $E_b = 0.3 \text{eV}$. Simulations are carried out on system sizes of 320x320; results remain essentially the same when the size is increased to 480x480. In Fig. 1 we plot island densities $N$ versus deposition rates $R$ for the growth temperature $T=780 \text{K}$. The solid curve shows results for MBE growth. We count islands comprising two or more atoms as stable; this lower limit of 2 does not seem to affect the numerical value of the growth exponent we get in our simulations. Using 3-5 atoms as the lower limit on the stable island size gives essentially the same results. We obtain an MBE growth exponent $\eta = 0.6$, corresponding to a critical island nucleus of $i^* = 3$. Over nearly two orders of magnitude in the deposition rate $R$, the $\ln(N)-\ln(R)$ plot in Fig. 1 is essentially a straight line, as discussed above. We also look at the distribution $N_s(\theta)$ of island size $s$. In Fig. 2 we display scaled island size distributions for two deposition rates $R = 1$ and 16 and coverage $\theta \sim 0.095$. The lines through points (squares, diamonds and circles) are due to a scaling ansatz proposed by Amar and Family

$$\frac{N_s(\theta)S^2}{\theta} = f_i(\frac{s}{S})$$

where $S(\theta) = \Sigma_s sN_s(\theta)/\Sigma N_s(\theta)$ is the average island size and $f_i(u) = C_i u^i \exp(-a_i u^{1/a_i})$ is a scaling function, with $a_i$ satisfying the relation $\Gamma[(i+2)a_i]/(\Gamma[(i+1)a_i] = (ia_i)^{a_i}, C_i = (ia_i)^{(i+1)a_i}/(a_i \Gamma[(i+1)a_i]$ and $i$ is the critical island size. We see that $i \leq i^*(=3)$ and is not constant over the range of $\theta$ investigated, which suggests that critical sizes obtained from
fitting island distributions with the scaling relation defined by Eq. 3 is less than those given by rate equations. In our simulations, in contrast to the work of Amar and Family\textsuperscript{11}, we do not impose the unnecessary constraint that atoms with \( i \) or more neighbors are not allowed to detach from an existing island.

In the second set of simulations, SiH is deposited on the substrate at various rates; the hydride is allowed to move as a complex with a hopping rate defined by the activation energy \( E_o = 1.0\text{eV} \). The hydrogen evaporates at certain rates, leaving bare Si atoms. Lone Si atoms diffuse fast enough so that they are immediately lost to a step edge (i.e. the atom is effectively removed). This is consistent with the manner in which the growth rate is estimated in the experiments of ref. 1. In Fig. 1 we display results of simulations for two evaporation rates \( R_e = 1200 \) and 2000. Both curves approach the MBE results at high deposition rates \( R \) and show higher slopes at lower \( R \) indicating higher rates of CVD exponents (at least) for lower deposition rates. These higher exponents are consistent with rate equation theory results for incomplete condensation\textsuperscript{2}. However, the exponents of Andersohn \textit{et al} are obtained from plots of island density \( N \) versus the effective growth rate \( R' \), not the deposition rate \( R \). The growth rate \( R' \) is estimated from the accumulating material that stays within the area imaged by the STM used in data analysis. When our results are replotted against \( R' \), the two curves rescale to the MBE results for all growth rates, and the effective CVD exponent for \( N(R') \) becomes the same as the MBE exponent for \( N(R) \). This effect can also be seen in rate equation theories which we discuss in Appendix B.

Andersohn \textit{et al}\textsuperscript{3} discuss the possibility of a strong growth rate dependence of the diffusion parameter \( D_o \), due to the presence of hydrogen. Kulkarni \textit{et al}\textsuperscript{5} show that among the various surface chemical reactions that can happen, there is one where a silicon dihydride complex breaks up into a monohydride complex and a hydrogen which saturates a neighboring dangling bond; at low coverages, this dangling bond is likely to be associated with a substrate Si atom with four Si nearest neighbors, which would make \textit{this} particular SiH complex essentially immobile. It is possible that this H atom, produced by the local chemical reaction \( \text{SiH}_2 \rightarrow \text{SiH} + \text{H} \), will reduce the effective mobility of a nearby mobile SiH complex.
We test this idea in our simulations by depositing SiH$_2$ which breaks up immediately into a monohydride and a hydrogen atom. This atom passivates a neighboring dangling bond site chosen at random within 2 lattice spacings from the monohydride; all lone monohydrides are allowed to move with hopping rates determined by the parameters above, no hydrogen evaporation is considered. We show these modified simulation results also in Fig. 1. The curves are parallel to the line for MBE; they are shifted towards higher densities, giving the same value ($\sim 0.6$) for the exponent $\eta$. It is as if the H has increased the effective deposition rate by a fixed percentage for all growth rates without in any way affecting the underlying island scaling behavior.

Andersohn et al$^1$ has noted that the presence of H changes the 7x7 reconstruction of the surface to a 1x1 H-terminated surface which may result in up to 20% of the material in island nuclei coming from the substrate itself. As noted above the result of increasing the effective deposition rate by a fixed percentage simply raises the curve by a constant amount without changing the growth exponent. Thus, this mechanism should not affect the exponent in any significant manner.

Finally we simulate growth due to the explicit presence of two species on the substrate. Kulkarni et al$^5$ show that above 250$^\circ$C, disilane decomposes to leave SiH$_2$ on the surface. This dihydride in turn breaks down to leave the monohydride plus hydrogen which may or may not desorb. Since this hydrogen does not affect the growth exponent, as we discuss above, we will neglect it in our simulation and simply allow it to desorb. Consider the two adatom species: SiH$_2$ which is first deposited has a very short lifetime and so we take SiH to be infinitely long-lived. We use the same bonding strength $E_n = 0.3eV$ for both and $E_o = 1.0eV$ for the diffusion of SiH; since SiH$_2$ is very much less mobile than SiH, we take $E_o$ for SiH$_2$ to be 2eV. The breakup rate of SiH$_2$ is given by setting $R_e=730$, chosen to optimize the exponent. Clearly, this parameter $R_e$ sets the proportion of SiH to SiH$_2$ on the substrate in the steady state. The results are not sensitive to this particular value of $R_e$. The experimental evidence is overwhelming that hydrogen is essential in maintaining growth with the high exponent value$^{1,6}$. If the flux of disilane is low or growth occurs at
high temperatures so that hydrogen desorption is fast enough to keep the surface essentially H free, then the CVD growth becomes essentially the same as the MBE growth in terms of the value of the islanding exponent. For this reason and due to the fact that large CVD exponents are seen in growth at 480°C and 500°C when H desorption is insignificant, we ignore the loss of H by SiH itself in our simulations. In Fig. 1, we plot the results of $N_s(\theta)$ versus deposition rate for this case of 2-species growth. The exponent $\eta = 0.9$ is higher than that for MBE of 0.6 (which corresponds to $i^* = 3$). On the basis of the old rate equation theories an exponent of 0.9 corresponds to a critical nucleus of $i^* = 20$, which is greater than the size of the majority of the islands for the high deposition rates, $R \geq 10$. In Fig. 3a, the island distribution results averaged over 40-50 samples, for $R = 1$ are displayed, together with the scaling relations for $i^* = 1, 2$ and 3. Clearly the results do not really fit any one relation but are closest to the $i^* = 2$ curve for $s/S \geq 1.5$, while they are closest to the $i^* = 1$ curve at $s/S \sim 1$; here the implication is that $i \sim 1$ does not agree with $i^* \sim 20$ as suggested by rate equation theories. In Fig. 3b, the corresponding curve for $R = 16$ shows no agreement with any of the scaling relationships at all. Island density declines monotonically to a tail longer than those due to scaling. Thus, in the presence of 2-species migration-induced islanding and growth, simple scaling relations break down and the effective scaling exponent $\eta$ becomes very large indicating a failure of the simple scaling relation.

IV. DISCUSSION AND CONCLUSION

Rate equation theories show that for 2 and 3D islanding, growth exponents of $\eta \geq 1$ occur in the steady state case, only under regimes of extreme incomplete and initially incomplete condensation. Our kinetic MC simulations, including those not covered by standard rate equation theories, indicate that it is not simple to obtain these high growth exponents from naive CVD simulations. Even in the case which involves evaporation of H, the high exponent at low effective growth rate reduces to the low exponent case when island density is plotted.
against growth rate $R'$ instead of deposition rate $R$. As we will see in Appendix B the case of initially incomplete condensation collapses into that of complete condensation when the island density is plotted against growth rate $R'$; the exponent $\eta = i/(i + 2), i/(i + 2)$ for 3D and 2D islanding respectively. In our simulations, we explored several physical processes and mechanisms suggested by the CVD experiments. We find that the mechanism of the change of surface reconstruction from 7x7 to 1x1, which can increase the effective deposition rate by a given percentage, cannot increase the exponent. Andersohn et al. suggest that a monomer diffusion constant that is strongly $R$ dependent could account for the high exponent; we explored a possible way - the codeposition of H in the neighborhood of a deposited monohydride - and found that this merely raised island densities without increasing $\eta$. It is interesting that this has the same effect as increasing the deposition rate by a fixed percentage. Based on the investigations of Kulkarni et al., who showed that at the growth temperatures of ref. 1 disilane deposits a dihydride on the substrate which subsequently breaks up into H and the monohydride, we investigate a growth model involving these two hydrides (“the 2-species migration model” for CVD). The important characteristics of this model are that each hydride is assumed to move as a complex, since the SiH bond is known to be very strong and that the dihydride, which moves much more slowly than the monohydride, has a much shorter lifetime. In our simulations of this two component system an effective growth exponent $\eta$ 50% higher than the corresponding MBE case ($\eta \approx 0.6$) is obtained. We find $\eta = 0.9$ for the square lattice 2-component CVD growth and expect to see still higher exponents for the realistic diamond lattice where the smallest stable clusters of size greater than three would be accessible to simulations within reasonable times. Our conclusion is, therefore, that this 2-component model of 2-species migration is operational in the CVD growth of ref.1, leading to very large CVD growth exponents.

In Appendix A we discuss the extension of Walton’s expression for the equilibrium density of critical clusters to the two component system that we study here. We then extend standard rate equation theories to these systems and show that the exponent goes as $i/2$ instead of $i/(i + 2)$ for 2D islanding and $2i/5$ instead of $i/(i + 2.5)$ for 3D islanding. Large
growth exponents have also been shown to arise when island edge barriers $E_B$ are present. Kandel suggests that these edge barriers may occur in surfactant mediated growth; an adatom can only be attached to the edge of an island after surfactant atoms have been removed. The energy barrier required for such an interchange may be very large. Kandel argues that the H in disilane CVD on Si plays the role of surfactant atoms. Kandel’s work has been discussed and criticised in some detail by Venables and Brune; they showed that this island edge barrier has significant consequences: Even a modest edge barrier would cause the steady state nucleation stage when the population of monomers $n_1$ has become constant, to be greatly delayed, that is, the transient stage $(n_1 = R(1 - Z)t = \theta(1 - Z))$ will become substantially extended. Here $Z$ is the coverage due to clusters excluding monomers. This is because the capture numbers $\sigma_1, \sigma_x$, which determine the rate of removal of monomers by clusters of size 1 and $x$ respectively, are reduced by the factor $\exp - \beta E_B$ and, therefore, nucleation times are enormously increased by the inverse of this factor. Our estimates are that, with the parameters we use in our simulations, a barrier of $E_B \sim 1eV$ is enough to move the transient regime up into the range of coverages of the order of 0.1ML. Venables and Brune conclude that the exponent of $\eta = 2i/(i + 3)$ obtained by Kandel, based on steady-state results may not be valid for his comparisons with experiments. Furthermore, we examine the assumption that H behaves as a surfactant. Kulkarni et al have shown that Si-H moves as a complex; as we have noted before, the Si-H bond is very strong, so that the H atom does not behave like a surfactant. There is no exchange of Si with hydrogen for the silicon atom to join an island at the edge of the island. It is known that once hydrogen passivates a dangling bond on the Si surface, there can be no further growth on top. Our conclusion based on our kinetic MC simulations is that the large CVD exponents reported in ref.1 arise from a failure of the simple island number scaling scenario in the 2-component migration condition prevailing under CVD growth. More experiments and simulations are obviously needed to settle the issue definitively.

This work is supported by the US-ONR and NSF-MRSEC.
APPENDIX A: TWO COMPONENT RATE EQUATIONS

We consider a system where only monomers are mobile. We have a two component system with monomer densities \(n_{1H}\) and \(n_{2H}\) and total density of monomers \(n_1 = n_{1H} + n_{2H}\). These two types of monomers move with diffusion constants \(D_{1H}\) and \(D_{2H}\), but in forming islands the monomers are linked to each other by bonds of the same strength \(E_b\), so that clusters of size \(i\) have energies \(E_i\), which are independent of the detailed composition of adatom complexes of type 1H and 2H. Under these conditions Walton’s equation\(^{12}\) for the equilibrium density, \(n_i\), of clusters of size \(i\), given by

\[
\frac{n_i}{N_o} = C_i \left( \frac{n_1}{N_o} \right)^i e^{E_i / kT}, \tag{A1}
\]

should apply. Here \(E_i\) is the energy of the cluster relative to the monomer state, \(N_o\) is the site density, and \(C_i\) is a weighting factor dependent on the lattice. Only monomers of type 2H are deposited; they have a lifetime of \(\tau_2\) and decay to type 1H monomers. Following Venables\(^2\), we write down the rate equations for this two component system,

\[
\frac{dn_{2H}}{dt} = R(1 - Z) - \frac{n_{2H}}{\tau_2} - \sigma_{2x} D_{2H} n_x n_{2H}, \tag{A2}
\]

where \(R\) is the deposition rate, \(Z = a_x n_x\) is the coverage due to clusters (whose average area is \(a_x\)), \(\sigma_{2x}\) is the average capture number by clusters of the 2H monomer and \(n_x\) is the density of stable clusters.

\[
\frac{dn_{1H}}{dt} = \frac{n_{2H}}{\tau_2} - \sigma_{1x} D_{1H} n_x n_{1H}, \tag{A3}
\]

where \(\sigma_{1x}\) is the average capture number by clusters of the 1H monomer. From Eqs. A2 and A3, we obtain

\[
\frac{dn_1}{dt} = R(1 - Z) - \sigma_{1x} D_{1H} n_x n_{1H} - \sigma_{2x} D_{2H} n_x n_{2H}
= R(1 - Z) - \sigma_x n_1 \left\{ \frac{D_{1H} n_{1H}}{n_1} + \frac{\sigma_{2x} D_{2H} n_{2H}}{\sigma_x n_1} \right\}, \tag{A4}
\]

where we have written \(\sigma_x\) in place of \(\sigma_{1x}\) for notational simplicity. We can write the second term of Eq. A4 as \(\sigma_x n_1 D\), where \(D\) is an effective diffusion constant. The equation for stable clusters is given by

\[
\frac{dn_1}{dt} = R(1 - Z) - \sigma_x n_1 D,
\]

where we have written \(\sigma_x\) in place of \(\sigma_{1x}\) for notational simplicity. We can write the second term of Eq. A4 as \(\sigma_x n_1 D\), where \(D\) is an effective diffusion constant. The equation for stable clusters is given by
\[
\frac{dn_x}{dt} = U_i - U_c, \quad (\text{A5})
\]

where \( U_i \) is the nucleation rate of stable clusters (i.e. clusters with size \( > i \)) and \( U_c \) is the rate at which stable clusters coalesce. \( U_i \) is given by

\[
U_i = \sigma_{1i} D_{1i} n_i n_{1i} + \sigma_{2i} D_{2i} n_i n_{2i}
= \sigma_{1i} n_i \left\{ \frac{D_{1i} n_{1i}}{n_i} + \frac{\sigma_{2i} D_{2i} n_{2i}}{\sigma_i} \right\}
= \sigma_{1i} n_i D, \quad (\text{A6})
\]

where we have written \( \sigma_{1i} \) as \( \sigma_i \) and the effective diffusion constant as the same \( D \) as in Eq. A4. This approximation is consistent with the one we will make below. We use an expression for \( U_c \) given by \( U_c = 2n_x dZ/dt^2 \). Eqs. A4, A5 and A6 are now identical to those in Venables\(^2\). Together with the 2D islanding equation for \( Z \), \( dZ/dt = \Omega^2/3 (\sigma_x D n_1 n_x + RZ) \), and Walton’s equation (Eq. A1) they lead to the following equations\(^2\),

\[
\frac{dn_1}{dt} = R(1 - Z) - \frac{n_1}{\tau}, \quad (\text{A7})
\]

where \( 1/\tau = \sigma_x D n_x \) and

\[
\frac{dn_x}{dt} = \gamma_i N_o^{1-i} D n_x^{i+1} \left( 1 - Z \right)^i - 2n_x \frac{dZ}{dt}, \quad (\text{A8})
\]

where \( \gamma_i = \sigma_i C_i \exp(\beta E_i) \) and \( N_o \) is the number\(^2\) of sites/cm\(^2\). Under steady state conditions Eq. A7 gives \( n_1 = R \tau (1 - Z) \). Using this result and the variables \( \mathcal{N} = n_x/N_o \) and \( \mathcal{T} = Rt/N_o \), Eq. A8 becomes

\[
\frac{d\mathcal{N}}{dZ} = (1 - Z) \gamma_i \frac{R}{D N_o^2} \frac{1}{\mathcal{N}} \left( \frac{1}{\sigma_x \mathcal{N}} \right)^{i+1} - 2\mathcal{N}, \quad (\text{A9})
\]

where we have used the result

\[
\frac{d\mathcal{T}}{dt} = \frac{R}{N_o} \frac{1}{dZ/dt} = \frac{1}{\Omega^2}. \quad (\text{A10})
\]

Under steady state conditions, we obtain from Eq. A3 the result \( n_{1H}/n_{2H} = 1/\alpha \), where \( \alpha = \tau_2 \sigma_x D_{1H} n_x \). This gives \( n_{1H}/n_1 = 1/(1 + \alpha) \) and \( n_{2H}/n_1 = \alpha/(1 + \alpha) \) and if we
assume that $\sigma_{2x} \sim \sigma_x$, then the effective diffusion constant in Eq. A4 is given by $D = (D_{1H} + \alpha D_{2H})/(1 + \alpha)$. We now consider two limits; first, (a) when $D_{1H} \ll \alpha D_{2H}$, $D = D_{2H} \alpha/(1 + \alpha)$. Here a growth exponent other than the standard one results when $\alpha < 1$. This leads to $\eta = i/(2i + 3)$. However the diffusion of the dihydride is much slower than that of the monohydride, so that the other limit (b) $D_{1H} \gg \alpha D_{2H}$ is applicable; then $D$ is well approximated by $D = D_{1H}/(1 + \alpha)$. Here there are two limiting cases that we can look at; the first is where the second term in the denominator is less than 1 and the second when it is greater than 1. The first case simply leads to the standard growth exponent for 2D islands for the complete condensation regime\textsuperscript{14}, $\eta = i/(i + 2)$. The second case may apply to the experimental results of Andersohn \textit{et al}. Using the parameters\textsuperscript{1,2}, $n_x \sim 10^{12}/cm^2$, $1 < \sigma_x < 100$ and estimating from the results of Mo \textit{et al}\textsuperscript{4} that $10^{-10} < D_{1H} < 10^{-8}(cm^2/sec)$ at $500^\circ C$ and assuming that $\tau_2$ is at least of the order of 1 second, we can see that the second term can be dominant. In this case Eq. A9 becomes

$$\frac{dN}{dZ} = (1 - Z)\gamma_i\left(\frac{R\tau_2}{N_o}\right)^i \frac{1}{\sigma_x N^2} N_o \Omega^2 - 2N, \quad (A11)$$

Setting $N = \zeta(Z)\left(\frac{\gamma_i}{N_o^{i+1} \Omega^2}\right)^{1/2}$, where $\zeta(Z)$ is a pure number satisfying a differential equation\textsuperscript{2}. This leads to the growth exponent $\eta = i/2$ for 2D islanding. A similar analysis for 3D islanding leads to $\eta = 2i/5$. In both cases the exponent could be larger than unity.

**APPENDIX B: RATE EQUATIONS IN TERMS OF GROWTH RATE $R'$**

We look at the standard rate equations in terms of the growth rate $R'$ rather than the deposition rate $R$. Eqs. A7, A8 remain the same but $\tau$ is now given by $1/\tau = 1/\tau_a + \sigma_x D n_x$, where evaporation is now considered and $\tau_a$ is the evaporation lifetime of the monomer. Eq. A10 becomes

$$\frac{dT}{dt} = \frac{1}{N_o \Omega^2} \delta, \quad (B1)$$

where $A = D\tau_a N_o$ and $\delta = (1 + \sigma_x AN)/(Z + \sigma_x AN)$. Eq. A9 becomes
\[
\frac{d\mathcal{N}}{dZ} = (1 - Z)\sigma_i B_i \left( \frac{A}{1 + \sigma_x A \mathcal{N}} \right)^i + 1 \frac{dT}{dZ} - 2\mathcal{N}, \tag{B2}
\]

where \( B_i = C_i e^{\beta E_i} (\frac{R}{N^2 D})^i \). From \( R' = R - n_1/\tau_a \) and the steady state relation \( n_1 = R\tau(1 - Z) \), we get \( R = R'\delta \). In terms of \( R' \), \( B_i = B'_i\delta^i \), where \( B'_i = C_i e^{\beta E_i} (\frac{R'}{N^2 D})^i \).

We obtain growth exponents for the following condensation regimes:

(a) for extreme incomplete condensation \( \sigma_x A \mathcal{N} \ll Z \). This leads to \( R = R'/Z \) and \( B = B'/Z \). The growth exponent plotted against \( R' \) remains the same as that plotted against \( R \), with \( \eta = i \).

(b) for complete condensation \( \sigma_x A \mathcal{N} \gg Z \). This gives \( R = R' \) and \( B = B' \) and so the exponent remains unchanged at \( \eta = i/(i + 2) \).

(c) for initially incomplete condensation \( 1 > \sigma_x A \mathcal{N} > Z \). We obtain

\[
\frac{dT}{dt} = \frac{1}{N_o \Omega^2} \frac{1}{\sigma_x A \mathcal{N}}, \tag{B3}
\]

\[
B_i = B'_i (\frac{1}{\sigma_x A \mathcal{N}})^i, \tag{B4}
\]

\[
\frac{d\mathcal{N}}{dZ} = (1 - Z)\sigma_i B_i' \left( \frac{A}{\sigma_x A \mathcal{N}} \right)^{i+1} \frac{1}{N_o \Omega^2} - 2\mathcal{N}, \tag{B5}
\]

This leads to the result \( \eta = i/(i + 2) \) like that for the complete condensation regime.
REFERENCES

1 L. Andersohn, Th. Berke, U. Kohler and B. Voigtlander, J. Vac. Sci. Tech. A 14, 312 (1996).

2 J. A. Venables, Phil. Mag. 27, 697(1973); J. A. Venables, G. D. Spiller, and M. Hanbucken, Rep. Prog. Phys. 47, 399(1984).

3 Bert Voigtlander and Andre Zinner, Surf. Sc. Lett. 292, L775 (1993); S. V. Ghaisas and S. Das Sarma, Phys. Rev. B 46, 7308(1992).

4 Y.-W. Mo, J. Kleiner, M. B. Webb and M. G. Lagally, Surf. Sc. 268, 275(1992).

5 S. K. Kulkarni, S. M. Gates, C. M. Greenlief and H. H. Sawin, Surf. Sc. 239, 26 (1990); J. Vac. Sc. Tech. A 8, 2956(1990); S. K. Kulkarni, S. M. Gates, B. A. Scott and H. H. Sawin, Surf. Sc. 239, 13 (1990).

6 M. H. von Hoegen and Anke Golla, Phys. Rev. Lett. 76, 2953(1996).

7 U. Kohler, L. Andersohn, and H. Bethge, Phy. Stat. Sol. (a) 159, 39 (1997).

8 D. Kandel, Phys. Rev. Lett. 78, 499(1997).

9 K. E. Khor and S. Das Sarma, Phys. Rev. B 62, 16657(2000).

10 B. Lewis and J. C. Anderson, Nucleation and Growth of Thin Films, Academic Press (1978).

11 J. G. Amar and F. Family, Phys. Rev. Lett. 74, 2066(1995);

12 D. Walton, J. Chem. Phys. 37, 2182(1962).

13 J. A. Venables and H. Brune, Phys. Rev. B 66, 195404(2002).

14 J. A. Venables, Surf. Sc. 299/300, 798(1994).
FIGURES

FIG. 1. Island density versus deposition rates $R$ in our kinetic Monte Carlo simulations as described in the text. Solid line with open circles: MBE; dotted line with open squares: SiH with hydrogen evaporation rate $R_e = 1200$; dot-dash line with solid diamonds: SiH with hydrogen evaporation rate $R_e = 2000$; double dot-dash and double dash-dot lines: SiH with H atom deposited randomly onto available nearest neighbor dangling-bond site and up to next-nearest neighbor sites respectively; dashed line with solid triangles: two component SiH, SiH$_2$ results.

FIG. 2. Scaled island distributions for Si MBE for (a) $R=1$ and (b) $R=16$. Curves with circles, diamonds and squares are due to the scaling function (Eq. 3) for $i=3,2$ and 1 respectively.

FIG. 3. Scaled island distributions for two component growth (SiH and SiH$_2$) for (a) $R=1$ and (b) $R=16$. Lines with circles, diamonds and squares are as in figure 2.
