Mechanisms of Stranski-Krastanov Growth

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Stranski-Krastanov (SK) growth is reported experimentally as the growth mode that is responsible for the transition to three dimensional islands in heteroepitaxial growth. A kinetic Monte Carlo (KMC) model is proposed that can capture many of the experimentally observed features of this growth mode. Simulations reveal that this model effectively captures the SK transition and subsequent growth. Annealing simulations demonstrate that the wetting layer formed during SK growth is stable, with entropy playing a key role in its stability. It is shown that this model also captures the apparent critical thickness that tends to occur at higher deposition rates and for alloy films (where intermixing is significant). This work shows that the wetting layer thickness increases with increasing temperature whereas the apparent critical thickness decreases with increasing temperature. Both of which are in agreement with experiments.

I. INTRODUCTION

Heteroepitaxy is a process in which a film is deposited on a substrate of a different material. The typical examples of film substrate combinations include Ge/Si, InAs/GaAs and InP/GaAs. The lattice mismatch between the film and substrate can lead to the growth of a strained film. The film often grows in a layer-by-layer fashion until a certain critical thickness, beyond which 3D islands form through what is known as the Stranski-Krastanov (SK) transition. In a strained film, the formation of islands is energetically favorable, as it reduces the strain energy in the crystal. The experimental observations on Ge/Si systems seem to show a critical thickness of about 3 monolayers (ML) for pure Ge on Si\textsuperscript{1,2}. Similar observations are made in InAs/GaAs systems\textsuperscript{3}. These 3D islands show potential to serve as quantum dots and are of great practical importance\textsuperscript{4,5}.

The instability of a planar film is understood in the context of the Asaro-Tiller-Grinfeld (ATG) instability\textsuperscript{5}. However, according to the ATG theory a strained film of any finite thickness is unstable i.e. it predicts a zero critical thickness. Currently two fundamentally different theories have been used to reconcile this. One is based on a kinetic stabilizing mechanism (the notion of an apparent critical thickness) and the other an energetic mechanism (use of a wetting potential).

The concept of an apparent critical thickness relies on the notion that the instability is present but not observed until the perturbations have grown large enough to be perceived as islands\textsuperscript{6,7}. It was further suggested by Tu and Tersoff\textsuperscript{8} that intermixing lowers the growth rate of the instability, leading to a delayed perception of the island formation. One possible problem with this interpretation is that the region between the islands will erode below the original substrate location and this does not appear to be observed in experiments.

On the other hand, Leonard et al\textsuperscript{9} observed that a critical thickness was observed when depositing InAs on GaAs even at very low fluxes. This suggests an energetic mechanism might be appropriate; to this end one can introduce a wetting potential, which arises naturally when assuming that the surface energy varies with height\textsuperscript{10}. This can give rise to a linearly stable flat film. Earlier studies on the wetting interactions date back to the work of Tersoff\textsuperscript{11,12}. More recently these calculations were repeated using density functional theory\textsuperscript{12}. It is argued in literature\textsuperscript{11,12} that approximately 1-3 ML of Ge on Si will be stable. In both cases this is based on calculating the energy per atom after each consecutive layer of Ge is added. One issue with this work is that the roles of entropy and intermixing, which can be significant at the temperatures typical of molecular beam epitaxy, are not included. As a consequence such an argument cannot predict the temperature dependence of the critical thickness observed in experiments\textsuperscript{13}.

In this, work we show that the issues discussed above can be well understood by using an oft-used solid-on-solid atomistic KMC model. The model uses a bond counting approach for short range interactions and a ball and spring model to account for the long range elastic interactions. This allows us to capture surface energy and elastic energy, the basic ingredients present in both approaches outlined above. Wetting interactions are put into place using a species dependent bond strength. This model not only predicts the existence of a kinetically limited apparent critical thickness (as in the work of Tu et al\textsuperscript{8}) but also a true critical thickness for the onset of the instability (not observed in Tu et al\textsuperscript{8}). Entropy is found to play a crucial role in stabilizing the wetting layer in this regime. The identification of the different stabilizing mechanisms and the role of entropy allows us to present a comprehensive theory that explains the Stranski-Krastanov transition under different growth conditions. This approach not only unifies the pre-existing theories but also recovers the experimental observations of temperature dependence and long term stability (to annealing) of the wet-
ting layer. This is the key contribution in this paper. The discussion and the model description are presented below for Ge/Si but are applicable to heteroepitaxial growth in general.

II. KMC MODEL

The KMC model used in this study was first presented by Orr et al. and later by Lam et al. An efficient method for solving the model which is used here was presented in our previous work. The model is an atomistic model in which the crystal occupies a semi infinite substrate of Si on top of which sits a film of deposited material. The atoms occupy sites on a cubic lattice.

In this work we consider a 1+1 dimensional system of atoms within the solid-on-solid framework (no overhanging atoms). Each atom in the system is bonded to its nearest (4 possible) and next to nearest (4 possible) neighbors by chemical bonds of strength $\gamma$ that depends on the species involved. There are three possible bonds have strengths $\gamma_{\text{Ge-Ge}}, \gamma_{\text{Ge-Si}}$ and $\gamma_{\text{Si-Si}}$. These bond energies account for the chemical energy of the system.

The atoms in the system are also connected to their occupied nearest and next to nearest neighbors by means of Hookean spring (linear stress strain relations). This accounts for the long range elastic interactions though linear elasticity. The lateral and vertical springs connecting nearest neighbors have spring constant $k_L$ and the diagonal springs connecting the next to nearest neighbors have strength $k_D$. The spring constants are chosen so that they satisfy $k_D = k_L/2$ corresponding to the case of isotropic linear elasticity. The natural bond lengths or lattice spacings of the atoms are denoted by $a_{ss}, a_{gs}$ and $a_{gg}$ corresponding to Si-Si, Ge-Ge and Ge-Si bonds. They are not equal in general and are chosen to reflect the Ge/Si system with a 4% misfit.

The hopping rate of a surface atom is given by

$$R_t = R_0 \exp \left( \frac{\Delta E + E_0}{k_B T} \right)$$

(1)

where $\Delta E$ is the total change in energy when the atom is removed from the system and $k_B T$ is the thermal energy. The parameters $R_0$ and $E_0$ are chosen to give physically relevant hopping rates. This choice of Arrhenius-like rates satisfies detailed balance. This has two parts the chemical energy (bond counting) and the elastic energy (springs) of the system.

$$\Delta E = \Delta E_{\text{chem}} + \Delta E_{\text{elas}}$$

(2)

The chemical energy of the system is accounted for by bond counting. It is simply the sum total of the energy in the bonds that need to be broken to remove the atom from the system. For example in the case of a pure Si system the change in chemical energy of the system is simply $-N \gamma_{\text{Si-Si}}$ where $N$ is the number of occupied neighbors. The hopping rate in this case is simply

$$R_t = R_0 \exp \left( \frac{-N \gamma_{\text{Si-Si}} + E_0}{k_B T} \right).$$

(3)

In the more complex case of a mixture of Ge and Si the change in chemical energy is calculated by adding the energies associated with each bond that is broken to remove the atom. The general form is written as

$$R_t = R_0 \exp \left( \frac{\Delta E_{\text{chem}} + \Delta E_{\text{elas}} + E_0}{k_B T} \right)$$

(4)

where $\Delta E_{\text{chem}}$ is the change in chemical energy (bond energy), $\Delta E_{\text{elas}}$ the change in elastic energy when the atom is removed from the system.

Not surprisingly a majority of the events during the course of a KMC simulation are adatom ($N \leq 3$) hops. This means the total computational time needed significantly depends on the treatment of the adatoms. To increase the simulation speed, the elastic contribution and the species type are ignored when evaluating the adatom hopping rates. Naturally, one should be concerned when making an approximation such as this; but nevertheless extensive tests revealed that little loss of fidelity was observed while the code was 3 to 5 times faster. For this reason, the results in this paper use the following rates

$$R_t = \begin{cases}  
R_0 \exp \left( \frac{\gamma_{\text{Ge-Ge}} + E_0}{k_B T} \right) & N \leq 3 \\
R_0 \exp \left( \frac{\Delta E_{\text{chem}} + \Delta E_{\text{elas}} + E_0}{k_B T} \right) & N > 3  
\end{cases}$$

(5)

The KMC simulation of this model is computationally very expensive since the elastic displacement field must be updated repeatedly. For the simulations presented in this study over $10^9$ updates are typically needed. Therefore it is particularly crucial to perform this operation with great efficiency. This is achieved by using both global and local updates of the displacement field. Local updates are computed using the expanding box method, and when this local approach fails global updates are used. The global approach is based on a multigrid algorithm combined with an artificial boundary condition (to incorporate the semi-infinite substrate). Our algorithm involves a reduced-rejection KMC, based on the use of upper-bounds for the rates and a rejection to compensate. The upper bounds are obtained from local (computationally inexpensive) overestimates of the change in elastic energies ($\Delta E_{\text{elas}}$). They are reasonably sharp, leading to rejection rates of under 5%. The reader is directed to our previous work for a comprehensive exposition of the algorithm and underlying theory.

III. STRANSKI-KRASTANOV GROWTH MODE

The above model sets stage for our discussion on the SK growth mode. Here we choose $\gamma_{\text{Ge-Ge}} =$
FIG. 1. Shows the snapshots of the growth of pure Ge on flat Si substrate at 600K under a deposition flux of 0.8ML/s. The plots show the film at 2, 4, 6 and 8ML of deposition. The simulation was performed on a periodic domain of 512 atoms in the horizontal direction.
Left - Bond strengths are equal: $\gamma_{\text{Si-Si}} = \gamma_{\text{Si-Ge}} = \gamma_{\text{Ge-Ge}} = 0.37$ eV
Right - Bond strengths are unequal: $\gamma_{\text{Si-Si}} = 0.37$, $\gamma_{\text{Si-Ge}} = 0.355$ and $\gamma_{\text{Ge-Ge}} = 0.34$ eV

FIG. 2. Shows the equilibrium configuration obtained upon annealing a flat film of 1ML, 2ML, 3ML and 4ML of Ge on a flat Si substrate at a temperature of 600K. The simulation was performed on a periodic domain of 512 atoms in the horizontal direction.

FIG. 3. Shows the equilibrium configuration obtained upon annealing a flat film of 3ML of Ge on a flat Si substrate at a temperature of 500K, 550K, 600K and 650K. The simulation was performed on a periodic domain of 512 atoms in the horizontal direction.

Growing on a Germanium rich layer of approximately 3 ML indicating presence of a stable wetting layer. We remark that there exists small trenches near the periphery of the islands. This growth mode persists even after 10 ML of deposition. These observations are consistent with SK growth.

To further validate our claim that this is indeed SK growth, we perform the following annealing experiments.
We consider an initial condition of $N$ ML of Ge placed on a substrate of Si which is then annealed for approximately 14 seconds (this is about $10^{10}$ KMC steps at 600 K). These simulations (see Fig. 2) indicate that Ge films that are $\lesssim 3$ ML are stable but at 4 ML islands will form. From this we conclude that it is reasonable to surmise that this KMC model has a true critical thickness and wetting layer thickness of 3 ML. This is indeed the observation made in experiments, that a sharp critical thickness is observed even at very low deposition rates. The low deposition rate ensures that the film is close to equilibrium and these observations are not the result of kinetically limited processes.

It should be pointed out that these stable films are stressed and so it is surprising, that islands do not form. We claim the reason that islands do not form is due to entropy. To validate this assertion we preformed a similar series of annealing simulations, this time we annealed 3 ML of Ge on Si at different temperatures (see Fig. 3). These simulations show that if $T \lesssim 550 K$ islands will form. On the other if $T \gtrsim 600 K$ islands do not form. Clearly if the temperature is too large entropy will prevent islands from forming even with the wetting layer being stressed. Also the true critical thickness increases with temperature as observed in experiments done at low fluxes.

It was first observed experimentally by Mo et al. that metastable 3D islands exist in the Ge/Si system well before the formation of stable 3D islands. This was also confirmed by Yam et al. using RHEED and AFM techniques. They conclude that the film loses stability before stable 3D islands can form by instead producing very small metastable 3D islands by strain relaxation. Similar observations were made by Floro et al. for alloy films.

This is consistent with our simulations, the reader is directed to the right hand side of Fig. 4 which shows tiny islands after 2 ML of deposition. Even though these small islands lower the strain energy, the energetic advantage of their formation is not quite enough to overcome entropy. Therefore, they are only metastable. Only when enough material has been deposited can islands form that are big enough to yield a reduction in strain energy that can overcome entropic effects. The annealing results, for a 2ML film shown in Fig. 2 reveal a smoother film with fewer tiny islands which is consistent with the assertion that the tiny islands in the growing film are indeed metastable.

Finally, we mention the last crucial ingredient contained in this model needed to capture SK growth is allowing the bonds strengths to be different. This can be understood by performing a simulation, the same as above, but with identical bond strengths: $\gamma_{Si-Si} = \gamma_{Ge-Si} = \gamma_{Ge-Ge} = 0.37 eV$. This simulation produces an apparent critical layer but as the film grows trenches form between the islands destroying the wetting layer. The result of growth are shown in Fig. 4 (left). The reason the trenches form in this case and not the other is twofold. Because all the bonds strengths are the same, there is a lower energy barrier to intermixing. Surprisingly, intermixing actually increases the total elastic energy which further drives the ATG instability resulting in the trench formation. Table 1 shows that after 8 ML of deposition the equal bond case has considerably more elastic energy than the case with different bond strengths. Thus elastic effects can make segregation to be energetically preferred since intermixing increases the elastic energy. This suggests that the intermixing is in fact entropically preferred and the use of different bond strengths provides the much needed energy driven pathway to segregation ultimately leading to the SK growth mode.

### IV. THE APPARENT CRITICAL THICKNESS

Intermixing plays a more significant role when depositing Si-Ge alloys as compared to pure Ge on Si. In this case, we initially observe an apparent critical thickness much like that reported by Tu and Tersoff. We have compiled a series of simulations where Ge$_x$Si$_{1-x}$ is deposited on Si with $\gamma_{Ge-Si} = 0.34 eV$, $\gamma_{Ge-Ge} = 0.355 eV$ and $\gamma_{Si-Si} = 0.37 eV$.

In order to quantify our observations, we introduce the quantity, $F$, which is taken to be the amplitude of the dominant mode of the discrete Fourier transform of the surface height function.

To perform a quantitative analysis of the dependence of the apparent critical thickness on temperature and film concentration, we define the apparent critical thickness to be the average thickness of deposited film, where the quantity $F$, is 1000 (roughly 5 times the magnitude of a kinetically roughened film ($\sim 200$)). This definition is similar to the one used by Tu and Tersoff. The Fig. 4 shows the apparent critical thickness as a function of concentration of Ge in the deposited material. These results were obtained by ensemble averaging the data obtained on a periodic domain of 1024 atoms over 4 independent runs.

These simulations show that apparent critical thickness can be as large as 11 ML for $x = .55$. They also demonstrate (see Fig. 4) that the apparent critical thickness increases with decreasing $x$ and decreasing temperature. This is also in agreement with experiments. This behavior is understood by noting that as the temperature increases the entropy driven intermixing dilutes the film further slowing the growth rate of the instability. The effect is found to be more pronounced in the case of dilute deposition flux. Due to the computational cost the temperature dependence is only shown.

| Equal Bond Strengths | $755.5602 k_B T$ |
| Different Bond Strengths | $637.4619 k_B T$ |
with equal bond strengths. Preliminary tests indicate a similar trend persists with unequal bond strengths. In addition our simulation show that subsequent growth sees this apparent critical layer disappearing with its contents being incorporated into the islands leaving behind a wetting layer of about 3 ML. This behavior was observed in experiments. Fig. 5 shows an example of this in a simulation of Ge$_{0.8}$Si$_{0.2}$ growth on Si. Here an apparent critical thickness of about 5 ML is observed (no islands at 5 ML growth). However at 8ML of growth well separated islands are formed where some of the material from the critical layer (first 5 layers) is incorporated into the islands. At 8ML of growth a wetting layer much smaller than 5 ML is observed between the islands.

FIG. 4. Shows the apparent critical thickness as a function of concentration of Ge ($x$) for deposition of Ge$_x$Si$_{1-x}$ on Si. The results were averaged over 4 independent runs. The simulation was performed on a periodic domain of 1024 atoms in the horizontal direction.

FIG. 5. This figure shows a simulation where an alloy (Ge$_{0.8}$Si$_{0.2}$) is deposited at 0.8 ML/sec on Si at 600K with bond strengths $\gamma_{Ge-Ge} = 0.34$, $\gamma_{Ge-Si} = 0.355$, and $\gamma_{Si-Si} = 0.37$ eV. The apparent critical thickness is 5 ML however further growth results in wetting layer much smaller than 5 ML. The simulation was performed on a periodic domain of 512 atoms in the horizontal direction.

In addition simulations also indicate a weak dependence of the apparent critical thickness at low flux regimes with the apparent critical thickness decreasing with the flux (toward the true critical thickness). Table II shows the apparent critical thickness of pure Ge on Si as a function of deposition flux. The trends are consistent with experiments.

| Deposition Flux in ML/s | 0.2 | 0.4 | 0.8 | 1.6 | 3.2 | 6.4 |
|------------------------|-----|-----|-----|-----|-----|-----|
| Critical Thickness in ML | 3.66| 3.79| 4.22| 4.73| 4.74| 5.40|

V. DIFFERENT MECHANISMS INVOLVED IN STRANSKI-KRASTANOV GROWTH

Based on the above results, we conclude there are primarily three different mechanisms responsible for the phenomena associated with Stranski-Krastanov growth. These are:

- Apparent Critical Thickness
- Wetting potentials
- Entropic stability

A. Apparent Critical Thickness

The first case we shall address is the mechanism related to the notion of an apparent critical thickness which tends to arise when the growth rate associated with the ATG instability and the deposition rate are comparable. We observe that kinetic roughening and the adatom diffusion lead to enough intermixing to reduce the strength of the elastic instability and thereby increasing the apparent critical thickness, also in agreement with Tu and Tersoff.

Our simulations suggest that strained film growth in this regime has three stages.

- **Stage I**: The first stage occurs when the film exhibits a planar layer-by-layer growth with three regions being observed: the substrate, an intermixing layer, and the film. The concentration of the Ge increases as one moves from substrate to surface. At the latter portion of this stage the film will have small islands (metastable) and/or ripples.

- **Stage II**: The second stage begins when the film thickness exceeds an apparent critical thickness marked by the growth of the small metastable islands into stable quantum dots.
B. Wetting Potentials

The introduction of wetting potentials\cite{10,11} allows one to include the possibility that the surface energy may change with film thickness due to film/substrate interactions. When chosen appropriately, the wetting potential can stabilize a thin film in the presence of strain. In our model these effect are naturally incorporated by the use of different bond strengths. The difference in bond strengths leads to the difference in surface energies between the two species. For our choice (physically relevant) the Ge surface energy is lower and it is cheaper to have a Ge rich surface.

When the temperature is low and as a consequence, entropy is not dominant we observe a wetting layer of one atomic layer thickness (see Fig. $\text{B}$, T= 500K). Even though this layer is strained it still energetically favorable because the Ge surface has less surface energy than a Si surface. However, at low temperatures the thicker film would not be stable because of strain relaxation, indeed if we again look at Fig. $\text{B}$ (T= 500K) we infer that film of thickness 3ML is not stable. However, as the temperature is increased this scenario changes due entropic contributions which provide a stabilizing mechanism discussed below.

C. Entropic Stabilization

The last mechanism we will discuss results from entropic contributions. The effects of entropy can allow a film that would be energetically unstable at low temperature to become stable at sufficiently high temperatures. Such a film would be linearly unstable by the Asaro-Tiller-Grinfeld instability (even accounting for the wetting potential). However, entropy can prevent the surface height perturbations from growing into islands.

In the regime, when films are grown at ultra low fluxes, entropic effects may be the dominant mechanism. The film, grows in a layer-by-layer fashion and the strain energy increases. Only, when the energetic advantage of island formation is enough to overcome entropy, will 3D islands form. The so formed islands sit on top of a wetting layer. The extreme case of zero flux is explored using annealing simulations as presented in Fig. $\text{A}$ and Fig. $\text{C}$. Our conclusions on this regime are consistent with experiments at ultra low fluxes\cite{10}.

VI. SUMMARY

The phenomena of SK growth is an interplay involving the aforementioned mechanisms, but overall SK growth can be understood as the competition between energy and entropy. Accounting for entropy allows one to bridge the two existing theories of apparent critical thickness and wetting potentials to formulate a comprehensive theory that also explains regimes not accounted for by the individual theories.

In conclusion, we have presented a simple KMC model that is able to capture many aspects of heteroepitaxial growth including wetting layers and apparent critical layers. The distinction between the apparent critical thickness and wetting layers thickness has been clarified. Finally the importance of the roles of entropy and intermixing has been identified.

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We choose parameters $E_0 = 0.53\text{eV}$, $R_0 = 2D_0/a_{ss}^2$ where $D_0 = 3.83 \times 10^{13}\text{Å}^2/\text{s}$. The Si-Si, Si-Ge, and Ge-Ge lattice spacings are taken to be $a_{ss} = 2.73\text{Å}$, $a_{sg} = 1.02a_{ss}$, and $a_{gg} = 1.04a_{ss}$ respectively. The spring constants are $k_L = 13.85\text{eV}/a_{ss}^2$ and $k_D = k_L/2$ These parameters are chosen to model Ge/Si system, but we note that Lam et al. used $\gamma_{Si-Si} = 0.4 \text{eV}$. Our choice of $.37 \text{eV}$ is physically reasonable and yields a reasonable amount of intermixing.

More likely the film is only metastable on very large time scales as discussed by Tersoff.

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