

Mechanisms of Stranski-Krastanov Growth

Arvind Baskaran*

Department of Mathematics, University of California Irvine, California 92697-3875.

Peter Smereka[†]

Department of Mathematics, University of Michigan, Ann Arbor, Michigan 48109.

(Dated: January 19, 2011)

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 replicate 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 for alloy films or at higher deposition rates. 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.

PACS numbers: 68.43.Jk, 68.65.Hb, 68.55.-a

Heteroepitaxy is a process in which a film of a certain material is deposited on 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. Similar observations are made in InAs/GaAs systems [11]. These 3D islands show potential to serve as quantum dots and are of great practical importance [1, 2].

The instability of a planar film is understood in the context of the Asaro-Tiller-Grinfeld (ATG) instability [3]. However according to the ATG theory a strained film of any finite thickness is unstable i.e. it predicts a zero critical thickness. One possible way to reconcile the inability of the ATG theory to predict a critical thickness is to posit that the instability is present but not observed until the perturbations have grown large enough to be perceived as islands. This led the authors in [12, 14] to introduce the notion of an apparent critical thickness. It was suggested in Ref. [12] that since the intermixing of the film and substrate dilutes the film the growth rate of the instability is lowered (as predicted by ATG instability [3]). This in turn leads to a delayed perception of the island formation (not the delayed onset of the instability). One possible problem with this interpretation is that the region between the islands will keep being eroded well below the original substrate location and it

does not appear to be the case in experiments. The authors in [23] found that a critical thickness was observed even when depositing InAs on GaAs at very low fluxes allowing the system to equilibrate. This however cannot be explained by a kinetic argument.

Another approach is to introduce a wetting potential which arises naturally if one assumes that the surface energy varies with height [4-6]. This can give rise to a linearly stable flat film. The earlier works on the wetting interactions dates back to the work of Tersoff [7] and later a similar calculation using techniques of Density Functional Theory were performed by [8]. It is argued in these Refs. [7, 8] 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 Ref. [25].

In this study, we use a solid on solid atomistic KMC model (for Ge/Si system) with bond counting approach for short range interactions and a ball and spring model to account for the long range elastic interactions. We will demonstrate that wetting interactions put in place by use of a simple species dependent bond strength is enough to capture a wetting layer. Different mechanisms are observed for the stability of the wetting layer and the SK transition at different temperatures. A mechanism similar to the one proposed in [7] is observed in low temperature regimes where energetics are dominant. At higher temperatures where alloy formation and intermixing are significant an entropic stabilizing mechanism is observed. Our model not only predicts the existence

of a kinetically limited apparent critical thickness (as in [12]) but also a true critical thickness for the onset of the instability (not observed in [12]). 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 is the key contribution in this paper. The discussion and the model description are presented below for the Ge/Si system for simplicity. However the key ideas and the theory are applicable in general to heteroepitaxial growth in general.

The KMC model used here is a solid-on-solid bond counting model in 1+1 dimensions [16, 19, 20], in which only the surface atoms are mobile. The model captures both elastic and surface energetics and surface diffusion, the essence of continuum models; it also naturally includes the discrete stochastic effects such as surface roughness, nucleation and intermixing. We briefly describe the model and the numerical scheme here and refer the readers to [16] for details. The atoms in the crystal occupy sites on a cubic crystal, within the solid-on-solid framework (i.e. no overhanging atoms). Each atom on the lattice is bonded to all of its occupied nearest and next to nearest neighbors by bonds of strength $\gamma_{\text{Ge-Ge}}$, $\gamma_{\text{Ge-Si}}$, or $\gamma_{\text{Si-Si}}$. The elastic interactions are modeled by a ball and spring system with Hookean springs connecting nearest and next to nearest neighbors. The details are carefully explained in Ref. [16].

The hopping rate of a surface atom is given by

$$R_{\ell} = R_0 \exp\left(\frac{\Delta E_{\text{chem}} + \Delta E_{\text{elas}} + E_0}{k_B T}\right) \quad (1)$$

where ΔE_{chem} is the change in chemical energy (bond energy), ΔE_{elas} the change in elastic energy when the atom is removed from the system, $k_B T$ is the thermal energy. The change in chemical energy ΔE_{chem} is simply the sum total of the energy of the bonds broken when removing the atom. For the case where all bonds are of equal strength ΔE_{chem} is simple $N\gamma$ where N is the number of occupied neighbors of the atom. The parameters R_0 and E_0 are chosen to give physically relevant hopping rates [15, 21]. This choice of Arrhenius-like rates satisfies detailed balance. For computational ease we neglect the elastic energies of the adatoms (atoms with $N \leq 3$), and treat all adatoms the same. This gives a model that is computationally faster with adatom hopping rates changed to $R_0 \exp\left(\frac{-3\gamma_{\text{Ge-Si}} + E_0}{k_B T}\right)$. This treatment of adatoms does not significantly change the results [16].

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 letter over 10^9 updates are typically needed. There-

fore 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 [16, 22]. The global approach is based on a multigrid algorithm combined with an artificial boundary condition (to incorporate the semi-infinite substrate) [17, 18]. 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 change in elastic energies (ΔE_{elas}). They are reasonably sharp, leading to rejection rates of under 5% [16, 22]. The reader is directed to [16] for a comprehensive exposition of the algorithm and underlying theory.

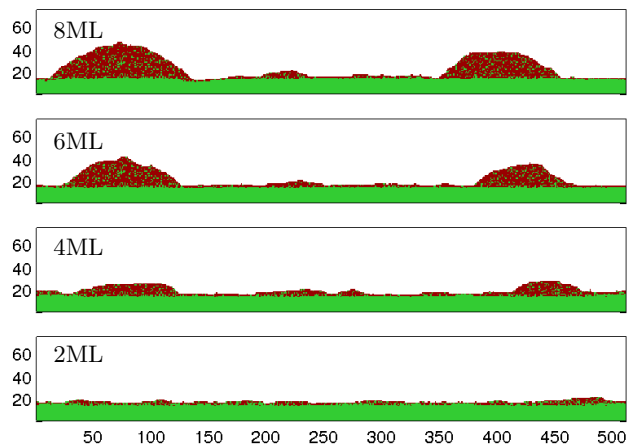


FIG. 1: Shows the snapshots of the growth of pure Ge on Si at 600K under a deposition flux of 0.8ML/s. The plots show the film at 2,4,6 and 8ML of deposition.

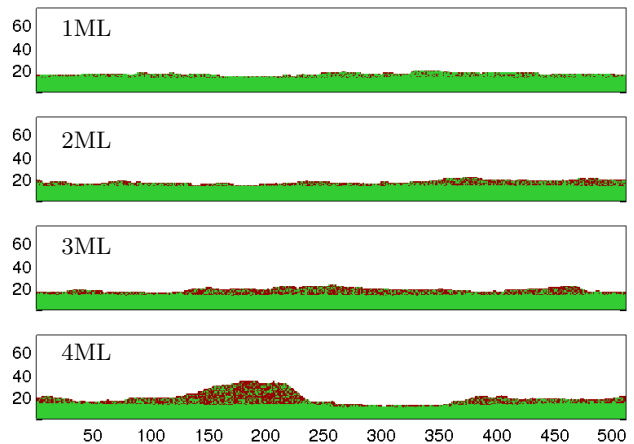


FIG. 2: Shows the equilibrium configuration obtained upon annealing 1,2,3 and 4 ML of Ge on Si at 600K.

The above model sets stage for our discussion on the mechanisms of SK growth. Here we choose $\gamma_{\text{Ge-Ge}} = 0.34\text{eV}$, $\gamma_{\text{Ge-Si}} = 0.355\text{eV}$ and $\gamma_{\text{Si-Si}} = 0.37\text{eV}$ (see [21], [16]). Four snapshots of the simulations are shown in

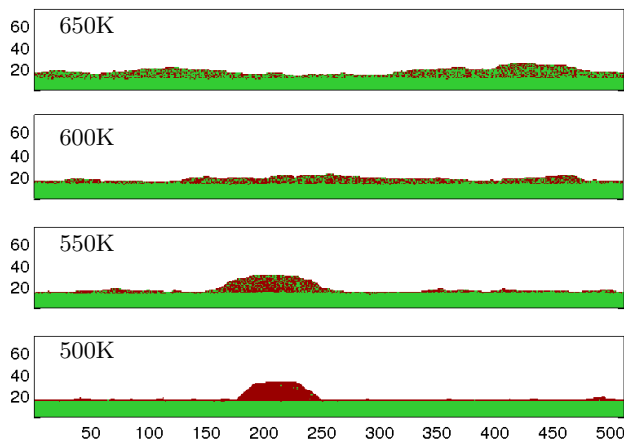


FIG. 3: Shows the equilibrium configuration obtained upon annealing 3ML of Ge on Si at a temperature of 500K, 550K, 600K and 650K.

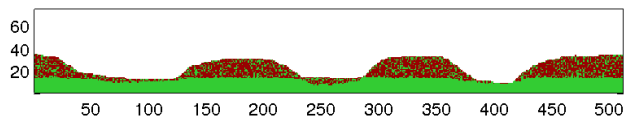


FIG. 4: Shows the configuration of a film of pure Ge grown on Si at 600K with a flux of 0.8ML/s with the bond strengths $\gamma_{\text{Ge-Ge}} = \gamma_{\text{Ge-Si}} = \gamma_{\text{Si-Si}} = 0.37\text{eV}$.

Fig. 1. We observe layer-by-layer growth up to approximately 3 ML after which time islands nucleate indicating the critical thickness is approximately 3 ML. Subsequent growth reveals islands 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 ≤ 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 [23] 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, at first sight, that islands do not form. We claim the reason that islands do not form is due to entropy. This is to say the energy advantage to forming an island cannot overcome entropy. To validate this assertion we performed a similar series of

annealing results, this time we annealed 3 ML of Ge on Si at different temperatures (see Fig. 3). These simulations show that if $T \leq 550\text{K}$ islands will form. On the other if $T \geq 600\text{K}$ islands do not form. Clearly if the temperature is too large entropy will prevent an islands from forming even with the wetting layer being stressed. Also the true critical thickness increase with temperature as observed in experiments done at low fluxes [25].

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: $\gamma_{\text{Si-Si}} = \gamma_{\text{Ge-Si}} = \gamma_{\text{Ge-Ge}} = 0.37\text{eV}$. This simulation produces an apparent critical layer but as the film grows trenches form between the islands destroying the wetting layer. The result after 8 ML of growth is shown in Fig. 4. The reason the trenches form in this case and not the other is twofold. First, 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 the trench formation. Table I 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.

TABLE I: Total elastic energy of 8ML of pure Ge on Si deposited at 0.8 ML/s at 600K

Equal Bond Strengths	795.5602 $k_B T$
Different Bond Strengths	637.4619 $k_B T$

Intermixing plays a more significant role when depositing Si-Ge alloys as compared to pure Ge on Si. In this case, we first observe a apparent critical thickness much like that reported by Tu and Tersoff. We have compiled a series of simulations where $\text{Ge}_x\text{Si}_{1-x}$ is deposited on Si with $\gamma_{\text{Ge-Ge}} = 0.34\text{eV}$, $\gamma_{\text{Ge-Si}} = 0.355\text{eV}$ and $\gamma_{\text{Si-Si}} = 0.37\text{eV}$. These simulations show that apparent critical thickness[28] can be as large as 11 ML for $x = .55$. They also demonstrate (see Fig. 5) that the apparent critical thickness increases with decreasing x and decreasing temperature. This is also in agreement with experiments [26, 27]. Due to the computational cost the temperature dependence is only shown with equal bond strengths. Preliminary test 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

[10]. The details will be presented in a forthcoming paper, nevertheless Fig. 6 shows one example.

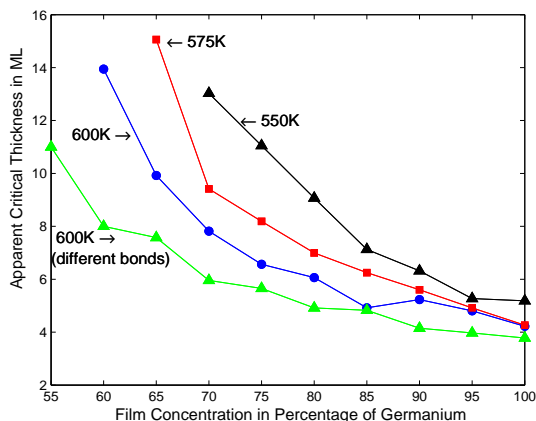


FIG. 5: Shows the apparent critical thickness as a function of concentration of Ge (x) for deposition of $\text{Ge}_x\text{Si}_{1-x}$ on Si. The results were averaged over 4 independent runs [28].

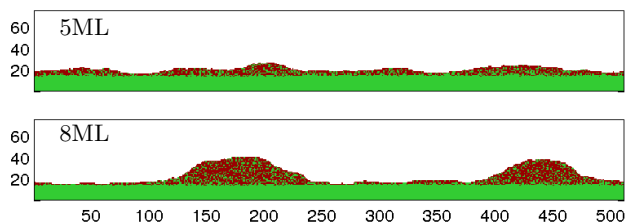


FIG. 6: This figure shows a simulation where an alloy (Ge_sSi_2) is deposited at .8 ML/sec on Si at 600K with bond strengths $\gamma_{\text{Ge-Ge}} = .34$, $\gamma_{\text{Ge-Si}} = .355$, and $\gamma_{\text{Si-Si}} = 0.37\text{eV}$. The apparent critical thickness is 5 ML however further growth results in wetting layer much smaller than 5 ML.

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

The authors gratefully acknowledge helpful conversations with Joanna Mirecki-Millunchick, Len Sander, Vivek Shenoy, and Jerry Tersoff. This research was supported, in part, with grants DMS-0553487, DMS-0509124, DMS-0810113, and DMS-0854870 from the National Science Foundation. One of the authors AB was supported in part by a postdoctoral fellowship from the Institute for Pure and Applied Mathematics and University of California Irvine. The authors also thank Bennet Fauber for help with computing resources.

* Electronic address: baskaran@math.uci.edu

† Also at : Michigan Center for Theoretical Physics, University of Michigan, Ann Arbor, Michigan 48109.; Electronic address: psmereka@umich.edu

- [1] V.A. Shchukin and D. Bimberg, Rev. Mod. Phys. **71**, 1125 (1999).
- [2] P. Politi et al Phys. Rep. **324**, 271 (2000).
- [3] R.J. Asaro and W.A. Tiller, Metall. Trans **3**, 1789 (1972); M.A. Grinfeld, J. Nonlinear Sci. **3**, 35 (1993).
- [4] M. Ortiz, E.A. Repetto, and H. Si, J. Mech. Phys. Sol. **47**, 697-730 (1999).
- [5] T.V. Savina, P.W. Voorhees, and S.H. Davis, J. Appl. Phys. **96** 3127-3133 (2004).
- [6] M. S. Levin et al, Phys. Rev. B. **75** 205312 (2007).
- [7] J. Tersoff, Phys. Rev. B **43**, 9377-9380 (1991).
- [8] M.J. Beck, A. van de Walle, and M.Asta, Phys. Rev. B, **70** 205337 (2004).
B. J. Spencer, P.W. Voorhees, and S.H. Davis, J. Appl. Phys. **73**, 4955 (1993).
W. H. Yang and D. J. Srolovitz, J. Mech. Phys. Solids **42**, 1551-1574, (1994).
- [9] T. Walther et al, Phys. Rev. Lett. **86**, 2381-2384 (2001).
- [10] J.A. Floro et al, Phys. Rev. Lett **79**, 3946 (1997).
- [11] P. M. Petroff and S. P. DenBaars, Super Superlattices Microstruct. **15**, 15 (1994).
- [12] Yuhai Tu and J. Tersoff, Phys. Rev. Lett. **93**, 126101 (2004).
- [13] B. J. Spencer et al, Phys. Rev. B. **64**, 235318 (2001).
- [14] B.J. Spencer, P.W. Voorhees and S. H. Davis, Phys. Rev. Lett. **67**, 3696 (1991).
- [15] D.E. Savage et al, in Semiconductors and Semimetals **56**, R. Hull and J.C. Bean Ed. (Academic Press 1999).
- [16] A. Baskaran, J. Devita, and P. Smereka, Continuum Mech. Thermodyn. **22**, 1 (2010).
- [17] G. Russo and P. Smereka, J. Comput. Phys. **214**, 809 (2006).
- [18] G. Russo and P. Smereka, Mult. Model. Simul. **5**, 130 (2006).
- [19] B.G. Orr, D.A. Kessler, C.W. Snyder, and L.M. Sander, Euro. Phys. Lett., **19**, 33 (1992); Also see : [20]
- [20] C.H. Lam, C.K. Lee, and L.M. Sander, Phys. Rev. Lett. **89** 16102 (1-4) (2002).
- [21] 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 $a_{ss} = 2.73$, $a_{sg} = 1.02s_{ss}$, and $1.04a_{ss}$ 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 [20] but we note [20] used $\gamma_{\text{Si-Si}} = .4$ eV. Our choice of .37 eV is physically reasonable and yields a reasonable amount of intermixing.
- [22] T. P. Schulze and P. Smereka J. Mech. Phys. Solids. **57** 512-538 (2009).
- [23] D. Leonard, K. Pond and P. M. Petroff, Phys. Rev. B. **54** 11687 (1994).
- [24] F. Patella et al, Appl. Phys. Lett. **88** 161903 (2006).
- [25] L. Sfaxi et al, J. Crystal. Growth. **290** 330-334 (2006).
- [26] D.C. Houghton, J. Appl. Phys. **70** 2136-2151 (1991). (see Figure 13).
- [27] X. Wang, G.L. Zhou, C. Sheng, and M.R. Yu, Mat. Tes. Soc. Symp. Proc. **220** 241-245 (1991).
- [28] The apparent critical thickness is calculated following [12] the thickness of the film, when the amplitude of the dominant Fourier mode becomes 5 times that of a kinetically roughened crystal of pure Si.