Hetroepitaxial Growth Using an Off-Lattice Kinetic Monte Carlo Model

Brian McGuigan, Anne Marie Tan, Jacob Gruber

May 7, 2013

Many of the modern semiconductor devices are fabricated through an epitaxially growth process such as molecular beam epitaxy (MBE) or chemical vapor deposition (CVD). When dissimilar materials are grown upon each other, the process is referred to as heteroepitaxial growth. It terms of electronic device performance, there can be many benefits of having dissimiliar junctions of materials. However, an inherent difficulty with heteroepitaxial growth processes is the lattice mismatch featured between the two substances which can be quantified by:

$$\epsilon_{mis} = \frac{a_f - a_s}{a_s} \tag{0.1}$$

where a_f and a_s are the lattice constants of the film and substrate respectively and ϵ_{mis} is the lattice mismatch strain. This strain can inevitably lead to the formation of quantum dot structures or defects such as dislocations, both of which can affect the electronic properties of the devices. There have been many on-lattice models to study the growth of such systems; however, lattice fixed atoms tend to have restricted motion. There is an inability to classify defects like dislocations since atoms are constrained to certain sites. In order to study the formation of such structures, we implement an off-lattice kinetic Monte Carlo model.

1 MODEL

For this project, our goal was to develop a simple model to simulate hetero-epitaxial growth, rather than to simulate any specific material systems. Therefore, we decided to just use a simple Lennard-Jones (L-J) pair potential to simulate the interactions between the different atoms. The L-J potential takes the following form:

$$U_{ij}(U_0,\sigma) = 4U_0\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{1.1}$$

where σ and U_0 are the L-J parameters and r_{ij} is the distance between atom i and j. The first term in the L-J potential equation represents the repulsive interaction between the atoms cores at close distances, while the second term represents the Van Der Waals attractive interaction. By changing the parameters σ and U_0, we can describe the interactions between different atom types in our model. The parameter sets (σ_s, U_s) and (σ_a, U_a) describe the interactions between two substrate or two adsorbate atoms, respectively. We approximated the interactions between atoms of different type with the parameters $U_{as} = \sqrt{U_s U_a}$ and and $\sigma_{as} = \frac{(\sigma_a+\sigma_s)}{2}$.
The L-J potential decays rapidly to close to zero at distances r > 3σ. Therefore, one can effectively ignore the interactions between atoms which are more than a distance of 3σ apart. In order to keep track of atoms within this interaction radius of any given atom, we have employed a "binning" method. Atoms are sorted in to "bins" of size 3σ, such that only interactions between atoms in the same bin and directly adjacent bins need to be considered when evaluating the forces or energies on any given atom. This enables us to carry out many steps in the simulation locally with ease and greatly reduces computation time. The bins are updated after every move.

Figure 1.1: Schematic of Binning/Cell Method

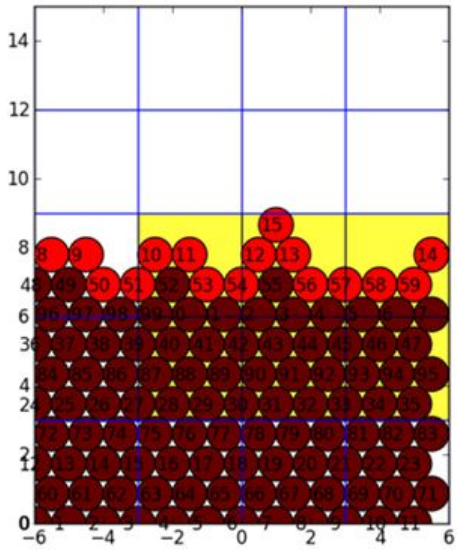


Figure 1.1 shows a schematic of the binning method for effective neighborhood listings. For example, to calculate the forces on atom 13, only those atoms within the yellow shaded bins are considered. In this project, we have considered only a 2-dimensional system, where atoms are deposited on a 1-dimensional surface. This

simplification makes the problem significantly more tractable, while still being able to capture many essential features of 3D hetero-epitaxial growth. We assume periodic boundary conditions in the lateral direction and fix the positions of the bottom layer of atoms.

2 N-Fold Kinetic Monte Carlo Method

In a Kinetic Monte Carlo (KMC) simulation, moves are carried out based on their relative rates. Here, we considered 2 basic types of moves: diffusion moves, and deposition moves. Each possible diffusion move has a different rate associated with it, calculated using the following formula:

$$R_{Diffusion} = \nu_0 \exp\left(-\frac{\Delta_E}{kt}\right) \tag{2.1}$$

where ν_0 is the attempt frequency, Δ_E is the energy barrier for the diffusion move, k is the Boltzmann constant, and T is the temperature. $\hat{I}_{i0}$ was set to a fixed value of 10^{12} m/s which corresponds to the typical vibrational frequency of an adatom, and the temperature T was set according to $kt = 0.03 => 460$K, based on a previous study. Meanwhile, the deposition rate is simply given by:

$$R_{Deposition} = \left(\frac{L_s}{a_s}\right) * (GrowthRate) \tag{2.2}$$

where L_s is the length of the substrate and the growth rate is in monolayers per second.All the rates corresponding to each possible move are put into a rate catalog, similar to that shown below. A random number is used to pick the move to be carried out; the likelihood of a particular move being chosen is proportional on its rate compared to the total rate of all possible processes. After the chosen move is executed, the time step is incremented and the rate catalog is updated. In order to maximize the efficiency of this updating step, we only recalculate the rates for those atoms which are within the interaction radius of the atom which underwent the move, as only these few rates would have been significantly altered by the move. Rates may be added or removed from the catalog at each step as appropriate. Figure 2.1 shows an example of how the rate catalog is structured.

3 Potential Energy Surface (PES) Scan

The fundamental difference between on-lattice and off-lattice KMC is that in the former, the atoms are constrained to occupy lattice positions; furthermore, the energy barriers between moving from one lattice site to another are fixed. In the off-lattice case, however, the atoms can in practice occupy any position along a continuum, and the energy at each position in a function of all other atoms in the system. In order to determine the energy barriers and final positions (local energy minima) of all possible diffusion moves, the following procedure is carried out.

Figure 2.1: Table Showing Structure of Rate Catalog

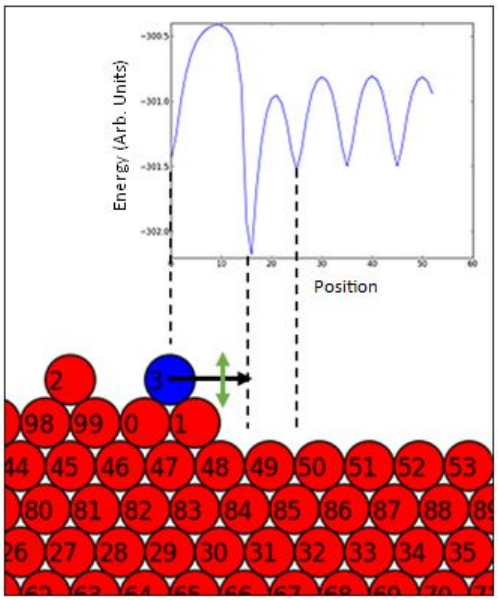
Event	Barrier Height ΔE	Final Position
Atom 1: Move Left	ΔE1	X1
Atom 1: Move Right	ΔE2	X2
Atom 2: Move: Left	ΔE3	X3
Atom 2: Move: Right	ΔE4	X4
.	.	
.	.	
.	.	
Deposition	-----	Xn

0

1

We first identify all atoms on the surface which are able to make a diffusion move, i.e. adatoms and atoms at step edges. For each of these atoms, we virtually move it along the x-direction (lateral direction) in small increments; at each fixed x-position, the total energy of the system is minimized with respect to this atoms position in the vertical direction. By doing so, the potential energy surface (PES) associated with the movement of this atom can be evaluated, from which the energy barrier as well as the final position of possible diffusion moves can then be determined. An example of this is shown in the Figure 3.1.
As the blue adatom is virtually moved to the right along the lateral direction, the total energy of the system is locally minimized with respect to the moving atoms vertical position. The resulting PES shows an increased energy barrier for moves down a step and a decreased energy barrier for attaching to a step from below, while away from the step edge, it is essentially periodic. Here our calculations are able to reproduce the well-know Erlich-Schwoebel barrier effect.
In our simulation, we consider that only single diffusion hops can take place. Therefore, for each virtual move, the PES need only be evaluated until the nearest local minimum in the given search direction is found. The position of this local minimum is taken to be the final position of the possible diffusion move, while the energy barrier is calculated by taking the difference between the maximum energy along the PES and the energy at the starting point of the move.
In evaluating the PES, we have employed the “frozen crystal approximation”. According to this approximation, all other atoms other than the atom making the virtual move are considered to be fixed in position, so that the energy has only to be minimized with respect to the moving atoms vertical coordinate and not the coor-

Figure 3.1: Potential Energy for Surface Atom at Different Positions

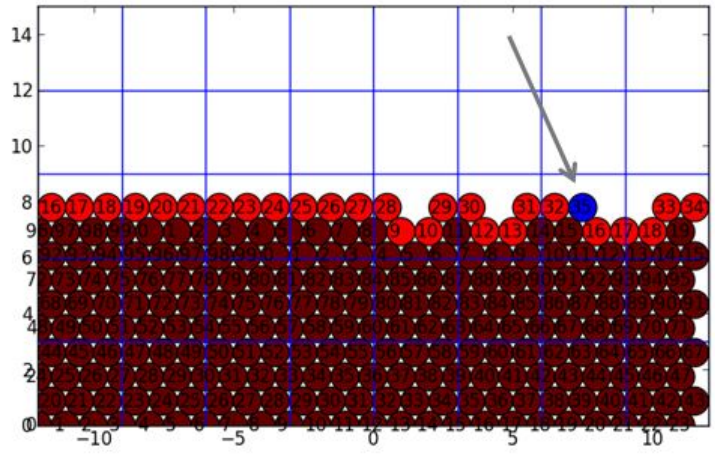


dinates of all atoms. This greatly simplifies the calculations and drastically reduces the computation time required. It has been reported in the literature [] that this approximation results in the overestimation of energy barriers by around 10 percent; however, as we are interested in the relative barrier heights and not the absolute barrier heights, this is an acceptable approximation.

4 Deposition Event

When a deposition event is randomly chosen from the rate table, the surface atoms of the system are identified. This is performed in an efficient matter where the surface bins are located first followed by classification of the topmost atoms. This method prevents the uncessary scanning of each atom embedded in the bulk substrate which helps reduce computation time. Upon classification of the surface atoms, a random atom is chosen as a deposition site where another atom is deposited half a lattice constant above and slightly left or right based on another random number. After placing this atom, a molecular statics calculation is performed locally to relax neighboring atoms into a minimum potential energy position. Figure 4.1 shows an example of the identified surface atoms in light red and a deposition atom in blue.

Figure 4.1: System With Highlighted Surface Atoms



5 Molecular Statics

After each deposition and surface move event, a molecular statics calculation is performed to move each atom to a local minimum energy. In this project, several techniques were enforced for this minimization of energy. The first technique used was the newton-raphson method which finds succesive better approximations to the roots or zeros of a function. This method ultimately equated to slow convergeance once the atoms reached their near equillibrium points and would oscillate heavily until final convergeance. The next attempted method was a slight variation of the newton-raphson method called the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method. This technique serves to imitate the newton-raphson method by approximating the hessian matrix of second derivatives used for finding the minimum. This Quasi-Newton provided a slight decrease in the computation time since the evaluation of the hessian matrix is not performed at each step but rather updated to a better approximate form. The conjugate gradient method for minimization was the method that provided the fastest computation time and did not send atoms into unrealistic positions when initialized too close. Rather than moving atoms along a direction of steepest decent, the conjugate gradient method attempts to move atoms along a path perpendicular to energy contours for fast convergence. The overall algorithm used is listed below and features a Polak-Ribiere formalism for determining the conjugate gradient direction.

5.1 Conjugate Gradient Algorithm for Molecular Statics

- Find force on each atom:$\Delta x_0 = -\bigtriangledown_x f(x_0)$
- Perform Initial Line Search: Determine α_0 for x and y direction of each atom such that $f(x_0 + \alpha \Delta x_0)$ is minimized

- Update Positions: $x_1 = x_0 + \alpha_0 \Delta x_0$
- Initialize Conjugate Direction: $s_0 = \Delta x_0$
    1. Determine the Steepest Direction: $\Delta x_n = -\bigtriangledown_x f(x_n)$
    2. Determine Conjugate Direction Step Size β_n According to Polak-Ribiere Formalism: $\beta_n = \frac{\Delta x_n^T(\Delta x_n - \Delta x_{n-1})}{\Delta x_{n-1}^T \Delta x_{n-1}}$
    3. Update the Conjugate Direction: $s_n = \Delta x_n + \beta_n s_{n-1}$
    4. Perform Line Search: Determine α_n for x and y direction of each atom such that $f(x_n + \alpha \Delta s_n)$ is minimized
    5. Update Positions: $x_{n+1} = x_n + \alpha_n s_n$
    6. Repeat 1-5 Until Forces on All Atoms are Sufficiently Small

6 Initial Problems With Slow Dynamics:Adaptive KMC

Upon implementing the above algorithm, the system would tend to hang on surface moves with a low Δ_E barrier between certain states. When the energy barrier between two states becomes too small, the rate for the corresponding move blows up. Consequently, the random number generator would choose this move continuously and the system would never evolve while oscillating between several shallow states. A simple fix to this is too keep track of repeated moves and rescale the corresponding rates upon each duplicated step. This was achieved by storing a table of all the moves that had been made and their relative frequency. When the rate for a previous move was calculated it was then scaled by

$$R_i' = R_i exp(-\kappa n) \tag{6.1}$$

where κ is a damping constant and n is the move frequency. Different values of κ changed the evolution of the system significantly. When κ was too large, the system did not sufficiently relax between successive depositions, and amorphous regions formed, even without strain. When κ was too small the system was not sufficiently damped and the vast majority of moves were oscillations between shallow states. Both these factors were minimized for $\kappa \approx 0.6$.

A more sophisticated way of reducing the frequency of shallow moves would be to combine shallow states into super basins, however, we did not have enough time to implement this.

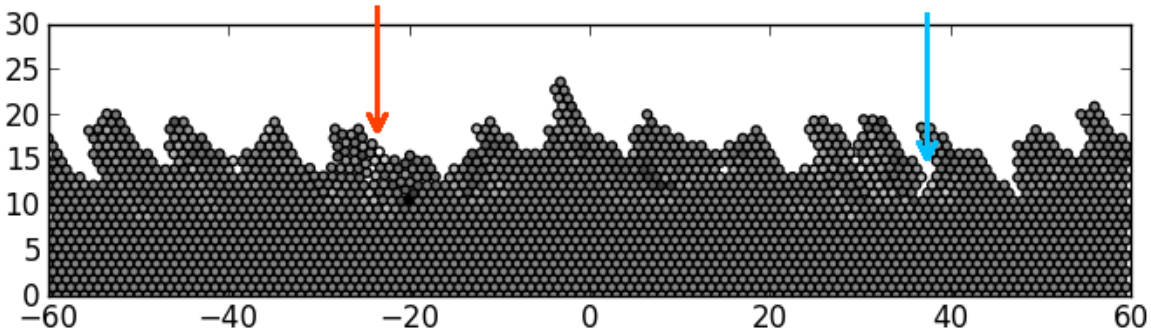
7 Results

Homoepitaxy was examined first in order to determine the quality of the simulated films without the added complication of strain (Fig. 7.1). The growth of a film of

moderate thickness was showin in this test, however the film did not fully relax beyond the fist few monolayers; small amorphous regions, vacancies and what looked like the beginning of dislocations were present. This implies that an insufficient number of diffusion steps took place between deposition steps to ensure epitaxy, resulting the equivalent of low temperature deposition. Unfortunately including a sufficient number of diffusion steps would require computing power beyond available resources.

Another effect that can be noticed in this simulation is the tendency of the film to form columnar structures angled to the left. This was noticed in almost all the simulations performed, and while the columnar structure is typical of low temperature deposition, the angle is likely due to bias. The cause of the bias within the code has not yet been determined.

Figure 7.1: Homoepitaxy Simuation after 3500 steps colored by local strain Farker atoms are under compression. Note the amorphous region (orange) and proto-dislocation (blue)

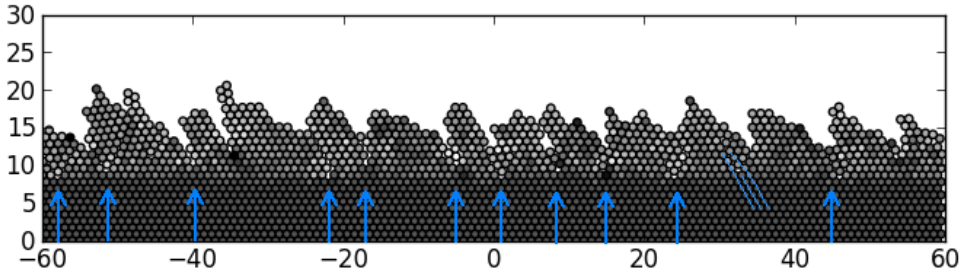


Simulations of heteroepitaxy were then performed in systems with lattice mismatches of $\epsilon = \pm 5\%$. These large mismatches were chosen so that we could see dislocation over a short length scale.
In the $\epsilon = 5\%$ system (Fig. 7.2), the formation of edge dislocations in which a row atoms is missing in the film is apparent. The dislocations present in sections of the film far from the surface were counted and a dislocation density of 0.1 dislocations per unit distance was calculated. This matches up well with theoretical calculations:

$$\rho_{edge} = \epsilon / b_x = 5\%/(a/2) = 0.1 \tag{7.1}$$

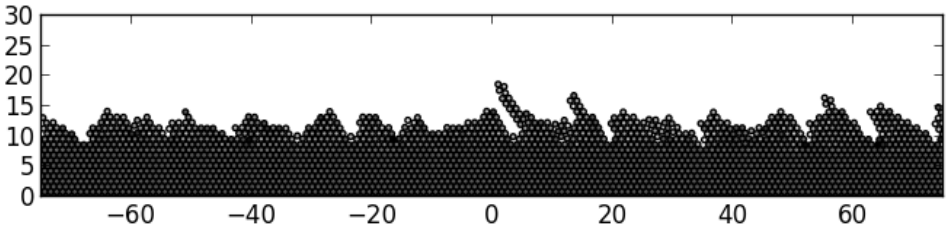
where ρ_{edge} is the linear dislocation density, b_x is the x component of the burger's vector and a is the lattice constant (here take to be unity). Despite the attractiveness of this result, more study is needed on this system, as there is some evidence of dislocation formation in progress near the surface of the film.
In the $\epsilon = -5\%$ system, no dislocation formation is apparent. This is due to the preferential growth in columnar structures, which for some reason is exacerbated for

Figure 7.2: 5% Lattice Mismatch System.



negative mismatch systems. This prevented the film from reaching the critical thickness required for dislocation formation. In order to solve this problem, the system needs to be simulated for a longer time at a higher effective temperature.

Figure 7.3: -5% Lattice Mismatch System.



8 Potential for Future Study

This method shows significant potential for the more detailed study of strained growth in films, but unfortunately the resources were not available to pursue all goals. By varying the effective deposition temperature (controlled by the temperature of the system and the adaptive damping rate), the effect of deposition rate on the formation of crystal structure could be investigated. Additionally, by simulating systems at higher temperature over longer time and length scales, the macroscopic formation of misfit dislocations could be studied.

By increasing the radius of the molecular dynamics relaxation step, the strain and stress field in the material could be studied. The movement of dislocations could also be studied by applying an external stress to the system (though this would both require immense computation time and a restructuring of the periodic boundary

conditions).

It was initially intended to study deposition of binary compounds, mimicking real systems such as SiGe on Si. This would require careful consideration of deposition rates, but preliminary results showed that this method can successfully model these films.
The ultimate goal for this project is too be able to extend this system to three dimensional systems and more complex potentials, allowing the first principles modeling of practical deposition processes. There are significant challenges in the optimizations and calculations required for this scope, however if those demands can be met this simulation method should be able to sucessful be applied to these situations.

9 CONCLUSION

There are many different combinations of growth parameters that can be used in this off-lattice KMC model. The growth rate, lattice constants, temperatures, and substrate lengths can be varied to give different, interesting results. This model is limited in the sense that it is two dimensional and, therefore, difficult to formally classify dislocations such as stacking faults. The Lennard Jones potentials used are also limited in the respect that they do not take into account anisotropic effects. However limited these factors may be, the model still serves to show the general method and versatility of the off-lattice algorithm. It can easily be extended to three dimensional cases with more complex potentials.