Anisotropic corner crossing barriers in nanorod growth

D N McCarthy ¹,², S A Brown* ¹,²

¹ MacDiarmid Institute of Advanced Materials and Nanotechnology
² Department of Physics and Astronomy, University of Canterbury, Christchurch, New Zealand
* simon.brown@canterbury.ac.nz

Abstract. The growth of quasi 1-dimensional bismuth rods from graphite step edges is modeled using kinetic Monte Carlo simulations. An anisotropic growth model is developed and tested against experimentally observed behaviour. The model incorporates adatom deposition, diffusion, and irreversible attachment of material to the aggregate. It is found that the best agreement between experiments and simulations occurs when anisotropic corner crossing barriers are introduced to the model.

1. Introduction
The growth of kinetically limited structures forms an interesting topic within the field of thin film deposition. Complex, non-equilibrium morphologies can develop due to imbalances within the growth environment. In general [1,2,3] these shapes are due to the interference of two or more processes, such as aggregation and diffusion. Understanding the evolution in aggregate morphology as a function of growth conditions can lead to better control of the growth and of the resulting structures.

Recently it has been reported [4] that the growth kinetics of bismuth nanorods on graphite surfaces depends on material flux. Anisotropic systems have been investigated previously using kinetic Monte Carlo (KMC) simulations, and a number of models have been proposed to describe chain-like growths on fcc-(110) surfaces [5,6,7]. The objective of this paper is to use KMC simulations to model the growth of Bi rods on graphite, and to explore the influence on rod growth of both anisotropic diffusion along rod facets and anisotropic corner crossing.

Example experimental results for the growth of bismuth nanorods on graphite are shown in Fig 1. These rods are very flat (heights ~ 1nm) with the Bi\{01-12\} plane parallel to the surface, and the Bi <11-20> direction of the rods is found to be parallel to the direction of growth [4]. The rods are typically aligned perpendicular to the graphite step edge. In this low flux example the rods have large aspect ratios. At higher fluxes the rods have much smaller aspect ratios. Experiments also show rods from neighboring step-edges growing into one another, indicating the transport of material from the long edges of the rods onto the rod tips. The suggestion given in [4] is that the growth is driven by the anisotropic rates of diffusion along the facets, due to the strong bonding at the end of the zig-zag chain shown in Fig 1. At low flux the equilibrium shape is an elongated structure, since material has ample time to be transported from the long facet to the short facet. In the high flux environment the arrival of new material occurs on similar time scales to the growth, causing the formation of relatively isotropic structures.

To better understand this growth, simulations were developed to test the proposed model, and to make comparisons with the experimentally observed behavior. The growth of elongated rods
Fig. 1 SEM image of bismuth rods growing perpendicularly from the graphite steps, flux=0.03Å/s, T=320K. The crystal orientation is depicted, showing the unsatisfied covalent bonds of the short facet.

from the step edges of graphite is modelled as a function of energy barrier, flux, and coverage. The aspect ratio of these rods is analysed.

2. The Model
Due to the complexity of the experimental system (rhombohedral Bi with &lt;11-20&gt; growth direction on a hexagonal graphite lattice) some simplifications were necessary to enable efficient coding. The chief approximations used are that both the bismuth and graphite crystals are modeled with a cubic lattice and any detachment/desorption processes are neglected. Attachment to an aggregate is therefore irreversible, and the growth of the aggregate is dictated by the efficiency with which this material can be transported around the aggregate edges. The KMC simulations were run using an adapted Bortz, Kalos and Lebowitz (BKL) [8] type algorithm. Event lists are compiled at the beginning of the simulation, and adjusted throughout. The events correspond to important growth processes, and a schematic of these processes is shown in Fig 2. The events are all activated jumps occurring at rates equal to \( h = \nu e^{-V/kT} \) where \( V \) is an energy barrier in electron volts, and \( \nu \) is the hopping attempt frequency, chosen to be the phonon frequency of \( 10^{13} \text{ s}^{-1} \). On bare areas of the terrace, atoms hop between adjacent nearest neighbour sites according to an activation barrier \( V_t \). Atoms incident on the step edge at the bottom of the image diffuse with a barrier \( V_s \). Once attached to an aggregate, the particles can move along edges with energy barriers \( V_e \), and around corners via \( V_c \). Corner crossing events are treated as direct exchanges between next nearest neighbour sites.

The simulations are performed on a 300 by 600 lattice, with periodic boundary conditions on the long edges, reflecting conditions on the top edge of Fig 2(b), and a terrace step on the bottom edge. The elongated lattice is used to reproduce the anisotropic diffusion field present in the experiments. Deposition onto the bare terrace occurs randomly with a flux \( F \), and for surface diffusion the atoms move randomly between nearest-neighbour sites. Parameters such as flux and temperature \( (T=300K) \) are chosen to be equivalent to those in the experiments [4]. To model the crystal growth a distinction between the two facets is made (labeled A and B in Fig 2(b)), so that diffusion barriers and bonding characteristics along the respective sides can be modified independently.

To standardize the nucleation process so that the growth can be studied as a function of flux and diffusion, without any competition between neighbouring rods, a small aggregate is initially fixed at the middle of the step edge. With the selection of a small diffusion barrier along the step \( (V_s) \), particles incident on the step are quickly transported to the defect, preventing the nucleation of extra islands and encouraging growth from the seed.
3. Results

We now describe the simulation results found for different combinations of energy barriers and parameters. Flux ranges from 0.001→ 0.2Å/s, and coverages up to 0.2ML.

We begin by demonstrating that the elongated aggregates of Fig. 1 cannot result solely from an anisotropically shaped diffusion field coupled with anisotropic edge diffusion barriers ($V^A_e=0.25-0.5\text{eV}$, $V^B_e=0.45-0.7\text{eV}$). Simulations were performed for a range of fluxes (0.001Å/s-0.2Å/s), and no corner crossing events were allowed ($V_c=1\text{eV}$). The resulting aggregates (not shown here), have large bases with multiple extensions, and do not exhibit the clean, single rod growth seen experimentally in Fig. 1. The isotropic structures observed experimentally at higher fluxes also cannot be reproduced. This result makes it apparent that material transport between the facets is an important process in the growth.

Next we use the model proposed by Scott et al [4], which allows the transport of material between the facets, while maintaining anisotropic edge diffusion barriers. This second scenario uses a coding method developed by Zhong et al [3] for growing compact structures on fcc (001) surfaces. The diffusion path around aggregate corners is opened up by reducing the corner crossing barrier $V_c$ to a level comparable with $V_e$, allowing material to be transported between the facets. Selecting energy barriers such that $V^A_e < V^B_e$ (typically $V^A_e=0.3\text{eV}$, $V^B_e=0.4\text{eV}$), we vary the corner crossing barrier $V_c$ through values less than $V^A_e$ to values larger than $V^B_e$. Representative results from this model are shown in Fig 3 (b) (filled circles, we have chosen $V^A_e=0.3\text{eV}$, $V^B_e= V_c=0.4\text{eV}$) where the aspect ratio never exceeds 1. Unexpectedly, no combination of these parameters produces the elongated structures of Fig 1, suggesting that the simple model proposed in [4] cannot in fact explain the experimental data.

In the next series of simulations we allowed anisotropic corner crossing barriers, i.e. $V^B_c=0.45\text{eV} > V^A_c=0.35\text{eV}$, while keeping the anisotropic edge diffusion barriers as $V^A_e=0.3\text{eV}$, $V^B_e= 0.4\text{eV}$. Figures 2(b) and 2(c) show results using this combination of energy barriers for different fluxes. If the bonding strengths of the A and B facets are different, then it can be expected that an atom traveling from the A facet to the B facet will diffuse at different rates to the inverse (B to A) process. This type of argument follows a line of reasoning used by Li et al [5] to describe the anisotropic aggregates grown on the fcc-(110) surface. The importance of anisotropic corner crossing barriers however was postulated as early as 1966 by Schwoebel [9], and more recently for the fcc-(111) surface by Brune et al [10]. Figure 3 (a) compares the coverage dependence in the model with results taken experimentally, for fluxes of 0.005Å/s and 0.2Å/s. Fig
Fig. 3 (a) Aspect ratios (AR) as a function of material flux for the basic corner crossing model (filled circles) and anisotropic corner crossing model (filled triangles) and experimental results (open triangles) 0.6ML. The filled squares are from the anisotropic corner crossing model now with $V_{B\rightarrow A}^{c}=0.5eV$ (b) AR as a function of surface coverage for the anisotropic corner crossing model (filled circles) and the experimental results (open circles) for $F=0.005Å/s$, filled squares (model) and open squares (expt) for $F=0.2Å/s$

3 (b) compares the flux dependence of the model with the experiment, as $F$ is increased over two orders of magnitude. Figures 3(a) and 3(b) show that anisotropic corner crossing can indeed generate anisotropic growth. The rods remain compact for high coverages and high fluxes, but larger aspect ratios are apparent for low flux, as was observed for the experiments [4].

4. Conclusion
Using KMC simulations we have shown for a model system that anisotropic edge diffusion and isotropic corner crossing cannot produce the anisotropic structures observed experimentally in Ref [4] for Bi on graphite. The aspect ratios of aggregates grown using this model never exceed 1. Instead, it is found the introduction of anisotropic corner crossing barriers is required in order to produce elongated aggregates, which exhibit similar trends with flux and coverage as the experimentally grown rods. The anisotropy in the experimental system is due to different bonding strengths along the two facets, as from the crystallographic data it is apparent that the short ends of the rods contain unsatisfied bonds, to which new adatoms are expected to form strong bonds.

Clearly the simple simulations presented here can be improved upon by adding detailed features of the epitaxial system (e.g. crystallography). However, the simulations capture the essential features of the system and demonstrate the key processes leading to the observed anisotropic growth.

References
Acknowledgements: Milo Kral and George Spanos for helpful discussions.
[1] Michely, T Phys. Rev. Letters 70, 3943 (1993)
[2] Witten, T. A. and Sander, L.M. Phys Rev B 27, 5685 (1983)
[3] Zhong, J. et al, Phys. Rev B 63, 113403 (2001)
[4] Scott, S. A. et al, Phys. Rev B 72, 205423 (2005)
[5] Yinggang Li et al, Phys. Rev B 56, 12539 (1997)
[6] Mottet, C. et al, Surf. Sci. 417, 220-237 (1998)
[7] Heyn, Ch. Phys. Rev B 63, 033403 (2001)
[8] Bortz, A. B. et al, J. Comput. Phys. 17, 10 (1975)
[9] Schwobbel, R. and Shipsey, E. J. Appl. Phys. 37, 3682 (1966)
[10] Brune, H, Surf. Sci. 349, L115 (1996)