Kinetic Monte Carlo Simulation of the Growth of Various Nanostructures through Atomic and Cluster Deposition: Application to Gold Nanostructure Growth on Graphite

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Abstract. A Kinetic Monte Carlo (KMC) method is presented to describe the growth of metallic nanostructures through atomic and cluster deposition in the mono–and multilayer regime. The model makes provision for homo- and heteroepitaxial systems with small lattice mismatch. The accuracy of the model is tested with simulations of the growth of gold nanostructures on HOPG and comparisons are made with existing experimental data.

1. Introduction

A vast amount of research has been conducted over the past few decades in the study of nanostructure growth processes [1]. Recently, this research area has intensified due to the development of new modeling methods, as well as the relevance of nanostructures as building blocks in self-assembled layers. Numerous methods have thus far been developed to simulate growth at various time scales. Depending on the size of the system studied, these methods are typically classified as microscopic, mesoscopic or macroscopic. In particular, nanostructure growth falls in the mesoscopic regime in which case Kinetic Monte Carlo can be employed. The advantage of KMC lies in the fact that it treats time evolution of the system in a discreet fashion and can provide information on the morphology of grown nanostructures, unlike macroscopic approaches. KMC is however not a standalone method and relies on results generated from microscopic methods like electronic and molecular dynamics (MD) to supply activation energies. These activation energies are the key ingredients in the calculation of the transition rates that ultimately determine the growth process.

Several variants of the originally proposed KMC scheme have developed since its formulation in the 1980’s [2]. These include specific event [3], bond-counting [4] and complete table KMC [5]. Specific event KMC prohibits certain events allowing for fast system evolution but is also prone to inaccuracy in the case of a relevant neglected event. In bond-counting KMC only nearest neighbours are considered, whether in the initial or final state, and the activation energy for an event to occur is ignored. The most accurate of the above algorithms is complete table KMC in which all possible events are catalogued in a table and the rate of each event is explicitly calculated. Due to the large amount of rates that needs to be calculated in complete table KMC, it is also the most difficult and time-consuming algorithm to implement.

In this paper, a combination of bond-counting and complete table KMC is used to simulate the growth of gold nanostructures on a graphite substrate through physical vapour deposition in the sub-
monolayer and multilayer regime. Although discussed in terms of the gold-graphite system, the model is applicable to other systems as well. The extension of this model to treat cluster deposition is also briefly addressed and some preliminary results on the cluster deposition are presented.

2. Kinetic Monte Carlo Method
The Kinetic Monte Carlo method discussed in this paper was initially developed to simulate the growth of gold nanostructures on a graphite substrate by means of atomic deposition. For a given surface configuration, a list of all the events and their respective rates are created. In the case of atomic deposition, five specific events are identified which are (i) deposition, (ii) diffusion on terraces, (iii) evaporation, (iv) diffusion along island edges (step diffusion) and (v) jumps up and down islands (Schwoebel jumps). An event is chosen with a probability proportional to its rate, or a new atom is deposited if the inverse of this rate is greater than the arrival time between two atoms, \( \tau = 1/A F \), with \( A \) the area of the substrate and \( F \) the deposition rate in ML/s. The rates of these events are given by \[ v^j = v_0 e^{-\Delta E_j/2k_B T}, \] with \( v_0 = 2k_B T / h \) the attempt rate, \( k_B \) Boltzmann’s constant, \( T \) the substrate temperature and \( h \) Planck’s constant. The term \( \Delta E_j \) is given by

\[
\Delta E = E' - E + \Delta E^j,
\]

with \( E' \) and \( E \) the total energy of a jumping atom in its initial and final state respectively and \( \Delta E^j \) the activation energy needed for such a jump. In the case of cluster deposition, the type of events that can occur is reduced to (i) – (iii). In this model however, clusters are treated as separate entities except when contact with other clusters or existing islands occur. Should this be the case, the movement of individual atoms in the clusters are considered and events (i) – (v) are included. The activation energies needed for event (i) – (v) to occur are summarized in table 1.

| Event                                      | Energy Barrier (eV) |
|--------------------------------------------|---------------------|
| Terrace Diffusion (Au on Graphite)         | 0.0197              |
| Terrace Diffusion (Au on Au(111))          | 0.124               |
| Step Diffusion (Au on Graphite)            | 0.191               |
| Step Diffusion (Au on Au(111) A-step)      | 0.34                |
| Step Diffusion (Au on Au(111) B-step)      | 0.22                |
| Schoewbel Jumps                            | 0.45                |
| Cluster Diffusion (13 atom Iscosahedral)   | 0.2                 |

3. Simulation Details
The simulations were performed on a triangular lattice representing either the graphite substrate or the gold islands grown on top of the graphite. The Sutton-Chen [7] and a modified Lennard Jones [8] potential were used to describe the interaction between the gold-gold and gold-graphite atoms respectively. In the case of atomic deposition, roughly 0.2 ML gold was deposited on a 1000 Å x
1000Å substrate at various deposition rates and substrate temperatures. For cluster deposition, the substrate size was decreased to 200 Å x 200 Å.

4. Results and Discussion

The discussion commences with the monolayer atomic deposition results. From figure 1 it is evident that a decrease in the deposition rate causes a decrease in the density of the islands. This observation is consistent with nucleation theory. Furthermore, an increase in the substrate temperature also leads to a decrease in the island density as well as a transition from fractal to compact island growth. At high enough temperatures and low enough deposition rates, the islands assume the morphology of the substrate.

For multilayer deposition, the same observations are made in terms of island density and deposition rate. However, at high enough temperatures and low enough deposition rates, the islands do not assume only a hexagonal morphologies representative of the substrate, but also triangular and small octahedral particles. For the higher deposition rates, the island morphologies are similar to the monolayer deposition, mainly because the atoms do not have enough time to jump up the islands. Occasionally a deposited atom can however land on top of an existing island. These results are in agreement with experimental work [9, 10], however the fractal islands obtained through experiments appear more directional.

| Temperature | R=1 ML/s | R=0.1 ML/s | R=0.01 ML/s |
|-------------|----------|------------|-------------|
| T=100K      | ![Image](a) | ![Image](b) | ![Image](c) |
| T=300K      | ![Image](d) | ![Image](e) | ![Image](f) |
| T=500K      | ![Image](g) | ![Image](h) | ![Image](i) |
| T=700K      | ![Image](j) | ![Image](k) | ![Image](l) |

Figure 1. Monolayer deposited gold on graphite. The deposition rates and temperatures varied as indicated. The total coverage after deposition was 0.2 ML.
For the cluster deposition, at a given substrate temperature, the islands coalesce completely at deposition rates lower than 1 ML/s. It also follows that lower deposition rates yield the equilibrium shape, as expected. This confirms the ability of the model to treat cluster deposition.

**Figure 2.** Multilayer deposited gold on graphite. The deposition rates and temperatures varied as indicated. The total coverage after deposition was 0.2 ML.

| T=100K | R=1 ML/s | R=0.1 ML/s | R=0.01 ML/s |
|--------|----------|------------|-------------|
| (a)    | (b)      | (c)        |
| T=300K | (d)      | (e)        | (f)         |
| T=500K | (g)      | (h)        | (i)         |
| T=700K | (j)      | (k)        | (l)         |

**Figure 3.** Illustration of how cluster coalescence depends on the deposition rate. The temperature was 600 K and the deposition rate was (a) 10 ML/s, (b) 1 ML/s, (c) 0.1 ML/s and (d) 0.01 ML/s.
5. Conclusions
A Kinetic Monte Carlo method capable of simulating nanostructure growth through atomic deposition in the mono- and multilayer regime was presented. The ability to adapt this model to make provision for cluster deposition was illustrated. The results obtained agree well with experiment and nucleation theory.

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