



Time-dependent Monte Carlo studies of Surface Diffusion  
by Ann Marie Bowler

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:

The fabrication of microelectronic devices is of universal interest. However, relatively little is known about the competing microscopic surface reactions involved in these thin layer growth processes. The microscopic details of the growth processes cannot be deduced from current experimental techniques because the measurements require time scales which are longer by orders of magnitude than the microscopic reaction time scales. Because many interesting and useful semiconductor devices are thermodynamically unstable, optimization of the governing kinetic parameters is desirable. We examine surface diffusion and ordering in our efforts to understand the epitaxial growth of semiconductor devices.

We examine diffusion using numerical algorithms which incorporate a kinetic treatment in conjunction with a time-dependent Monte Carlo formalism. Our method is based upon a probabilistic description of adparticle jump events. The diffusion rate is determined by the energetics of adparticle interactions on the lattice. The rare event problem associated with other theoretical techniques is overcome by our highly efficient algorithms. Consequently, we are able to observe events, including ordering and island formation, which occur on time scales which are longer by orders of magnitude than those for simple adsorbate diffusion.

We have developed algorithms to examine surface defects, steps, adparticle interactions, concentrations, etc. Our approach is readily applied to a wide range of substrate/overlayer systems. We conclude that the experimental techniques currently employed to examine diffusion are fundamentally flawed in that they fail to deduce anything about the microscopic diffusion mechanisms. Furthermore, the relatively simple picture of diffusion on which experimental analyses are based are grossly inappropriate in many situations. Even small concentrations of surface defects radically alter diffusion rates and mechanisms.

Our most recent studies have been of the III-V semiconductor (110) surfaces. We have coupled our time-dependent Monte Carlo algorithm to a simple kinematic model for LEED profiles and find that the results of our TDMC analyses are in close agreement with projections based on the macroscopic experimental behavior of these systems. We can now begin more in depth efforts to simultaneously describe the predominant competing surface reactions in epitaxial growth processes.

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Doctor of Philosophy  
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Chemistry

MONTANA STATE UNIVERSITY  
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## ABSTRACT

The fabrication of microelectronic devices is of universal interest. However, relatively little is known about the competing microscopic surface reactions involved in these thin layer growth processes. The microscopic details of the growth processes cannot be deduced from current experimental techniques because the measurements require time scales which are longer by orders of magnitude than the microscopic reaction time scales. Because many interesting and useful semiconductor devices are thermodynamically unstable, optimization of the governing kinetic parameters is desirable. We examine surface diffusion and ordering in our efforts to understand the epitaxial growth of semiconductor devices.

We examine diffusion using numerical algorithms which incorporate a kinetic treatment in conjunction with a time-dependent Monte Carlo formalism. Our method is based upon a probabilistic description of adparticle jump events. The diffusion rate is determined by the energetics of adparticle interactions on the lattice. The rare event problem associated with other theoretical techniques is overcome by our highly efficient algorithms. Consequently, we are able to observe events, including ordering and island formation, which occur on time scales which are longer by orders of magnitude than those for simple adsorbate diffusion.

We have developed algorithms to examine surface defects, steps, adparticle interactions, concentrations, etc. Our approach is readily applied to a wide range of substrate/overlayer systems. We conclude that the experimental techniques currently employed to examine diffusion are fundamentally flawed in that they fail to deduce anything about the microscopic diffusion mechanisms. Furthermore, the relatively simple picture of diffusion on which experimental analyses are based are grossly inappropriate in many situations. Even small concentrations of surface defects radically alter diffusion rates and mechanisms.

Our most recent studies have been of the III-V semiconductor (110) surfaces. We have coupled our time-dependent Monte Carlo algorithm to a simple kinematic model for LEED profiles and find that the results of our TDMC analyses are in close agreement with projections based on the macroscopic experimental behavior of these systems. We can now begin more in depth efforts to simultaneously describe the predominant competing surface reactions in epitaxial growth processes.

## INTRODUCTION

Historically, investigations of surface diffusion have played a fundamental role in the understanding of a number of significant phenomena including the catalysis, crystallization, and annealing processes. A number of excellent reviews on the topic of surface diffusion are available.<sup>1-8</sup> Surface diffusion may, in many situations, dictate the natural time scale for the interaction between chemical reactants and, thus, control reaction rates.<sup>1</sup> The first significant evidence for the existence of lateral interactions between adsorbed species came with the observation of adsorbate ordering on single crystal metal surfaces.<sup>2</sup> Such ordering in the adsorbed layer may have a profound influence on adsorption and desorption kinetics.<sup>2</sup> Furthermore, the preference for specific adsorption sites illustrates that adsorbate migration is an activated process. Therefore, an examination of adparticle migration can provide information about the topography of the potential energy contours of a surface.<sup>2</sup> More recently, surface diffusion has been probed in an effort to gain a fundamental understanding of processes such as molecular beam epitaxial growth. This process plays a crucial role in the fabrication of semiconductor devices; but relatively

little is known about the microscopic details of the problem.<sup>1</sup>

A variety of experimental techniques have been, and still are, used to examine surface diffusion. Among these are field emission microscopy (FEM),<sup>1,3,5,9-11</sup> field ionization microscopy (FIM),<sup>1, 5, 12-16</sup> laser induced thermal desorption (LITD),<sup>17-34</sup> low energy electron diffraction (LEED),<sup>33-34</sup> and, most recently, scanning tunneling microscopy (STM).<sup>35-43</sup> The primary experimental objective is to determine the Fick's Law diffusion coefficient for the system under investigation. This is generally done by introducing a sharp, initial concentration gradient of adsorbed gas on the substrate and subsequently monitoring the time evolution of the system. The diffusion coefficient is then obtained from an acceptable solution to Fick's second law:<sup>1</sup>

$$\frac{dc}{dt} = \frac{d}{dx} \left( -D \frac{dc}{dx} \right) \quad (1)$$

Field emission microscopy<sup>1,3,5,9-11</sup> and field ionization microscopy<sup>1,5,12-16</sup> are powerful methods for examining the motion of individual atoms or atomic clusters on a surface. However, these methods provide little, if any, information about ordering in a diffusion system.<sup>68</sup> Similarly, low energy electron diffraction (LEED) can provide much information about whether or not an adsorbate is ordered,<sup>33,34</sup>

but little information about the actual kinetics of the ordering phenomena can be ascertained. In order to obtain information about the kinetics of adsorbate ordering using LEED techniques, the sample must be repeatedly heated and cooled in rapid succession. The time scale for such a heating cycle is much longer than the time scale for diffusive motion and ordering.<sup>76</sup> Consequently, much information about the diffusion process is lost.

One of the more common recent probes of surface diffusion is the laser induced thermal desorption method (LITD) where an adsorbate is deposited on a substrate. A laser beam is used to rapidly desorb the adparticles from a region of the surface which has a simple, well defined geometric shape. This creates a sharp concentration gradient; and particles begin to migrate into the vacated region. After a predetermined time period, the same region of the lattice is heated once again with the laser beam. The adsorbate is desorbed once again. The amount of adsorbate which has diffused into the region of interest can be determined; and a diffusion coefficient for the process can be calculated.

Although the LITD method is currently extensively used to measure diffusion rates, it is also limited in that no specific information about lateral interactions or individual particle motion can be obtained.<sup>75</sup> Laser induced thermal desorption measures the combined effects of

adparticle interactions, surface steps, surface traps, and other lattice defects. Therefore, no direct, quantitative information about lateral interactions can be deduced. In fact, surface defects which significantly alter diffusion phenomena can be introduced by the repeated laser heating of the surface.

Scanning tunneling microscopy (STM) provides precise information about individual particle positions; but, once again, no information about the kinetics of ordering can be obtained from this approach due to the relatively long experimental time scale involved. We can, however, use our diffusion model to extract information about the microscopic details of the process which leads to the configuration of adparticles observed by STM experiments.

Theoretical diffusion studies employ a wide variety of techniques. These range from thermodynamic descriptions,<sup>1,67</sup> to molecular dynamics simulations<sup>44-55</sup> to transition state theory<sup>4,56-65</sup> to Monte Carlo methods.<sup>66-75</sup> Some characteristic limitations of these theoretical models are included here for purposes of comparison.

Many authors have attempted to describe surface diffusion using various thermodynamic approaches.<sup>1</sup> This is true of the Metropolis Monte Carlo method where only the energy differences between the initial and final states are considered in the description of adparticle hopping.<sup>67</sup> Such treatments ignore the fact that surface migration is an

activated process. Although the method has been somewhat successful, the true picture of the thermally activated diffusion process can hardly be assessed from such a perspective. Other thermodynamic approaches assume that diffusion (flux) occurs in response to a gradient in the chemical potential, rather than to the concentration gradient specified in Fick's first law:<sup>1,72</sup>

$$J = -D \frac{dc}{dx} \quad (2)$$

Other authors have used molecular dynamics techniques utilizing classical equations of adparticle motion with appropriate interatomic potentials.<sup>44-55</sup> This analysis, in essence, reduces to the calculation of the velocity autocorrelation function from which the diffusion constant can be ascertained. These methods have also been somewhat successful; but some major limitations are inherent. More specifically, the application of these methods is restricted to systems of only a few particles. Much computation time is spent "watching" events that never materialize into adparticle hops. This computational obstacle is known as the "rare event" problem; and it is present in a similar form in other time-dependent Monte Carlo (TDMC) techniques where much computation time is spent addressing particles which don't move during the time interval of the current

computational step.<sup>66-68</sup>

All of these methods are also fundamentally limited by the inability to provide information about adsorbate ordering or island formation. Only very small model systems have been described using these methods. Consequently, much of the predominant physics of diffusing systems has entirely evaded analysis. We have developed a unique time-dependent Monte Carlo (TDMC) approach which enables us to examine both the adatom migration and ordering processes.

Many of the difficulties inherent in the methods described above are resolved by our approach. Most importantly, the "rare event" problem has been overcome; and processes that occur over much longer time scales than diffusion, specifically overlayer ordering and growth phenomena, can be described in microscopic detail. We are also able to study systems of thousands of interacting particles. Therefore, we are able to study one of the largest theoretical model systems to date. We are able to observe both the diffusion and ordering processes. In addition, we are able to deduce the microscopic diffusion mechanisms in systems with a variety of adparticle interactions.

Our investigations begin with diffusion on perfect surfaces. Although the results for perfect surfaces are quite valuable, they describe only the most simple model for surface diffusion. In reality, the best surfaces used in

experimental studies of diffusion contain a significant amount of steps and other defects. We have extended our TDMC method to more complicated systems which include surface steps and traps or poisons.

Specific geometries for the desorption area in laser induced thermal desorption experiments are selected because the mathematical solutions to the diffusion equations are known; and a diffusion coefficient can be readily calculated. Typically, the mathematical solutions possess radial symmetry. We will demonstrate that such an analysis is inappropriate for systems with surface steps even at relatively low step concentrations.

We also examine systems of particles diffusing in the presence of a minority of traps, or entities which are strongly bound to the surface and have a significant affinity for the diffusing particles. Impurities or poisons such as these have a large influence on diffusion rates and ordering phenomena in the systems we examine.

We also have the ability to monitor the diffusion behavior of two distinct adparticle types at comparable concentrations. Studies of coadsorbate systems such as these can provide considerable insight into catalysis and chemical reactions between heterogeneous adsorbed species on a solid substrate. In addition, we examine the diffusion/recombinatory desorption process which is involved in these and many other chemical processes.

At an even greater level of complexity, we have extended our approach to examine diffusion in more complicated systems such as the (110) surfaces of the III-V semiconductors. We have developed algorithms which examine the ordering of bismuth on the GaAs and InSb (110) surfaces. The ordering and growth mechanisms in these metal/semiconductor systems are of great importance in the fabrication of microelectronics.

The primary goal of molecular beam epitaxy is to prepare a wide variety of non-equilibrium surface morphologies. This indicates that, under a wide range of epitaxial conditions, the growth of the III-V semiconductor surfaces is kinetically, rather than thermodynamically controlled. Epitaxial growth of these surfaces is controlled by fundamental chemical processes (i.e. physical adsorption, migration, dissociative chemisorption, incorporation, and desorption.) There is no comprehensive understanding of these competing microscopic processes. The details of the growth process can only be ascertained from a microscopic, theoretical analysis such as the one we have developed.

Although we only begin the process here, our goal is to understand the growth processes for the III-V semiconductor surfaces and their associated mechanisms. We will explore the relationships between adparticle interactions, reactant concentration, and gas and surface temperature. We wish, also, to determine the relationships between the growth

mechanism and the kinetic parameters.

Using the time-dependent Monte Carlo method developed here, we can begin to examine the mechanisms of crystal growth phenomena and ultimately make theoretical predictions that will allow us to optimize the growth and ordering processes.

The first step in our analysis of metals on III-V semiconductor surfaces is to extract information from the experimental LEED profiles for metals adsorbed onto these substrates. Both the position and width of the LEED profiles provide information about overlayer growth and ordering. We examine experimental LEED profiles for Bi on GaAs (110) and InSb (110). These data provide one link between experiment and theory. We have utilized an algorithm which incorporates the most simple model of LEED diffraction. Thus, we are able to compute LEED spectra for the overlayer structures produced in our TDMC analysis and use this information to understand the overlayer ordering phenomena.

The simple TDMC method described here is applicable to multitudes of diffusion systems. We are able to describe the effects of surface imperfections, adparticle interactions, concentration, temperature, kinetics, and energetics. Thus, we assert that the TDMC models described below are superior in many respects to previous theoretical techniques.

**TIME-DEPENDENT MONTE CARLO STUDIES OF PERFECT SURFACES**Time-Dependent Monte Carlo Method for Perfect Surfaces

Our analysis begins with adparticles bound to a four-fold symmetric lattice. Our initial choice of substrate surface geometry is arbitrary. Our TDMC method has also been applied to more complex surface geometries with equal ease. A predetermined number of particles can be deposited either randomly or in a prescribed initial configuration on the surface. The binding energy of each adsorbed species to the surface is influenced by both the number and magnitude of its nearest and next-nearest neighbor interactions. Thus, the presence of adparticle interactions becomes of paramount importance in surface diffusion kinetics. The interactions, which are assumed to be pairwise additive, can either be attractive or repulsive. Therefore, the binding energy of a particular adatom may be higher or lower than the binding energy of an isolated adatom to the surface. Equation 3 gives the binding energy of a typical particle to the surface.

$$E_{ij} = E_b^0 - i \cdot E_{nn} - j \cdot E_{nnn} \quad (3)$$

Indices  $i$  and  $j$  are the number of nearest and next-nearest neighbor adparticles, and  $E_{nn}$  and  $E_{nnn}$  are the nearest and next-nearest neighbor interaction energies, respectively. The binding energy of an isolated adatom to the substrate is given by  $E_b^0$ .

In our lattice gas model, migration is allowed only to vacant nearest neighbor sites. An activation barrier to migration must be overcome to accomplish each particle hop. The assumption that particles diffuse by single lattice unit nearest neighbor jumps has been verified experimentally.<sup>5</sup> In addition, recent work by Cohen and Voter<sup>57</sup> illustrates that multiple hops only have a significant impact on diffusion dynamics at higher temperatures than those used in our analysis. In addition, multiple hops should only be of significance in a relatively small number of chemical systems. Under ordinary conditions, the desorption rate will not only compete with but will begin to dominate multiple hop diffusion at these higher temperatures. The activation barrier, which is calculated from the intersection point between harmonic potential wells centered on adjacent lattice sites, is defined in Equation 4.

$$E_{ijkl} = E_m^0 + (E_{kl} - E_{ij})/2 + (E_{kl} - E_{ij})^2/16E_m^0 \quad (4)$$

Indices  $i$  and  $j$ , respectively, refer to the number of nearest and next-nearest neighbors in the initial configuration. Indices  $k$  and  $l$ , respectively, refer to the neighbor numbers in the final configuration. The migration barrier for an isolated adatom is given by  $E_m^0$ . The curvature of the potential is related to the frequency of the frustrated translation of the adsorbed particle. The vibrational frequency associated with this frustrated translation mode can be determined experimentally for many systems.

The first step in the diffusion simulation process is to determine all possible initial and final states for the adsorbed species and then to assign a transition type to each potential adatom hop. Each unique initial and final state combination is referred to as a transition type. For a square lattice with nearest and next-nearest neighbor interactions, there are 25 possible initial states and 25 possible final states. Hypothetically, this leads to a total of 625 transition types; but, because certain of these can be eliminated, there are actually only 196 allowed transition types. For example, because migration is only allowed to vacant nearest neighbor sites and because the initial site from which a particle migrates is necessarily left empty, a particle can never have four nearest neighbors in the initial or final states.

It is also true that there are a significant number of particle neighborhoods that differ only in the arrangement of the neighboring particles around the particle of interest. For instance, in a configuration of two nearest neighbors, the neighboring particles may either be adjacent to one another or opposite to one another. This clearly represents two non-equivalent configurations. Because the transition type includes the initial and final particle configuration, these configurational differences are explicitly included in the transition type assignments.

As the calculation proceeds, each filled site on the lattice is addressed in sequence; and each particle is placed on the population lists of its corresponding transition types. Because there are four possible directions for migration, each particle may be placed on as many as four population lists. Each transition type is characterized by an activation energy. From this activation energy, an occurrence probability is computed. The occurrence probability is simply the product of the transition type occupation number and a Boltzmann factor as represented in Equation 5.

$$P_{ijkl} = N_{ijkl} e^{(-E_{ijkl}/kt)} \quad (5)$$

Now, each transition type is addressed with a frequency proportional to its probability of occurrence. Once a transition type is selected, a particle is chosen randomly from its population list to undergo migration. Individual particles are not addressed, nor are individual lattice sites. This is a dramatic difference between our method and those discussed previously. The probabilities as determined from potential surface energetics govern the diffusion rate. Thus, an adsorbed particle migrates in each time-dependent Monte Carlo (TDMC) cycle.

When a particle reaches its final destination, the lattice occupation map and the population lists of all affected transition types are updated. A transition rate is also calculated using Equation 6 where  $k_m$ , the rate constant, is assumed to be the same for all transition types. In all of our investigations described in this dissertation, the rate constant is given a value of  $1 \cdot 10^{10}$ .

$$W_{ijkl} = k_m P_{ijkl} \quad (6)$$

In actuality, the rate constant is dependent on the transition type or neighborhood of the migrating particle. However, we contend that different particle neighborhoods have rate constants that differ only by a "kinetic isotope effect." More specifically, changing a particle neighborhood only slightly changes the vibrational frequency

of the particle. We argue that this change is insignificant in comparison to the differences in Boltzmann factors. Therefore,  $k_m$  is assumed to be equivalent for all transition types. The transition time for a single adparticle hop is simply the inverse of the transition rate, as Equation 7 illustrates.

$$T_{ijkl} = 1/W_{ijkl} \quad (7)$$

The sequence begins again with the selection of a new transition type and particle. When the calculation is complete, the real time for the process is computed using Equation 8.

$$time = \sum T_{ijkl} / NT \quad (8)$$

Here NT represents the total number of adparticles on the substrate surface. The mean square displacement and the diffusion coefficient are then calculated assuming random walk and Fick's law behavior. The diffusion coefficient certainly has a spatial dependence which we could compute in the diffusion simulation. However, this spatial dependence cannot be measured experimentally.

The diffusion coefficient is also dependent on the value we select for the hopping frequency, or rate constant.

Although we don't know the precise value of this parameter, a simple scaling algorithm would allow us to compute the actual diffusion coefficient given the experimentally determined value for a particular system.

No current discussion of surface diffusion is complete without the inclusion of correlation effects. Our model explicitly includes some correlation effects in the transition type assignments. More specifically, each time a particle migrates, the neighborhoods of all affected particles are updated. The new occurrence probabilities contain the "memory" of the previous hop. Therefore, a particle may be more likely to move if a neighboring particle has recently moved. The activation barrier for a second hop is clearly influenced by the first. This correlated behavior, which parallels the phenomena observed by Landman, et al.,<sup>77</sup> in their studies of dimer diffusion, is clearly included in the model.

Tsong and Gao<sup>76</sup> have also proposed that full rows of atoms migrate simultaneously in the (1X1) to (1X2) surface reconstruction of fcc (110) planes. A phenomenon such as the simultaneous reconstruction of the fcc (110) planes could clearly not be modeled using our approach. However, the conceptual and computational difficulties encountered in applying the TDMC method to surface reconstruction may center fundamentally on semantics and the definition of the term simultaneous. It is certainly possible that the

reconstruction proceeds via a series of highly correlated hopping events that occur on a time scale much shorter than that observed by the experimental probe. Thus, the time scale for particle hopping must be considered here. Typical particle hops occur in our model on a time scale of roughly a tenth of a nanosecond; and experimental time scales may be on the order of several nanoseconds.<sup>76</sup> Therefore, it is possible that several individual hops lead to the surface reconstruction observed above.

We do not consider the sort of correlation where a single particle, driven by its momentum in a certain direction, makes multiple hops. In our model, the particle is assumed to thermally equilibrate with the lattice after each hop. In most systems of interest, heat transport between a particle and the lattice takes place on the order of a few picoseconds. This is far faster than the atomic hopping rate; therefore, our assumption should be valid. Tully, et al.,<sup>51</sup> concluded from molecular dynamics studies that 70% of particle hops in a system at moderate temperature were individual, uncorrelated ones.

Voter and Doll<sup>59</sup> also propose that, in order for a second hop to be directionally oriented, it must take place within a few vibrational periods of the first; or the memory of the event is lost. We expect thermal equilibration to take place more rapidly than this at the temperatures we are examining. As mentioned above, multiple hop correlation is

not expected to play a significant role unless the temperature is large in comparison to the activation barrier for migration. This is not true for the systems under investigation. Furthermore, because we are dealing with significant concentrations, a particle is not likely to be able to make multiple hops before it feels the influence of other adparticles. Consequently, consecutive, multiple hop correlation does not play a significant role in the adsorbate overlayer systems under investigation.

An algorithm which incorporates this diffusion methodology on perfect surfaces has been developed and tested. We currently have the capacity to study systems of thousands of particles on a lattice composed of tens of thousands of lattice sites using a VAX 8550. We have been able to simulate diffusion in systems with a variety of adparticle interactions.

The coordinates of each particle on the lattice are saved at regular intervals throughout the calculation. Thus, maps of particle locations can be generated at any phase of the diffusion process. This allows us to directly observe the influence of adparticle interactions and long range ordering. These maps of overlayer structure can also be directly compared with scanning tunnelling microscope experiments.

Another powerful probe of adsorbate ordering is the correlation function. Tabulation of correlation values is

quite similar to computing the Fourier transform of the overlayer. In order to generate the correlation function, we address each filled site on the lattice in sequence. The number of neighbors of each "type" surrounding each particle are counted according to the scheme in Figure 1. A neighbor "type" is simply defined by its displacement from the particle of interest. There are either four or eight equivalent neighbors of each type on the square substrate. The neighbor types are numbered consecutively with increasing distance from the particle of interest. Neighbor types one through eight, or A through H as they are labeled in Figure 1, are included in the analysis.

When a particle is addressed, the occupation number of neighbors one through eight are tabulated. We then move to the next filled site and add the occupation number of each neighbor type surrounding the particle of interest to the previous total.

After all of the filled lattice sites have been addressed, we have the total number of neighbor types one, two, three, et cetera. These occupation numbers are normalized. The normalization constant for each neighbor type is simply the product of the total number of particles in the system and the number of equivalent sites for that neighbor type. The resulting normalized quantity is called the correlation function. The correlation function provides an additional method for describing ordering and island















































































































































































































































































































































































































































































































