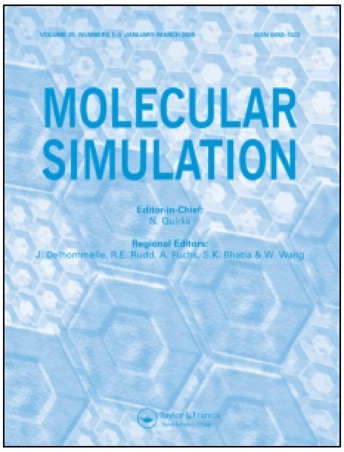

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D. A. Faux[a]; C. K. Hall[a]; J. Bernholc[ab]
[a] Department of Chemical Engineering, [b] Department of Physics, North Carolina State University, Raleigh, NC, USA

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A NEW MONTE CARLO SIMULATION TECHNIQUE FOR THE STUDY OF EPITAXIAL CRYSTAL GROWTH

D.A. FAUX, C.K. HALL and J. BERNHOLC*

*Department of Chemical Engineering, *Department of Physics, North Carolina State University, Raleigh, NC 27695, USA*

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A new type of Monte Carlo simulation is described which models epitaxial crystal growth on non-lattice-matched substrates. The model allows adatoms to immediately occupy positions of local potential minima which are defined by the particle-particle interactions. Adatoms make discrete hops from one minimum to another. This model therefore combines some of the flexibility of continuous-space Monte Carlo with the speed associated with lattice-like simulations. Details of the Monte Carlo procedure are presented for a two-dimensional system where the particle-particle interactions are assumed to be of the Lennard-Jones type. Some results are presented for the case where the adsorbate crystal lattice is larger than the substrate lattice by 2% and 8%.

KEY WORDS: Monte Carlo simulation, mismatched interfaces, crystal growth, two-dimensional systems.

1 INTRODUCTION

There has been considerable interest in the last decade in the properties of strained-layer superlattices. A strained-layer superlattice is a material consisting of alternating ultrathin layers of two different semiconductors. If the layers are thin enough, the artifical periodicity induces fundamental changes in the band structure, thereby leading to a new class of electronic materials. These devices have received attention because they display novel optical and electronic properties which can be tailored to specific needs, for instance, by varying the layer thickness [1–3].

The devices are generally fabricated either by molecular-beam epitaxy or by chemical vapour deposition. In both techniques atoms are deposited onto the surface of a substrate. If the mismatch between the lattice constants of the substrate and the overlayer atoms is not too large, the deposited layers will initially grow in registry with the substrate. However there will be a residual strain at the interface between layers of the two different materials because the overlayer stretches (or compresses) so as to have the same lattice parameter as the substrate. If the deposited layer exceeds a certain critical thickness, the strain energy becomes sufficiently large for the lattice spacing of the adsorbate to revert to its bulk value. This leads to misfit dislocations at the interface between the substrate and adsorbate which impair device performance.

Computer simulation is a useful way to investigate the formation of misfit dislocations in strained-layer superlattices. Starting with a set of certain assumptions concerning the nature of the particle-particle interactions, the bulk behaviour of large numbers of deposited adatoms may be studied.

The first full computer simulation of epitaxial growth was performed by Schneider *et al.* [4]. They investigated a 3-dimensional Lennard-Jones system using molecular dynamics. These authors [5] later extended this work to simulate the growth of Si on a Si substrate using an interatomic potential developed by Stillinger and Weber [6]. However, they did not consider lattice-mismatched systems. The first attempt to simulate the growth of a strained-layer interface was made by Dodson and Taylor [7]. They used a continuous-space Monte Carlo technique and investigated a 2-dimensional Lennard-Jones system. These authors have also performed molecular dynamics simulation of the same system and have recently extended their Monte Carlo work to silicon potentials [4,5].

We have embarked on a theoretical study of the deposition process and have developed discrete-space Monte Carlo algorithms capable of simulating deposition on non-lattice-matched substrates. This paper describes a new type of Monte Carlo computer simulation which has the advantage that it is inherently faster than continuous-space Monte Carlo or molecular dynamics techniques, whilst retaining the essential physics of the adsorption process. Another algorithm suitable for the simulation of strained-layer growth will be described elsewhere [8]. The significant speed-ups obtained allow us to investigate the full range of parameters, and thereby to gain an insight on an atomic level of the role of factors such as temperature, lattice mismatch, material type, layer thickness and deposition kinetics on the formation of misfit dislocations. A full discussion of the results will be published elsewhere.

The present model, which we call the potential-minimum model, assumes that adatoms adsorb at local minima (potential wells) defined by interactions with previously deposited adatoms (or between adatoms and substrate atoms). The time-of-flight of an adatom as it moves from one potential well to the next is assumed to be negligible when compared to the time spent in the well. Jumps to new locations may thus be represented by an instantaneous discrete hop to a new well. This has similarities to the lattice-gas model in which atoms make hops between sites on a predetermined lattice. Unlike a lattice gas simulation, however, the sites which may be occupied by an adatom are not defined *a priori*, but develop as the simulation proceeds.

In the following section we describe an application of the potential-minimum model to the adsorption of two-dimensional Lennard-Jones particles of one size parameter onto an ordered substrate of Lennard-Jones particles with a different size parameter. The results are presented in section 3 and compared to the calculations of Dodson and Taylor [7,9]. The conclusions, including a discussion of the extension of the model to three dimensions, are given in section 4.

2 DESCRIPTION OF THE POTENTIAL-MINIMUM MODEL

(i) Parameterisation

The atoms of a two-dimensional Lennard-Jones crystal occupy the sites of a triangular lattice. The substrate is therefore represented by a triangular arrangement of atoms with lattice spacing a_S as illustrated in Figure 1. The substrate atoms are kept fixed throughout the simulation. The adsorbate atoms to be deposited onto the

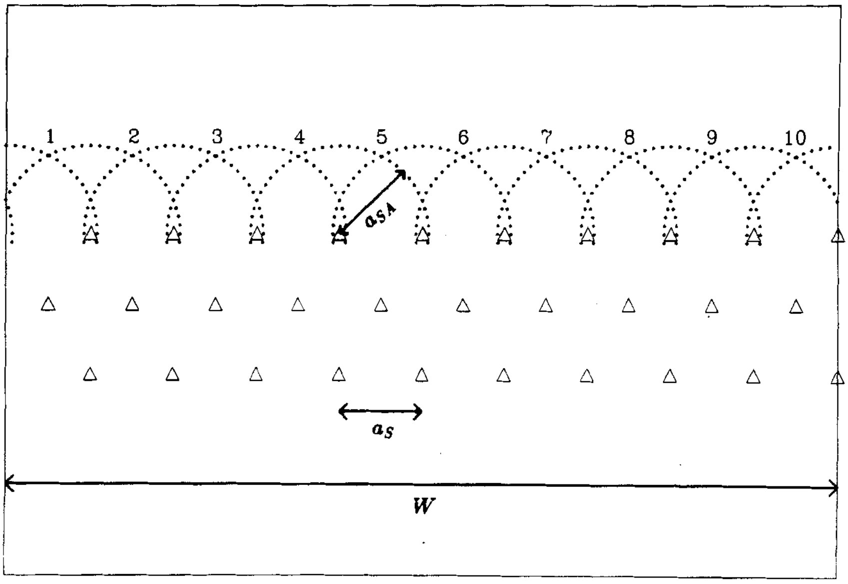

Figure 1 Three layers of substrate atoms are indicated (Δ). Circles are drawn around each surface substrate atom of radius α_{SA} (· · · ·). These represent the minimum in potential due to the Lennard-Jones interaction. The potential wells occur at the intersection of these circles and are labelled from 1 to 10. Sites 1–10 are available for occupation to deposited adatoms.

substrate, have a bulk lattice spacing a_A. Thus the lattice mismatch f is given by the expression,

$$f = \frac{a_S}{a_A} - 1 \tag{1}$$

Periodic boundary conditions are incorporated at the sides of the box and so W, the width of the simulation box, must accommodate an integer number of lattice spacings a_A and a_S. If $a_A = 1.05a_S$, for instance, the minimum value of W is $20a_A$, which is equal to $21a_S$.

The substrate-substrate (SS) and adsorbate-adsorbate (AA) interactions are each approximated by a Lennard-Jones potential of the form

$$U(r) = \frac{\varepsilon}{\alpha^2}[r^{-12} - \alpha r^{-6}] \tag{2}$$

The prefactor ε determines the temperature scale and is assumed to be unity. All distances are normalized to the substrate-substrate lattice spacing a_S which is arbitrarily set equal to 1. The AA and SS potentials, U_{AA} and U_{SS}, are given by Equation 2 with an interaction parameter α_{AA} and α_{SS} respectively. Both are truncated at the distance where the potential reduces to 1% of the value at the minimum. This occurs at $r = 2.71$.

Following Dodson and Taylor [7], we assume that the substrate-adsorbate (SA) potential is the average of the AA and SS potentials. Thus,

$$U_{SA}(r) = \frac{U_{AA}(r) + U_{SS}(r)}{2} \tag{3}$$

The interaction parameter α_{SS} is chosen so that the crystal phase with a lattice parameter of unity has the minimum energy. Although the minimum in the pair potential for the SS interaction occurs at $r = 1$ when $\alpha_{SS} = 2$, this value of α_{SS} does not give the minimum energy for the triangular crystal when the pair potentials are summed over the more distant lattice sites. Instead, the value of α_{SS} is chosen to equal 1.8926 since a numerical calculation shows that this value yields a minimum in the total energy for the crystal when the lattice parameter is unity and when the pair potential is truncated at $r = 2.71$. (Note that the nearest-neighbours are now slightly offset from the minimum in the Lennard-Jones potential which occurs at $r = 1.00924$).

The determination of α_{AA} for the AA interaction is on the same basis as described above. Thus the expression for α_{AA} is

$$\alpha_{AA} = \frac{\alpha_{SS}}{a_A^6} \tag{4}$$

(ii) Addition and Movement of Adatoms

The potential-minimum model assumes that the adatoms may only occupy positions

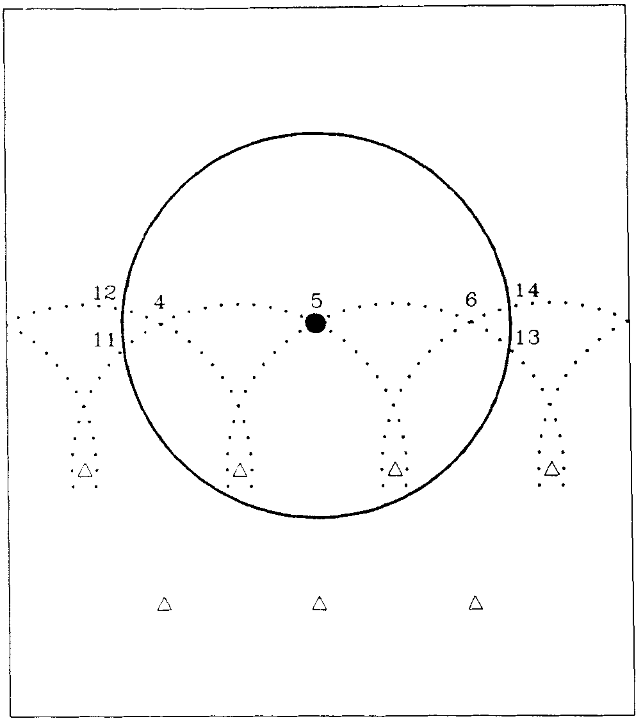

Figure 2 The first adatom occupies site 5. New potential wells are formed due to the intersection of a circle of radius a_A around the adatom and circles of radius a_{SA} around substrate atoms. These are locations 11–14.

of local potential minimum. The locations of the potential wells are readily defined for a Lennard-Jones system. These occur at the intersections of circles of radius a_A centered at the adatoms and circles of radius a_{SA} centered at the substrate atoms. The value of a_{SA} is taken to be the value of r corresponding to the minimum in the potential defined by Equation 3.

The addition and movement of adatoms can best be described by referring to Figures 1–3. In Figure 1 the well positions prior to the addition of the first adatom are labeled 1–10. These are the intersections of circles of radius a_{SA} about each substrate atom. An adatom is introduced to one of the available wells at random. In Figure 2 the first atom has been added to well 5. The presence of this adatom causes the formation of additional potential minima labeled 11–14. These are formed by the intersections of circles of radius a_A around the adatom and of radius a_{SA} about each substrate. This adatom is then permitted to hop to any well within a certain distance from its current position. In these simulations the maximum jump distance was fixed at $1.1 \times \max(a_{SA}, a_A)$. This adatom cannot, however, hop to a well which has been formed as a result of its own presence. Thus, in Figure 2, the atom cannot jump to sites 11–14 and may only hop to site 4 or 6.

A new configuration is accepted with the usual Monte Carlo criterion. If the energies of the initial and final states are U_i and U_f respectively, then the new configuration is accepted if $R < \exp[(U_i - U_f)/kT]$ where R is a random number

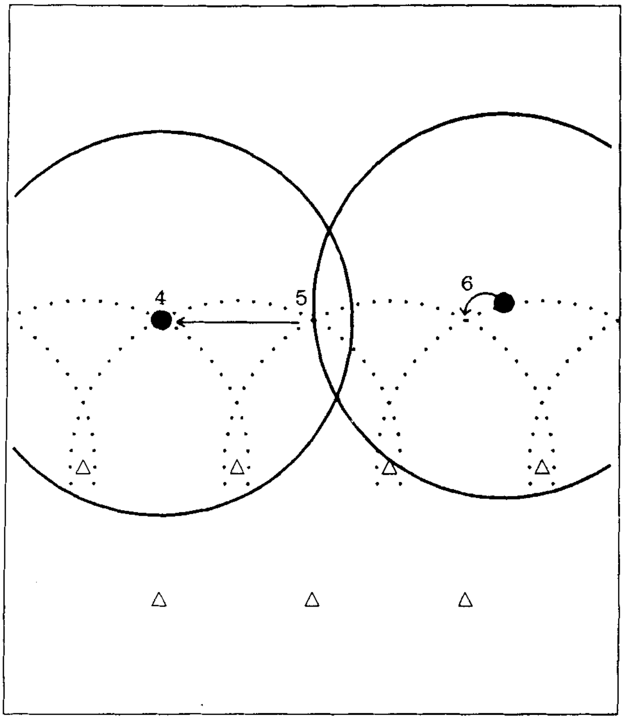

Figure 3 The second adatom is deposited on site 14. If the first adatom jumps to site 4, the potential well at site 14 disappears and the second adatom is moved to its nearest available site. Note that new potential wells have appeared due to the intersection of the two solid circles.

between 0 and 1. The probability that a proposed jump is successful thus depends only on the energies of the initial and final sites and not on the height of the potential barrier between the two sites.

The sites labeled 11–14 in Figure 2 will disappear when the adatom jumps to a new site because these sites no longer form a potential well. A fresh set of well positions will be formed. For the moment we assume that this adatom remains at location 5 and that a second adatom is to be added to the system. The second adatom may now be added to one of wells 1–14, chosen at random. Of course the energy of some of the wells will be too high to permit occupation, such as well 5 which is already occupied. The probability of accepting a new adatom at a specific location is made on the same basis as described above with $U_i = 0$.

Note that a hop of one adatom can leave a second adatom in a state where it is no longer in a potential well. For example, suppose a second adatom is added to site 14 in Figure 2. If the first adatom then jumps to site 4, the second adatom is no longer in a potential well (Figure 3). In this case the second atom is moved immediately to the nearest available site (site 6). Thus a single hop of one adatom can lead to a series of rearrangement hops by surrounding adatoms. This rearrangement simulates somewhat crudely the reconstruction which follows atomic motion.

3 RESULTS

The performance of the simulation is assessed at two different values of the mismatch f. The values of $|f|$ chosen were 0.02 and 0.08 with $a_A > a_S$ (the modulus signs are ignored hereafter). A full study as a function of mismatch, temperature and deposition kinetics will be published elsewhere.

The interaction parameters α_{AA} and α_{SS} are determined as described in section 2(i). The value of α_{AA} is equal to 1.6765 and 1.1476 for $f = 0.02$ and 0.08 respectively, and α_{SS} equals 1.8926 throughout. The temperature is fixed at 0.09 which corresponds to approximately 75% of the melting temperature ($kT_{melt}/\varepsilon \sim 0.11$ [11]). The width of the simulation cell W was sufficient to accommodate 50 substrate atoms and 300 atoms were deposited. In Dodson and Taylor's continuous-space Monte Carlo simulations [7], they chose the number of Monte Carlo steps (MCS) per atom between atom additions to equal 100. We presume this to be the number of attempted moves as opposed to the number of successful transitions, although this is not clear from their paper. In continuous-space Monte Carlo an adatom will make many hops locating a potential minimum and moving from one location to another. In these simulations the potential minimum is located directly and jumps to new minima are made in one move. It would therefore be expected that the number of MCS required in our simulations would be considerably less than for continuous-space Monte Carlo. Here the adatoms were allowed to make 10 successful jumps per atom between depositions.

A section of the crystal grown at $f = 0.02$ is plotted in Figure 4. The plot shows 3 layers of substrate atoms although the substrate atoms do not move during the simulation. The adsorbate has clearly grown in registry with the substrate. In contrast, at the very large mismatch $f = 0.08$, misfit growth is observed and the dislocation is indicated in Figure 5. These observations are in agreement with the published results of Dodson and Taylor [7].

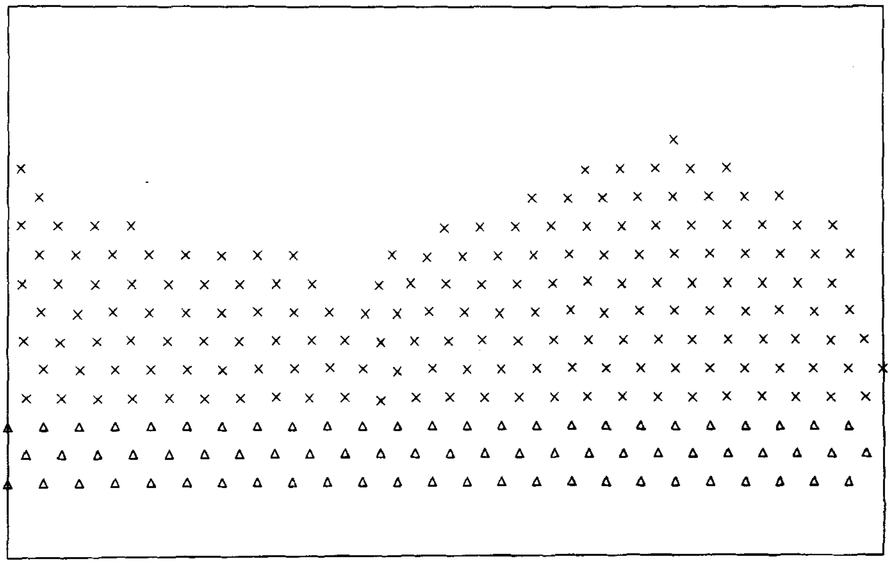

Figure 4 Approximately 6 layers of adatoms have been deposited at $f = 0.02$. The crystal has grown in registry with the substrate. Substrate atoms (Δ); adatoms (×).

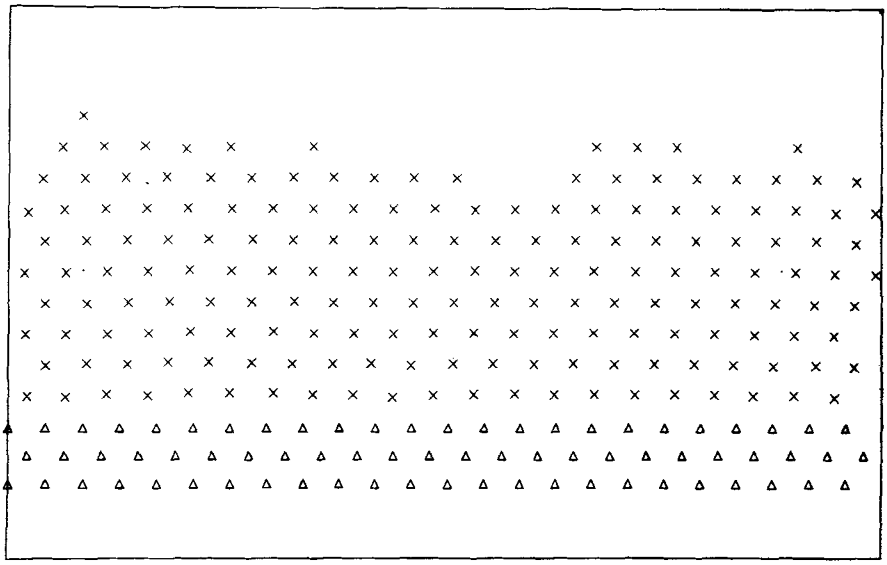

Figure 5 Approximately 6 layers of adatoms have been deposited at $f = 0.08$. Misfit growth is observed. Substrate atoms (Δ); adatoms (×).

A more quantitative presentation of these results is given in Figure 6. Here we consider only the first layer of adatoms and plot the mean nearest-neighbour distance as a function of the number of atoms deposited. At $f = 0.08$, the mean adatom spacing corresponds to a_A throughout and there is no tendency for the crystal to grow

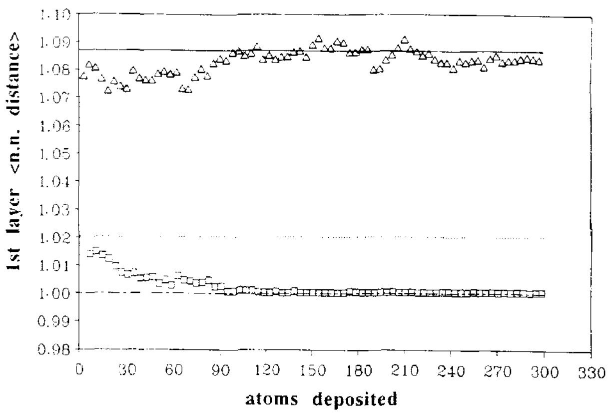

Figure 6 The average nearest-neighbour distance for atoms on the first layer is plotted as a function of the total number of atoms deposited. The Monte Carlo results at $f = 0.08$ are shown (△) and at $f = 0.02$ (□) both with 10 jumps/atom. The ideal spacings α_S (–·–·–), α_A at $f = 0.02$ (· · · ·) and α_A at $f = 0.08$ (———) are also indicated.

in registry with the substrate. At $f = 0.02$ the mean separation is greater than a_S until approximately 1 layer has been deposited. As the first layer fills up the separation corresponds to a_S indicating that the adsorbate crystal is growing in registry with the substrate.

A direct comparison of the amount of CPU time used here as compared to previous work is difficult because of its dependence on certain parameters and the different machines used for the simulations. Each simulation described here took about 11 hours on a micro VAX II or approximately 17 minutes on a CRAY X-MP to deposit 200 atoms. This appears to be about a factor of at least 2 faster than continuous-space Monte Carlo or molecular dynamics work [7,9].

4. CONCLUSIONS

The study of two-dimensional Lennard-Jones systems can give qualitative agreement with experimental observation and is an ideal test case for new simulation methods. The results obtained using the potential-minimum model show registered growth at a mismatch of 2% and misfit growth at 8%. These are in agreement with previous continuous-space Monte Carlo and molecular dynamics simulations but require less computer time.

The primary interest, however, lies in the study of 3-dimensional systems. The conversion to three dimensions with spherical potentials would be straightforward because the location of local potential minima are readily defined as the intersection of three spheres. This would be relevant to the study of metal-metal interfaces, for instance, where strongly directional bonding is not present. Highly coordinated bonding is present in semiconductor systems and we are currently investigating the possibility of incorporating semiconductor potentials into the model.

Although the technique has a number of advantages, it also has three limitations which should be pointed out. First, since new adatoms are placed directly at sites of potential minima, the technique does not take into account those transient kinetic effects which result from the conversion of the energy of adsorption into lattice vibrations near the site of impact. Second, the effect of thermal vibrations on the potential minima is not included. Third, Monte Carlo jumps are accepted or rejected based on residence probability rather than on barrier penetration probability. This is equivalent to assuming that barrier heights are small or that the timescale for barrier penetration and for successful Monte Carlo hops are much less than the time scale for addition of new adatoms. These limitations are of little consequence for the two-dimensional Lennard-Jones depositions considered but may be more significant for other applications.

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