PHYSICAL REVIEW B VOLUME 34, NUMBER 4 15 AUGUST 1986

Monte Carlo simulation of continuous-space crystal growth

Brian W. Dodson and Paul A. Taylor
Sandia National Laboratories, P.O. Box 5800, Albuquerque, New Mexico 87185

(Received 8 January 1986)

We describe a method, based on Monte Carlo techniques, of simulating the atomic growth of crystals without the discrete lattice space assumed by conventional Monte Carlo growth simulations. Since no lattice space is assumed, problems involving epitaxial growth, heteroepitaxy, phonon-driven mechanisms, surface reconstruction, and many other phenomena incompatible with the lattice-space approximation can be studied. Also, use of the Monte Carlo method circumvents to some extent the extreme limitations on simulated timescale inherent in crystal-growth techniques which might be proposed using molecular dynamics. The implementation of the new method is illustrated by studying the growth of strained-layer superlattice (SLS) interfaces in two-dimensional Lennard-Jones atomic systems. Despite the extreme simplicity of such systems, the qualitative features of SLS growth seen here are similar to those observed experimentally in real semiconductor systems.

INTRODUCTION

The current interest in superlattices composed of many thin ($\ll 100$ nm) layers of different materials suggests that an atomic scale understanding of crystal-growth mechanisms in such systems will be of increasing importance in the future. The enormous number of interesting material combinations requires us to attempt to systematize and to develop predictive capability concerning the likelihood of and probable conditions for growth of high-quality epitaxial interfaces between various materials. An increased capability in atomic scale modeling of crystal growth is one tool which may be used to deal with such issues.

At present, most simulations of crystal growth have depended on the definition of a natural lattice system by the substrate crystal.[1] This is usually done in the context of a solid-on-solid (SOS) model,[2] wherein one considers a lattice-gas model of the crystal, the spatial lattice being defined by the substrate lattice. Atoms of the crystal normally are constrained to interact only with nearest neighbors, although this is not a fundamental requirement of the SOS method. The resulting model is analogous to constructing a crystal with building blocks of fixed size and shape, with rules to determine which configurations of the blocks have the lowest energy. This sort of model can usually be mapped onto some version of the Ising model, which renders analysis of the model very tractable. Such models have proven useful in the study of growth kinetics, the roughening transition, nucleation of adsorbed layers, genesis and growth of screw dislocations, and many other topics.

The SOS and other lattice-gas models of crystal growth, however, cannot be used to study phenomena which fundamentally depend on a continuous interaction potential acting on atoms moving in real space. Examples of such phenomena would include epitaxial growth (especially heteroepitaxy), surface reconstructions, phonon-driven diffusion, growth of defective and/or amorphous layers, etc. These include problems which have become of considerable fundamental and applied importance in systems, such as strained-layer superlattices (SLS), in which characteristic distances are sufficiently small that reasonable numerical simulations seem possible. Our primary interest is in modeling the growth of semiconductor SLS interfaces to determine the conditions under which registered heteroepitaxial growth could occur in these strained systems. To treat such problems, we have developed a Monte Carlo technique to simulate vapor-phase crystal growth of mismatched materials, given only the interaction potentials of the two materials and the crystal structure and orientation of the substrate. This method will be described in the present paper and will be demonstrated by modeling the growth of SLS interfaces in a two-dimensional Lennard-Jones system.

MONTE CARLO CRYSTAL-GROWTH SIMULATIONS

The procedure to be described will model the vapor-phase growth of new crystal onto a substrate crystal. The substrate consists of a crystal lattice whose atoms interact through the spatially continuous potential AA (for simplicity we are considering only the case where the substrate and the vapor are monoatomic). The substrate lattice is subjected to periodic boundary conditions perpendicular to the direction of growth so that correlation effects can be modeled over longer effective distance. The substrate is equilibrated using conventional Monte Carlo techniques[3] at the desired substrate temperature, so that surface reconstruction and thermal-expansion effects can be allowed for.

Adatoms of the material being deposited are added in the following manner. A random position over the substrate is chosen, sufficiently distant from the substrate that the adatom-substrate interaction is negligible. The adatoms interact with each other through a continuous interaction potential BB and with the substrate atoms through a continuous potential AB. An adatom is placed at the random position and is lowered normal to the surface of the substrate until some criterion for interaction with the surface is satisfied. We generally choose that the adatom-substrate interaction be 10% of the bulk-binding energy of the adatoms, but the final results are quite insensitive to the details of the chosen criterion. The crystal atoms are held fixed during the approach of the new adatom, which is why the initial interaction with the substrate must be constrained to be so small.

When the adatom is sufficiently close to the substrate, the complete system, including the adatom, is equilibrated at the substrate temperature using the Monte Carlo method.[3] The Monte Carlo method consists of generating a representative group of states from the canonical ensemble of a system at a given temperature. This is accomplished by generating a new atomic configuration from the current one by randomly moving one particle. If the total energy of the system is reduced by the move, the new configuration is accepted. If the total energy increases, the configuration may be accepted according to a probability that is proportional to the Boltzmann factor $\exp(-E/k_BT)$. This procedure is iterated until an acceptable approach to equilibrium is achieved. The effect in the current case is that the new adatom drifts down to the surface under the influence of the substrate potential, and then the local structure comes into thermal equilibrium with the substrate. At this point, the next adatom position is chosen, and the process is repeated until a sufficient thickness of the second material is grown. In real molecular-beam-epitaxial (MBE) growth of semiconductors, the deposition rate corresponds to adding one adatom every few milliseconds on a substrate of tractable size (a few hundred surface atoms). The assumption of independent adatom adsorption used above is therefore reasonable.

The procedure outlined above represents a relatively benign method of adding atoms to a substrate and ensuring that a reasonable state in local equilibirum is attained. However, it is not a particularly accurate model of vapor-phase growth, since the initial transient behavior of the adatom-surface interaction is largely ignored. Two effects are being lost in the outlined procedure, those being the thermal energy of the vapor atoms and the energy gained by the adatom as it approaches the surface. In an accurate representation, this excess energy is converted first into the potential energy of a distorted local atomic configuration surrounding the point of impact of the adatom, and then the excess energy is dissipated throughout the crystal by phonons in a few characteristic vibrational periods. This transient behavior is a primary factor in the existence of characteristic "sticking coefficients" in vapor-phase deposition, and is also a source of adatom-induced surface diffusion and/or reconstruction. By contrast, the Monte Carlo procedure outlined above changes the abrupt nature of the transient behavior, resulting in a much "gentler" deposition process. The excess energy corresponding to the temperature of the vapor is just ignored, and that due to the integrated adatom-surface interaction disappears because there is no kinetic energy in a Monte Carlo computation. Thus the transient effects from these sources do not appear in the simulation. It is possible to model more accurately these transient processes within the context of the Monte Carlo simulation, essentially by artificially placing the adatom close to the surface, so that the excess potential energy is that which would be expected in a real adsorption. However, recovering the transient effects then requires very small attempted Monte Carlo moves, which are accompanied by a large increase in the computational effort. In the course of examining the importance of such transient effects, we have found that, in general, the qualitative significance of accurate treatment is rather small. We therefore suggest, in the interest of computational tractability, that the adatom deposition procedure outlined in the current section is a reasonable approximation, but we emphasize that the intrinsic limitations of the approximation must be examined when it is applied to a new system.

GROWTH OF TWO-DIMENSIONAL LENNARD-JONES SLS INTERFACES

We illustrate the implementation of the Monte Carlo vapor-phase crystal-growth technique by modeling the growth of mismatched two-dimensional Lennard-Jones (LJ) crystals. This pairwise interaction potential is spherically symmetric, and has been modified from the usual LJ potential so that we may model materials with different equilibrium radii but equal binding energies. The pair potential used is

$$\phi(r)=(r^{-12}-\alpha r^{-6})/\alpha^2 , \qquad (1)$$

where α, the radial size parameter, controls the interatomic spacing through $r_{\text{eq}}=(2/\alpha)^{1/6}$ ($\alpha=1$ recovers the conventional LJ potential in dimensionless units). The pairwise binding energy at equilibrium is the same for all positive values of α. The AB interactions were taken to be the average of the AA and BB interaction. Thus the substrate-substrate, adatom-adatom, and adatom-substrate interactions have equal strength at their respective equilibrium distances. For computational economy, the three potentials were placed in look-up tables with cutoffs of three scaled distance units.

The substrate was an 80×4 trigonal lattice with periodic boundary conditions along the long axis chosen so that the substrate is stress-free at the appropriate substrate temperature. From 200 to 400 adatoms of material B were then grown on the substrate, representing roughly 3–5 new layers of material. One-hundred Monte Carlo steps per atom (MCS/atom) were found to provide sufficient equilibration between adatom introductions to insure overall equilibration at the conclusion of the simulation; that is, 1000 MCS/atom between successive adatoms gave the same qualitative results. An average growth simulation therefore required roughly 3×10^6 MCS, requiring about 40 CPU (central processing unit) hours on a VAX Digital Equipment Corporation 11/780-class minicomputer.

The first case considered was that of homoepitaxy (see Fig. 1). The AA, BB, and AB interactions were all represented by modified LJ potentials in the form of Eq. (1) with $\alpha=1$. By using the procedure described in the preceding section, 200 adatoms were grown on the top surface of the substrate. The substrate temperature was varied in successive growth simulations over the range

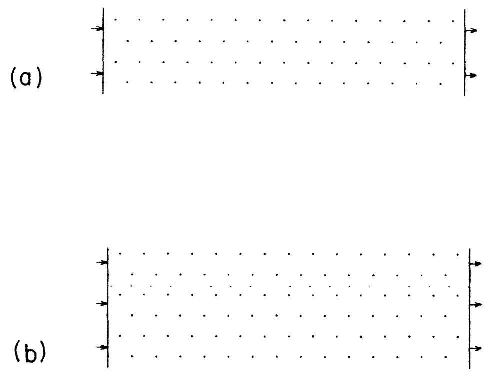

FIG. 1. The triangular two-dimensional Lennard-Jones substrate upon which growth from the vapor is modeled. (a) represents the initial substrate, where the periodic boundary conditions are indicated by the vertical lines and arrows. (b) is the (schematic) result of homoepitaxial growth of two new monolayers on the substrate of (a). The substrate studied in the paper is actually 80 atoms long rather than the 15 atoms shown in this figure.

$T=0$–0.15. (The melting point of the substrate is 0.12, as determined by MC calculations using the same Hamiltonian as the growth simulations.) We found good epitaxy to occur for all temperatures below 0.12, at which point the melting of the system made the question academic. However, a small density of interfacial dislocations was observed for temperatures below 0.02. Accurate homoepitaxial growth without defects or dislocations was observed in the temperature range 0.02—0.09 energy units, resulting in a perfect single crystal. In all cases below the melting point the surface of the final crystal is rather rough, having random modulations with an average period of about 10—15 atomic spacings and a depth of 1—2 layers. This is perhaps not surprising, since the ratio of the *BB* and *AB* interaction potentials is 1, which is the qualitative criterion for the transition between layer and island growth.[4]

Having demonstrated that the MC crystal-growth procedure does indeed simulate homoepitaxial single-crystal growth under reasonable conditions, we investigated the growth of mismatched layers next, with special attention paid to the growth of SLS interfaces. The authors have previously examined the limits of stability and metastability of two-dimensional Lennard-Jones SLS interfaces as a function of lattice mismatch.[5,6] The limit of metastability, or of spontaneous zero-temperature loss of registry, is closely related to the problem of ultimate strength of perfect materials under the uniaxial strain, where one calculates the degree of uniaxial strain that can be supported by a perfect crystal before dislocations are nucleated and grow. For the LJ system under consideration here, this limit occurs at about 12% lattice mismatch.[5] However, the limit of stability when subjected to finite temperatures and reasonably long times will be considerably less than this. This limit has been studied by calculating the energies of registered and defective interfaces in mismatched LJ systems by using Monte Carlo techniques to relax the atomic configuration to a local energy minimum.[6] By using this method, it was demonstrated that a two-dimensional LJ SLS system with layers three atoms thick is stable (not metastable) up to 8% mismatch (the stability limit will decrease with increasing layer thickness). Thus a LJ SLS system can be stable under reasonably large mismatch values and layer thicknesses.

Although our model system will, under some conditions, have a registered SLS geometry as the most stable state, this does not imply that such a geometry will result from a particular growth procedure. Therefore, the emphasis in the current simulation of vapor-phase heteroepitaxial growth is to determine the limits of mismatch within which a perfect LJ SLS interface can be grown by the current model of vapor-phase growth. The substrate used for these calculations is identical to that used earlier, having in particular $\alpha=1$. We take the adatoms to be larger than the substrate atoms, so that $\alpha<1$. Vapor-phase growth simulations were undertaken for the parameter matrix defined by $T=0.06$ and 0.09, and mismatches of 1%, 2%, 3.5%, and 5%, representing a total of 10 growth simulations. The substrate temperatures are 50% and 75% of the melting point.

At a substrate temperature of 0.06, imperfect interfaces are grown at all values of the lattice mismatch. The imperfections take the form of conventional misfit dislocations occurring roughly every 100/ (% mismatch) atoms, with the strain energy being localized near the interface. We are not able to consider smaller mismatches within the constraint of the chosen substrate geometry. The new crystalline layer still shows the surface roughness referred to in the earlier discussion of homoepitaxial growth. However, when the substrate temperature is raised to 0.09, we find that properly registered SLS interfaces can be grown at mismatches of 1% and 2%, but not at 3.5% or 5% (see Fig. 2). The defective interfaces are similar to those resulting from growth at $T=0.06$. We therefore conclude that a two-dimensional (2D) LJ SLS interface can be grown by our model-growth procedure, but the limiting mismatch value is not greatly in excess of 2%.

DISCUSSION

We have described a Monte-Carlo-based method for simulation of vapor-phase crystal growth in continuous space and have demonstrated its use on two-dimensional Lennard-Hones materials. The power of using Monte Carlo methods on such problems is that, by substituting an evolutionary path in phase space given by stochastic dynamics for that given by Newtonian dynamics, it is possible to effectively and efficiently simulate the end result of physical processes characterized by two or more disparate characteristic time scales. In the context of the growth simulations considered in the present paper, the processes are those of surface adsorption, occurring on a picosecond time scale, and surface diffusion, with a time scale of nanoseconds or more at the substrate temperatures used. Note that the basic principle here is not limited to crystal-growth simulations, but may be applied to

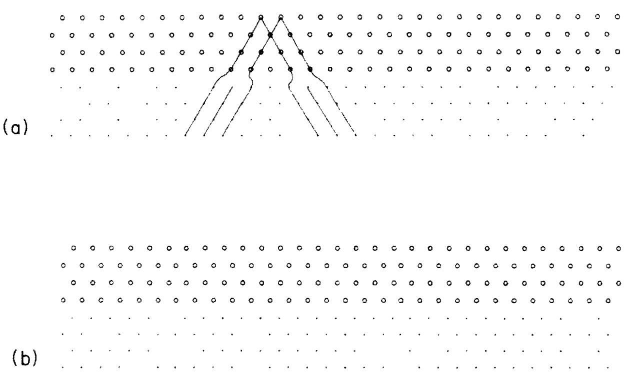

FIG. 2. Heteroepitaxial growth on a triangular two-dimensional Lennard-Jones substrate such as described in Fig. 1 and in the paper. (a) is the result of growing overlayers with atoms 5% larger than the substrate atoms. The resulting misfit dislocations are easily seen. By contrast, the registered overlayer in (b) is formed of atoms 2% larger than the substrate atoms. Both growth simulations were carried out at $T=0.09$ (about 75% of the melting temperature.) Again, to enhance clarity, only a portion of the entire system is shown.

many scenarios where a nonequilibrium system is freely relaxing towards a (at least locally) stable condition of interest. It is also worth noting that the Monte Carlo procedure can be replaced by implementation of Langevin dynamics, where the particles are subject to both a viscous damping force and a randomly fluctuating force, and the path in phase space is calculated by molecular-dynamics techniques.[7] Similar to Monte Carlo procedures, Langevin dynamics yields an equilibrium thermal distribution of the system such that the time average of any physical quantity is equivalent to its real-space ensemble average. The resulting path through phase space is thus characteristic of thermal equilibrium, although differing from those predicted by either Monte Carlo or Newtonian dynamics.

The primary limitation of this class of stochastically based evolutionary simulations is that use of the stochastic dynamics removes all information concerning the physical time scale associated with the real dynamics. Thus, for example, such methods cannot be used to determine directly dynamical properties such as diffusion coefficients or deformation rates. In many cases, however, such properties can be determined by a second stage of modeling wherein the parameters of the model come from stochastic simulations. (An example might be calculation of the vibrational properties of a dilute monolayer, wherein the system would be modeled as an equivalent system of oscillators with masses and effective spring constants for the "floppy" regions determined from a stochastic simulation.) It might be suggested that in the limit of very small step size, there is some current evidence that one can associate a real-time scale with the Monte Carlo stochastic dynamics.[8] However, in this limit the ability to treat disparate physical time scales disappears, and then we are no better off than by using molecular dynamics.

The immediate application of this technique to growth of SLS systems is of considerable interest. The successful growth of registered mismatched interfaces is controlled by the two standard parameters, mismatch and substrate temperature, even in the very simple 2D Lennard-Jones model system. The results reported above form a qualitative pattern of regimes suitable for growth of SLS structures that is in reasonable agreement with that obtained through experimental experience in growing semiconductor SLS systems. This correspondence underscores the potential significance of examining more closely the problem of growth of novel layered structures.

ACKNOWLEDGMENTS

This work was performed at Sandia National Laboratories and was supported by the U.S. Department of Energy under contract No. DE-AC04-76DP00789.

---

[1] See, for example, H. Muller-Krumbhaar, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, New York, 1979).

[2] T. L. Hill, J. Chem. Phys. **15**, 761 (1947).

[3] K. Binder, *Monte Carlo Methods in Statistical Physics*, Ref. 1.

[4] D. Kashchiev, J. P. v.d.Eerden, and C. v.Leeuwen, J. Cryst. Growth **40**, 47 (1977).

[5] B. W. Dodson, Phys. Rev. B **30**, 3545 (1984).

[6] B. W. Dodson and P. A. Taylor, Superlatt. Microstruc. (to be published).

[7] See, for example, R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975).

[8] R. Ettelaie and M. A. Moore, J. Phys. A **17**, 3505 (1984).