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Molecular-dynamics simulation of cluster and atom deposition on silicon (111)

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The deposition of Si atoms and Si-atom clusters on a silicon (111) surface has been studied with molecular-dynamics simulations using two- and three-body interatomic Si potentials. The energy deposition and dynamics of Si-atom deposition have been studied as a function of substrate temperature, incident atom energy, and substrate thickness. Epitaxial Si(111) layers have been grown by single-atom deposition. The energy deposition and spreading of Si-atom clusters is characterized as a function of substrate temperature, initial cluster velocity, cluster temperature, and cluster size. A range of deposition parameters has been characterized that lead to high spreading of clusters, a feature that is necessary for achieving epitaxial thin-film growth.

I. INTRODUCTION

The growth of high-quality epitaxial semiconductor films has led to numerous recent advances in semiconductor technology. Molecular-beam epitaxy (MBE) is among the most extensively used techniques for epitaxial semiconductor film growth. Relatively recently, Takagi and co-workers[1–4] have demonstrated that the ionized-cluster-beam (ICB) technique is a viable deposition process for growth of thin films. In the ICB method atomic clusters are generated by an adiabatic expansion of the vapor through a nozzle. An energetic electron beam causes impact ionization of the clusters. The positively charged clusters can be accelerated by an electric field, towards the deposition surface. Metals, semiconductors, and insulators have been successfully deposited on a variety of substrates, as discussed in the review articles.[1,2]

The ICB process is characterized by a control over the incident kinetic energy of the cluster and by the presence of charge on the deposited species. A general feature is that high-quality epitaxial films can be grown at lower substrate temperatures with the ICB process than with other deposition methods. Lower substrate temperatures are very desirable for maintaining sharp interfaces and for limiting diffusion of dopants. Silicon and germanium, as well as aluminum, have been epitaxially grown on the Si(111) and Si(100) substrates.[1,2,4,5]

Many aspects of the ICB growth process are not fully understood. In this paper we theoretically investigate the dynamics of clusters impinging on a silicon substrate. An important criterion for obtaining epitaxial film growth is that each cluster should dissociate on the substrate and spread into a uniform layer. We explore the sensitivity of the cluster dissociation and spreading on the substrate to the deposition parameters such as substrate temperature, cluster velocity, cluster temperature, and cluster size. We have attempted to model experimental trends. We discuss an interpretation of why high-quality growth may be achieved at lower substrate temperatures with the ICB technique, rather than with other methods.

Simulations of deposition and film growth are difficult since the film growth represents a process that is far from equilibrium, and also very substantial computational times are required for realistic simulations. Recently, a few molecular-dynamics (MD) simulations of the MBE process have been performed. Schneider, Schuller, and Rahman[6] (SSR) have simulated epitaxial growth on a Si(111) substrate using the Stillinger-Weber[7] (SW) potential. At intermediate substrate temperatures ($T/T_m \sim 0.4$, where T_m is the bulk melting temperature of the SW model) epitaxial growth was achieved, whereas low substrate temperatures ($T/T_m \sim 0.01$) led to the growth of amorphous layers.[6] The presence of overlayer atoms was found to improve the crystallinity of the lower layers. These results contrast with the results of simulations using Lennard-Jones potentials[8] which led to epitaxial close-packed layers at both intermediate and low substrate temperatures, with a number of voids and defects present at the lower-temperature simulation.

Recently, Gawlinski and Gunton[9] have simulated the growth on a Si(100) substrate using a scheme in which 256 Si atoms [comprising eight Si(100) layers] were deposited over $(12-19)\times 10^3$ time steps (98–143 ps) and then allowed to anneal over 50×10^3 time steps (383 ps). They confirmed the presence of an epitaxial temperature below which amorphous growth was found. Dodson[10] has studied the dynamics and trajectories for atoms incident on Si(111) at incident energies exceeding 10 eV, and found surface channeling of the incident atoms for incident angles less than an energy- and orientation-

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dependent value. Dodson[11] also investigated the growth with Monte Carlo simulations, and found that the adsorbate displayed a metastable structure at a coverage of 0.33 monolayer (ML) that precluded epitaxial growth. Using molecular dynamics, Khor and Das Sarma[12] have studied the surface diffusion of adsorbed atoms on silicon surfaces and found that dimer diffusion is comparable to single-adatom diffusion. Kobayashi and Das Sarma[13] have modeled the conditions necessary for growing epitaxial Si_xGe_{1-x} overlayers with Monte Carlo simulations. Monte Carlo simulations including those of Singh and co-workers,[14] and Ghaisas and Madhukar,[15] have simulated the semiconductor film growth and calculated the intensity of reflection high-energy electron-diffraction (RHEED) oscillation spectra during the growth.

All of the simulations mentioned so far involved studies of single atoms deposited on silicon surfaces. On the other hand, Muller[16] has simulated the deposition of clusters on a close-packed substrate using two-dimensional molecular-dynamics simulations with Lennard-Jones pair potentials. Muller[16] found that incident cluster kinetic energies per atom of the order of the bond strength were needed to produce homoepitaxial films which were close packed and almost defect free. It is hard to generalize these results directly to the silicon ICB case since (i) atomic diffusion is quite different in two dimensions than in three dimensions, and (ii) the dynamics of open covalent systems differs substantially from that of the close-packed systems. Blaisten-Barojas *et al.*[17] have studied the melting and freezing of Lennard-Jones clusters absorbed on a surface with three-dimensional molecular-dynamics calculations, and identified a transition temperature T_m, of the cluster, above which the cluster melts and wets the surface. The dependence of T_m on the strength of the cluster-substrate interaction was studied.

In this paper we study the dynamics of cluster deposition, which has not been addressed in the previous simulations[8-15] that primarily involved deposition of single atoms. We identify growth conditions that lead to a high surface diffusion and spreading of the clusters—a feature necessary for epitaxial growth. These simulations have been performed with a view toward initiating a longer-range theoretical study of epitaxial growth from cluster-beam deposition as well as exploring the feasibility of such a computational program.

Prior to studying the cluster-deposition process, we investigate the conceptually simpler problem of the energy relaxation and dynamics of single-atom deposition (Sec. III). This serves both as a comparison and a calibration for the cluster results. The dynamics of atom adsorption has an important bearing on what the acceptable theoretical deposition rates are for MBE simulations. Owing to limitations of computer time, theoretical deposition rates are larger than experiment, by as much as several orders of magnitude.[13] Theoretically, it is important for simulation times to be long enough to adequately account for surface diffusion. Further, it is often difficult to achieve a steady-state growth mode in the simulations,[9] and some energy-transfer processes (e.g., channeling) may be very slow.[10] We estimate the times needed for a steady-state growth process with the single-atom–deposition simulations and compare these times to those employed in earlier simulations.

The computational model and system used in the simulations is discussed in Sec. II. The dynamics of single-atom–deposition and film-growth simulations from atom deposition are described in Sec. III. The cluster-deposition results are discussed in Sec. IV. Finally, we give a brief summary and outlook for future work regarding epitaxial growth simulations from cluster-beam deposition in Sec. V.

II. COMPUTATIONAL METHODS

The simulation of semiconductor thin-film growth processes requires a model that is capable of describing the structural energy of a semiconductor over a wide range of structural configurations. An atom impinging on the substrate during a film-growth process experiences a variety of bonding configurations, ranging from the initial nonbonded state to a partially bonded surface atom state to a more fully bonded bulklike atomic site after film growth. At the outset, then, classical models fitted to small deviations to the diamond structure are inappropriate for film-growth studies. Recently, a number of classical models that globally describe a range of silicon structures have been developed, by Stillinger and Weber,[7] Biswas and Hamann,[18,19] Tersoff,[20] Dodson,[21] and Baskes,[22] among others. *A priori,* all these models may be equally suitable for simulations of thin-film growth processes. We have selected to employ the Biswas-Hamann[18] model of separable two- and three-body interatomic Si potentials. A strengthening of the three-body potential by a factor of 2.50, compared to that originally used in Ref. 18, has been adopted. This change in the three-body strength was found to be necessary for describing amorphous silicon.[23,24] The model was originally developed by fitting to first-principles total-energy calculations for bulk-, surface-, and defect-Si configurations. Relative to the original model,[18] the factor 2.50 makes the metallic-Si phases (with coordinations equal to or greater than 6) energetically more unfavorable than in the original model.

In the molecular-dynamics calculations, Newton's equations of motion have been integrated in time, with the Gear algorithm, for a collection of substrate and deposited Si atoms. We used a molecular-dynamics time step (Δt) of 0.0037 ps, which is significantly smaller than the Si–optical-phonon period of 0.0638 ps. In earlier simulations we estimated the melting temperature of the original Biswas-Hamann potential model to be between 0.24 and 0.26 eV. This estimate was based on calculations of the pair-correlation function $g(r)$, the energy, and the diffusivity of bulk-Si systems, as a function of temperature. This is somewhat higher than the experimental melting temperature $k_B T_m$ of 0.147 eV. In our simulations temperatures are often expressed in terms of the melting temperature of the original model (0.24 eV), since this represents the relevant physical comparison.

A significant advantage of the molecular-dynamics simulation method is that no *a priori* assumptions about

the bonding energies, adsorption sites, or crystallinity of the deposited atoms are needed. The microscopic energetics depends on the underlying classical model used.

We have studied the dynamics and energy relaxation of single-atom and cluster deposition on Si(111) substrates. The simulation system (Fig. 1) consisted of N_1 movable (111) layers above N_2 immobile (111) layers that modeled the underlying crystal. Systems with $N_1=8, N_2=4$ ("thick substrate") and $N_1=2, N_2=4$ ("thin substrate") were examined. Single atoms or clusters with center of mass velocity v_z in the $-z$ direction were incident on the substrate. A rectangular cell, with dimensions 24.3 and 28.04 Å, consisting of 96 Si atoms per (111) double layer, was used, with periodic boundary conditions in the x and y directions. An in-plane lattice spacing of 4.05 Å was used for the Si(111) substrate. Methods used to control the substrate temperature are discussed in the following section.

III. SINGLE-ATOM-DEPOSITION RESULTS

A. Dynamics and energy relaxation

With a view toward simulating the growth of thin films and understanding the physical processes important in film growth, we have studied the energy relaxation and dynamics of a single Si atom deposited on a substrate that is maintained at a controlled temperature T_s. The deposition parameters that are studied are T_s, the incident velocity v_z, the angle of incidence, the deposition site, and the thickness of the substrate system. These studies are with the Biswas-Hamann Si potential model. A brief comparison is made later with the Stillinger-Weber potential. The deposition of a single atom is conceptually easier than the deposition of a continuous stream of atoms, as in the MBE process. We expect the dynamics of the single-atom simulations to be extremely useful in further studies of the MBE process, particularly in defining acceptable theoretical growth rates. We expect these results to be very useful to other simulation studies, in calibrating other theoretical classical models.

A Si atom with velocity v_z towards the substrate was introduced in the system from a large enough height so that it was outside the range of interaction (5.0 Å) of the substrate atoms. In any thin-film growth experiment heat energy is added to the surface by the deposited species. The thermal conductivity of the substrate allows this heat to be transported into the bulk of the substrate material. In our simulations we model this thermal-conduction process by monitoring the average temperature of the N_1 substrate layers every m steps, m conveniently chosen to be 10. If this substrate temperature exceeds the desired temperature T_s, the atom velocities in the N_1 layers are rescaled to maintain a constant T_s. This amounts to controlling the single (111) double layer for the thin substrate and the upper four (111) double layers for the thick-substrate simulations. Values of m between 10 and 30 appeared to produce similar results, whereas values larger than 100 made the energy-transfer process considerably slower. The substrate layers act as a heat reservoir that absorbs heat through collisions with the deposited species. Other schemes to control the substrate temperature are studied later in this section.

The effect of depositions at two different substrate temperatures (0.06 and 0.12 eV) are shown in Fig. 2, where

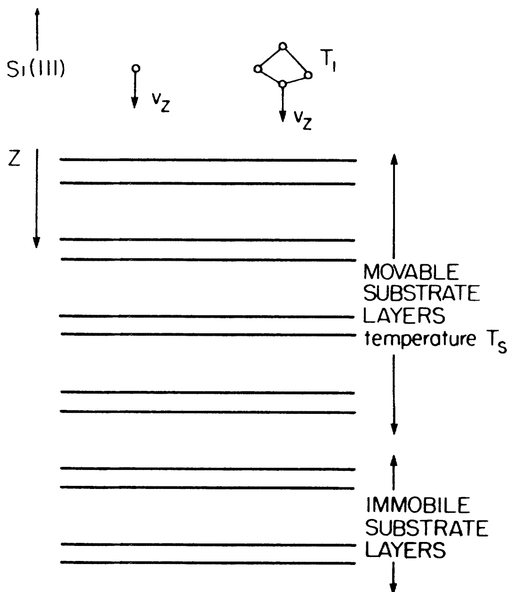

FIG. 1. Schematic diagram of the system used for the simulations. The substrate consists of four Si(111) double layers, below which are two fixed Si(111) double layers. Atoms or clusters (with internal temperature T_i) are incident with center-of-mass velocity v_z on the substrate.

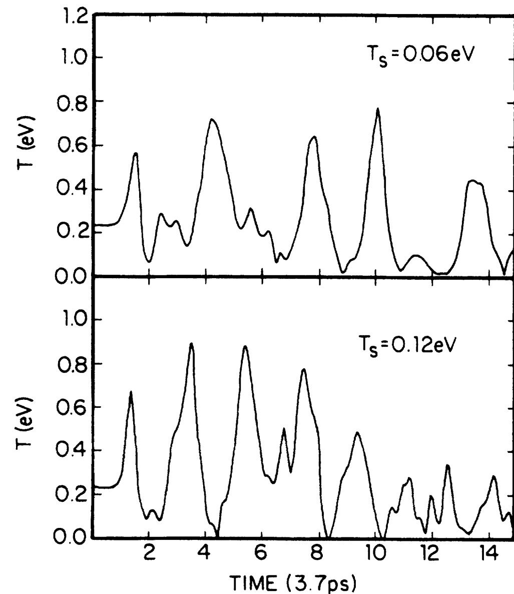

FIG. 2. Temporal variation of the translational temperature (i.e., $\frac{2}{3}$ of the kinetic energy) of an atom deposited on an eight-layer Si(111) substrate, for two different substrate temperatures T_s, displaying the slow equilibration of the deposited atom. The three-fold hollow site was employed in both cases. As in Figs. 3–7, the kinetic energies are averages over every 10 time steps, and 3.7 ps represents 1000 molecular-dynamics time steps.

the kinetic energy of the deposited particle is plotted as a function of time. The thicker eight-layer movable substrate was utilized, and the atoms were chosen to be incident on the three-fold hollow site. In both cases the predominant features are the large kinetic-energy oscillations and a heating of the incident particle to temperatures above 0.6 eV; that is, well above its energy at the bulk melting point. The oscillations persist beyond 10 000 time steps (37 ps), and large fluctuations of the kinetic energy are present even at the end of the simulations. These features of the energy oscillations are generally independent of the specific deposition site, as illustrated by Fig. 3, which shows depositions on two random positions over the substrate.

The initially large energy gain of the incident particle is not surprising since the atom traverses down a deep potential-energy well as it approaches the surface. This potential-energy well describes the bonding with the substrate atoms and has a depth of 1.0–2.0 eV, i.e., of the order of the bond energy. It is surprising, though, that the oscillations of the atom above the surface are only weakly damped. The period of the energy oscillations ranged from ~6.3 to 7.0 ps, representing a mode with frequency ~0.14–0.15 THz. We analyzed the nature of this low-frequency surface vibration mode by plotting the z and x positions of the atom as a function of time (Fig. 4). Oscillations of the x coordinate have a period that is twice the value of the z-coordinate oscillations. This suggests that the atom is vibrating between the two wells of a double-well potential on the surface. As illustrated in Fig. 3, the minima (maxima) of this well correspond to the maxima (minima) of the kinetic energy.

We investigated whether the energy oscillations were more damped when the impinging atom was incident obliquely on the surface, by choosing an angle of incidence of 45° with the surface normal, with results illustrated in Fig. 5. The atom heats up to a somewhat higher temperature than previously, simply because of its higher initial kinetic energy. Similar energy oscillations are found although the atom traverses along the surface.

The oscillations of the impinging atom were only damped slowly for all deposition cases considered. We note that these results hold only for a smooth surface.

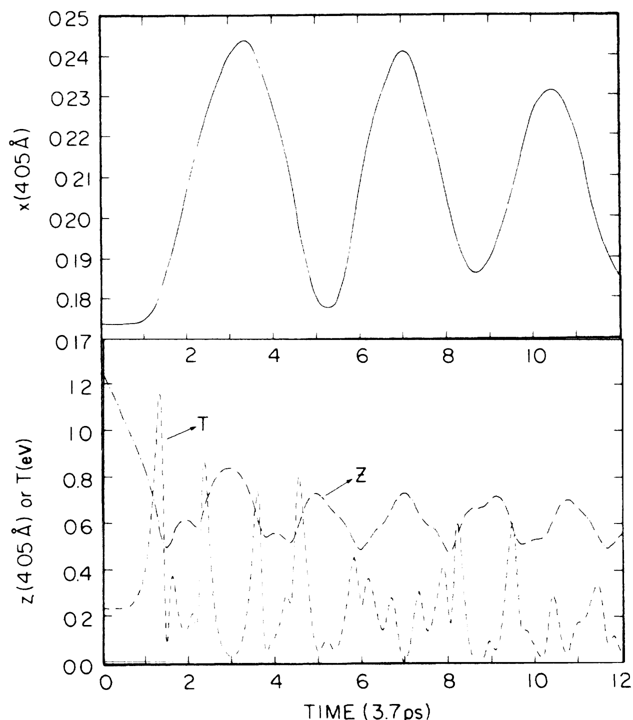

FIG. 4. Temporal variation of the x coordinate (upper panel) and the z coordinate and translational temperature (lower panel), for an atom deposited on the Si(111) substrate.

We expect the energy-transfer rates to be considerably faster for a rough or amorphous surface where collisions in the surface plane would also transfer energy to the substrate.

All the simulations described (Figs. 1–5) utilized the "thick"-substrate system. Simulations with the "thin" substrate led to similar results, except that longer equilibration times were observed. We expect the "thick" substrate to be more realistic since it allows for heat transport normal to the substrate. The damping of phonons normal to the substrate may lead to faster equilibration times.

In view of the long damping times, we considered another cooling scheme that has led to faster energy-

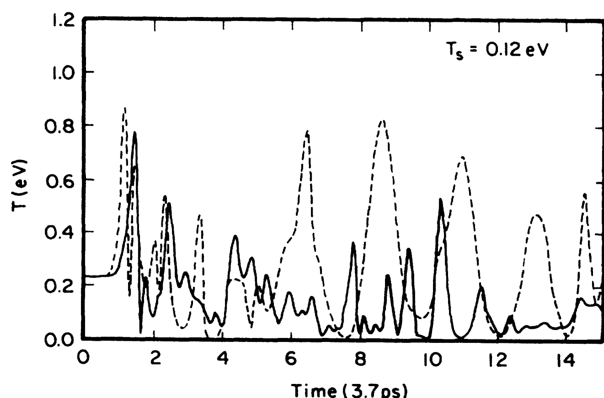

FIG. 3. Variation of the translational temperature of an atom deposited on the eight-layer Si(111) substrate. Depositions on two random sites are shown.

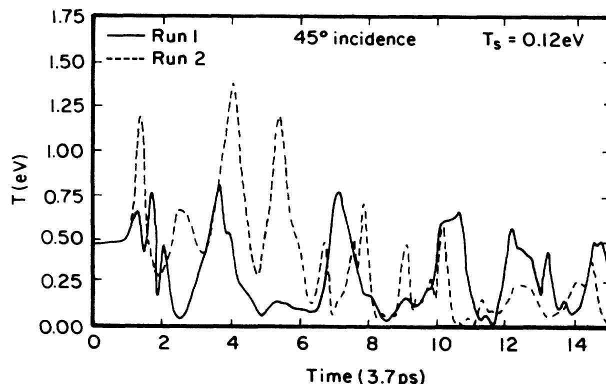

FIG. 5. Variation of the translational temperature of two atoms incident at an angle of 45° to the surface normal.

transfer rates. In this scheme the velocities of all the atoms (substrate and deposited atom) were rescaled if the average kinetic energy of the entire system (substrate and deposited atom) exceeded the desired value (0.18 eV). As expected, the incident atom cools more rapidly, as illustrated in Fig. 6. However, the direct damping of the incident-atom velocity affects its dynamics and inhibits the surface diffusion, a feature we feel may not be desirable for epitaxial growth simulations. We expect this scheme to lead to growth of amorphous layers.

We also considered a Langevin-dynamics method for the substrate atoms, where these atoms are connected to a heat bath that provides a stochastic force and viscous friction. Newton's equations of motion without any damping were solved for the deposited atom. Generally, this scheme maintained the substrate temperature at its desired value very well, but was even slower in damping the velocity of the incident atom than the velocity rescaling scheme.

For comparison, we show atom-deposition results with the shorter-range Stillinger-Weber potential in Fig. 7, for two values of the incident velocity. The deposited atom initially heats up to a higher temperature, but equilibrates with the substrate significantly faster than deposition with the Biswas-Hamann potential. Large energy oscillations are absent, and equilibration times are of the order of 8000–10 000 time steps (30–37 ps). The vibrational frequencies of the SW potential may be softer than the BH model, leading to a higher-energy transfer rate with the SW model. Such energy-relaxation calculations may serve as useful calibrations of molecular-dynamics models.

B. Growth simulations

In the MBE simulations of Schneider *et al.*[6] using the Stillinger-Weber[7] Si potential, atoms were continuously deposited with times between successive depositions that were much shorter than the equilibration times found here. The deposition rate used was 1 atom every 0.14 ps in a substrate of 448 atoms. We have found that under similar deposition rates the system does not equilibrate

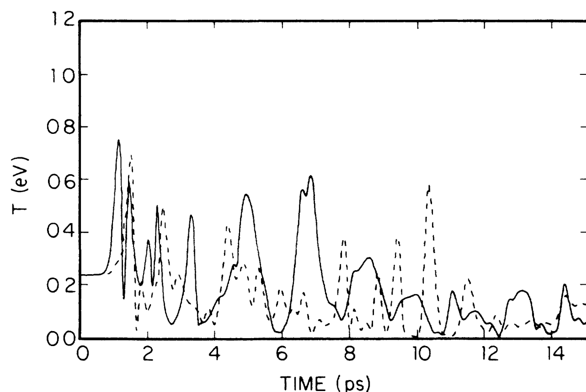

FIG. 6. Variation of the temperature of a normally incident particle where the temperature was controlled by damping the velocities of both substrate and deposited atoms every 10 time steps.

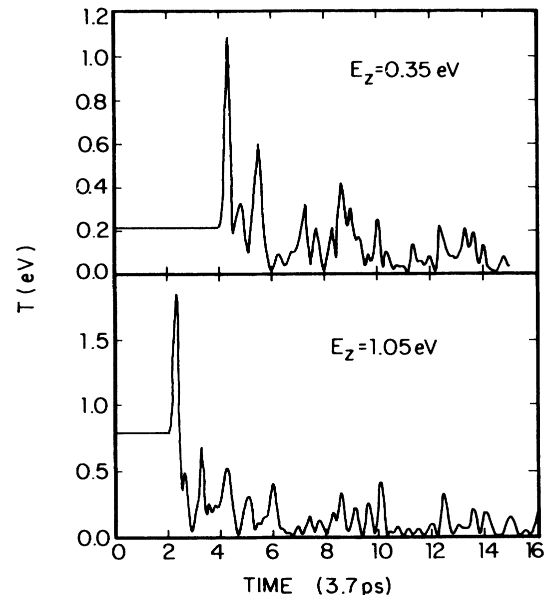

FIG. 7. Variation with time of the kinetic energy of an incident atom using the Stillinger-Weber Si potential model, for two initial kinetic energies E_z.

after each deposition event, but, instead, the entire deposited layer heats up above the melting temperature. Our interpretation of the results of SSR (Ref. 6) are that they were observing a solid growing into a liquid instead of the MBE-type growth. This may be why three to four deposited layers were necessary to achieve crystal growth at the interface.

Our interpretation of the SSR results are also based on two simulations where we continuously deposited atoms at rates comparable to those used by SSR. The "thin" substrate, similar to that employed by SSR, was employed. In the first case we used a deposition rate of 1 atom every 0.65 ps. After deposition of the first double layer, the temperature of the deposited atoms was 0.40–0.60 eV, i.e., well above the melting point. Annealing, i.e., allowing the system to run without further deposition, for ~237 ps (64×10^3 time steps) was needed to cool the deposited atoms back to the substrate temperature. The crystallinity of the deposited layer was improved by deposition of a second double layer of atoms with similar deposition and annealing times. The resulting first deposited layer (Fig. 8) is epitaxial with deposited atoms exhibiting a wurtzite stacking above the substrate. There are four vacancies in this epitaxial layer, which otherwise has a continuous array of sixfold rings. The second (111) double layer above the substrate did not crystallize since it was still mobile with temperatures of the order of 0.22–0.26 eV, i.e., close to melting at the end of the simulation. The wurtzite stacking is not surprising since in the BH Si model the bulk-diamond structure is only 0.01 eV/atom more stable than wurtzite.

We achieved another epitaxial growth simulation by a similar deposition-and-anneal method, using a slower deposition rate of 1 atom per 2.96 ps followed by ~92 ps of annealing. A total simulation time of 376 ps was in-

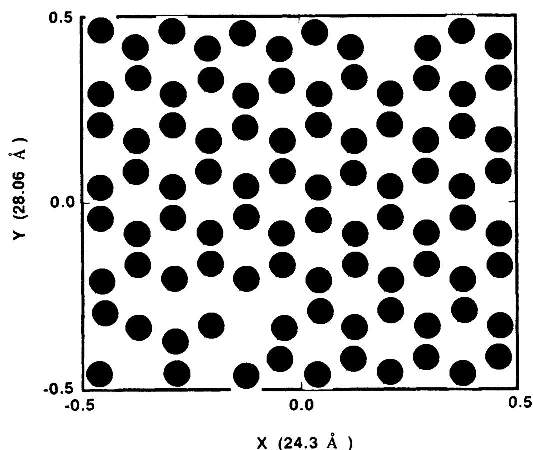

FIG. 8. Projection of the atoms in the first deposited layer using a faster deposition rate of 1 atom per 0.65 ps (175 time steps). Not shown is the modulation in the z direction, which is similar to a Si(111) surface. The atoms primarily show a wurtzite-type stacking above the substrate.

volved for each layer, compared to 299 ps in the previous case. Good epitaxy of the first deposited layer (Fig. 9) was achieved with a diamond-structure stacking. The deposited atoms reach temperatures of $\sim 0.3-0.4$ eV, i.e., they are not as hot in the earlier simulation, but the deposited atoms remain hot and mobile for a longer time than in the earlier simulation. In both these simulations crystallization occurs at a solid-liquid interface.

The long equilibration times found here indicate a crucial difference between growth of silicon and Lennard-Jones systems. Equilibration of close-packed Lennard-Jones systems is considerably faster, whereas open covalent sytems are more floppy owing to the orientational ordering needed for crystallization and the soft bond-bending modes of crystal Si.

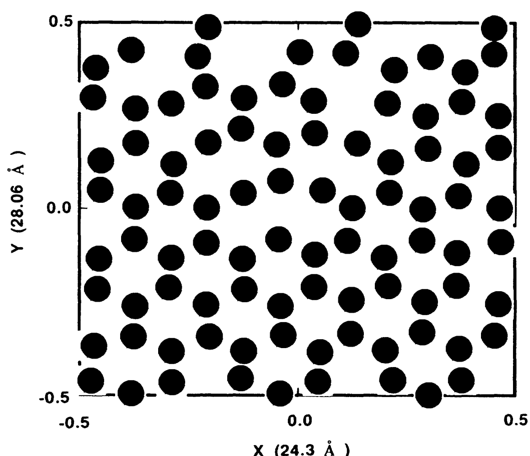

FIG. 9. Projection of atoms of the first deposited layer using a slower deposition rate of 1 atom per 2.96 ps (830 time steps). The atoms are primarily show a diamond-structure stacking above the substrate.

In the following section we study cluster deposition with the BH potential and find the energy relaxation of clusters to be significantly faster than for single atoms.

IV. DYNAMICS OF CLUSTER DEPOSITION

We have studied the energy deposition and dynamical evolution of Si-atom clusters deposited on the Si(111) surface. All simulations were performed with the thick-substrate system ($N_1=8$, $N_2=4$). The simulations described in this section should be viewed as the first step towards a full simulation of the film-growth process from a continuous beam of clusters. We demonstrate in this section that a simulation of cluster beam growth is feasible, and make estimates of the theoretical growth rates and computational times needed for such simulations. We present results that define a range of optimum deposition parameters and cluster sizes for high-quality film growth from cluster beams.

We first compare the dynamics of cluster deposition with that of single-atom deposition in Fig. 10, which shows the average temperature of N-atom clusters as a function of time, compared to the single-atom case, for $N=8$, 33, and 50. In all cases the thick substrates were maintained at the temperature of 0.12 eV, and all clusters had the same center-of-mass velocity as the single atom (4890 m/s equivalent to a translational energy of 0.23 eV). To ensure that the results were not biased by a particular choice of the initial cluster structure, we chose amorphous clusters that were fragments of previously generated bulk amorphous-silicon networks, with average internal temperatures of $\sim 0.5 k_B T_m$, 0.12 eV).

The dominant difference between cluster and single-atom depositions is that the large energy oscillations of the deposited atom are absent for the clusters. Some higher-frequency energy oscillations are present for the eight-atom cluster, but these get smoothed out for the 33- and 50-atom clusters. The clusters initially heat up to a much lower temperature (0.4–0.5 eV), and also equilibrate much faster to the substrate temperature (in $\sim 10^4$ time steps, or 37 ps) than the single-atom case.

There are two physical reasons for these effects. Firstly, the atoms within the cluster interact strongly with each other as the cluster approaches the surface. These strong interactions occur especially when the cluster atoms nearer the substrate have passed through the surface bonding potential well and are "feeling" the repulsive interactions with the substrate, resulting in a velocity away from the substrate, whereas the cluster atoms further from the substrate are still traversing towards the bottom of the potential well (towards the substrate) and are heating up. This process results in strong collisions between the cluster atoms which destroy the coherent energy oscillations that are present for the single-atom case. The cluster becomes liquidlike as it approaches the substrate, although it had an initial glassy structure. As the results of Fig. 8 indicate, thin-film–growth simulations

with cluster deposition may require significantly less computer time than single-atom deposition, because the adsorbed atoms equilibrate with the substrate more rapidly, allowing the next cluster to be deposited sooner than with single-atom–deposition simulation.

Initially, the clusters have a considerable amount of binding energy. As the cluster adsorbs, a smaller increase in the binding energy per atom is involved than for the single-atom case, which leads to less kinetic energy gained or less heating of the cluster than the atom.

We believe that an important requirement in growing defect-free epitaxial films from the cluster deposition is that each impinging cluster on the substrate should dissociate and spread in a uniform layer on the substrate. The following cluster will then impinge on a relatively smooth substrate. If the surface diffusion of the cluster atoms is low, the clusters will stick on the surface and the resulting film will consist of a inhomogeneous collection of such clusters, as found previously by Muller[16] in two-dimensional simulations. We explored the parameter space of deposition parameters that is needed for high cluster spreading. Since small clusters (e.g., $N=8$) are expected to dissociate more easily upon deposition, we confined our initial investigation to the larger $N=33$ atom cluster. We found that the surface diffusion of the cluster could be conveniently characterized by mean-square transverse positions of the atoms in the cluster relative to the cluster center of mass, defined as

$$\eta(t)=\sum_{i=1}^{N}[x_i(t)-x_{\mathrm{c.m.}}(t)]^2+[y_i(t)-y_{\mathrm{c.m.}}(t)]^2 . \quad (1)$$

$x_i(t)$, $y_i(t)$, and $z_i(t)$ are the coordinates of the ith atom in the cluster at time t, and $(x_{\mathrm{c.m.}}(t), y_{\mathrm{c.m.}}(t), z_{\mathrm{c.m.}}(t))$ is the dynamical position of its center of mass. It is convenient to normalize η by the value of η for the most compact N-atom cluster of an ideal Si(111) double layer.

We studied the diffusivity of the cluster as a function of the cluster internal temperature, the initial cluster velocity, and the substrate temperature. Experimentally, the cluster velocities can be easily controlled by varying the acceleration voltage in the ICB technique. The normalized index of spreading (η_{norm}) and the height of the center of mass ($z_{\mathrm{c.m.}}$) are plotted as a function of time in Figs. 11 and 12, for a sequence of five deposition simulations. In each simulation one of the three deposition parameters was varied from the parameters of the previous run.

As evident from the sequence of simulations 1, 3, and 4, the high initial center-of-mass velocity was the crucial variable necessary to achieve a high surface diffusion and consequent dissociation of the cluster. Concurrent with the large velocity v_z, it was necessary to maintain a surface temperature of about half the melting temperature (0.12 eV). When the initial translational temperature T_z was maintained at a high value (1.05 eV), but T_s was reduced by a factor of 4 (simulation 5), the surface diffusivity was considerably inhibited. This indicates that

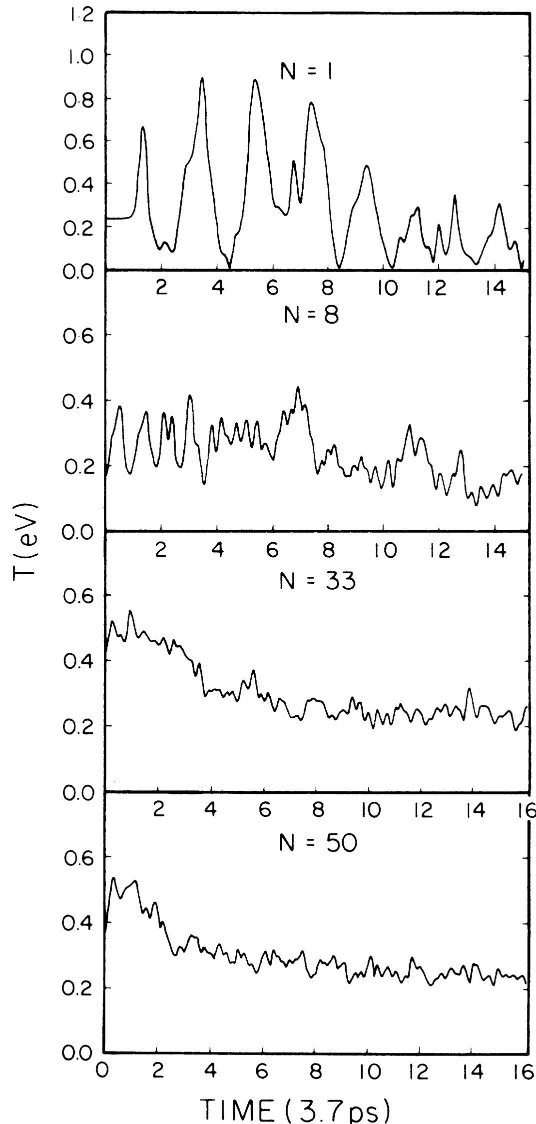

FIG. 10. Comparison of the temperature of N-atom clusters as a function of time during deposition simulations. In each case the substrate was maintained at the same temperature (0.12 eV).

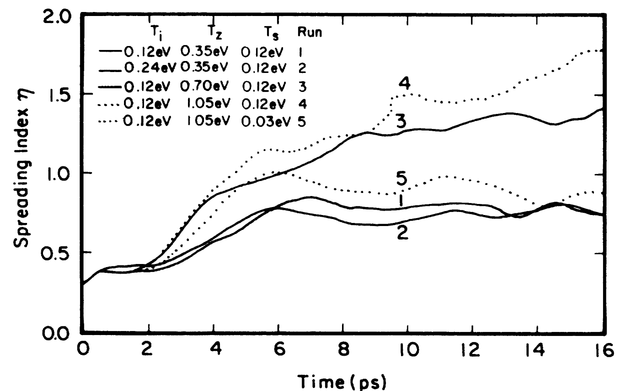

FIG. 11. Time evolution of the normalized spreading index [Eq. (1)] for 33-atom clusters. The deposition conditions, consisting of the cluster internal temperature (T_i), cluster translational temperature (T_z), and surface temperature (T_s), were varied in each case.

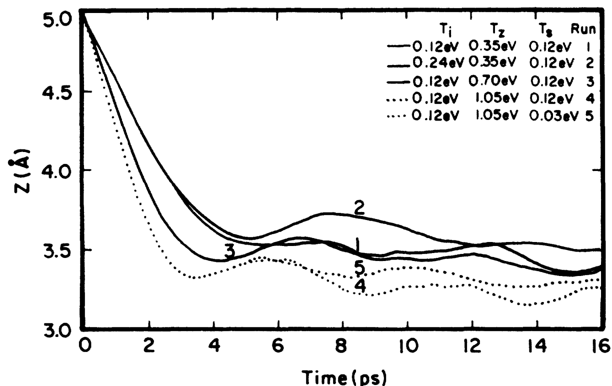

FIG. 12. Time evolution of the z coordinate of the center of mass of the clusters deposited under different deposition conditions. See caption for Fig. 11. The simulations are the same as in Fig. 11.

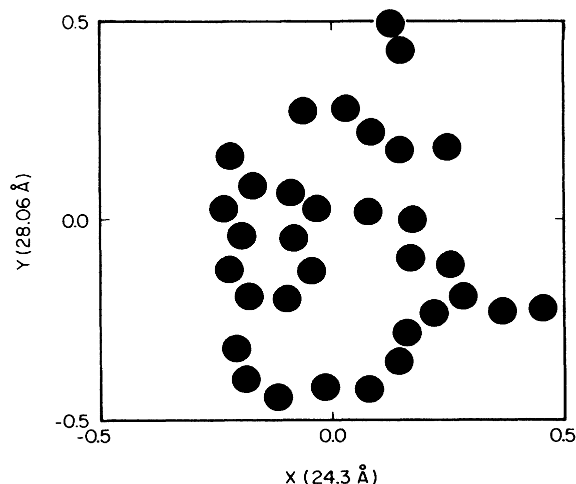

FIG. 13. Projection of the atoms in the x-y plane after the deposition process for a 33-atom cluster that displayed large surface diffusion (run 4, Fig. 11).

there may be a strong coupling or tradeoff between the variables T_s and T_z—a larger diffusivity may be obtained by increasing the surface temperature rather than the incident velocity. This feature provides an interpretation of the fact that good epitaxial growth may be obtained at lower substrate temperatures with ICB than with other growth processes. The incident velocity of the ionized cluster can be much higher than the thermal velocities achieved in other growth processes. With a higher cluster velocity it is possible to reduce the surface temperature and achieve the same surface diffusivity.

The cluster translational energy of 1.05 eV/atom (run 4), which achieved good surface diffusion, is about 3 times the energy of the atoms at the melting temperature and compares well with experimental estimates of the cluster kinetic energies of $\sim 1.0-10$ eV/atom by Kuiper *et al.*[25]

For the clusters that diffused poorly on the substrate (runs 1 and 2), we found that having an initially molten cluster had little effect on the cluster spreading. This is presumably because even clusters that are initially below T_m heat beyond their melting point as the surface is approached, and "memory" of its initial configuration is lost. The conclusions for the cluster dynamics are also illustrated in Fig. 12, where the cluster that diffuses the most on the surface has the smallest mean height above the surface.

The difference between the cluster that spread (run 4) and the cluster that did not spread is visually evident in Figs. 13 and 14, which shows the projected (x,y) coordinates of the cluster atoms well after deposition. The highly spread cluster has all its atoms in a single double layer above the substrate, with atoms having diffused to the edges of the cell (Fig. 13). A six-member ring appears in Fig. 13, but clearly deposition of further clusters would be required to form an epitaxial layer. However, the cluster with small surface diffusion displays a layering into two distinct deposited layers, with the formation of five and sevenfold ring structures (Fig. 14).

We have investigated the sensitivity of these results to the cluster size N, and have estimated an optimum cluster size for efficient growth simulations. The finite size of our simulation system (96 atoms per double layer) limits the maximum possible cluster size to about 60 atoms. For clusters larger than 60 atoms the cluster atoms may interact with the periodic images of other atoms of the cluster, a feature which is unphysical. Depositions were performed for $N=12$ and 50, for two values of the initial translational energy (0.23 and 1.05 eV), corresponding to simulations 1 and 4 in Fig. 11. The 12-atom cluster exhibited large spreading with $\eta > 2$, whereas the 50-atom cluster exhibited limited spreading with $\eta < 1$. In Fig. 15 we have plotted the efficiency of the simulation, defined as the reciprocal of the simulation time, for deposition of a full Si(111) double layer. The simulation time was estimated by assuming that clusters could be deposited successively with the time interval between successive clusters being the equilibration times estimated from Fig. 10.

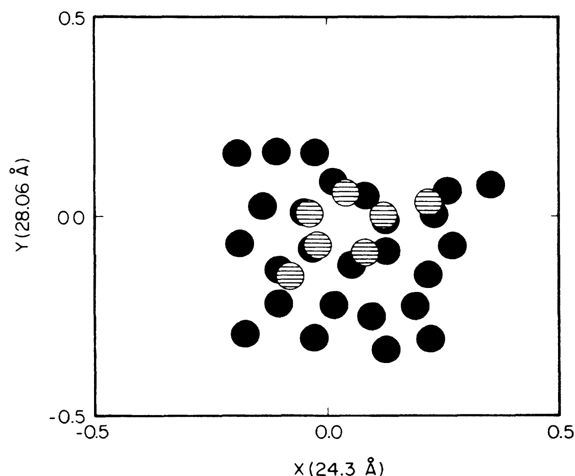

FIG. 14. Projection of the atoms in the x-y plane after the deposition process for a 33-atom cluster that displayed limited surface diffusion. Second-layer atoms above the surface are represented by hatched circles, first-layer atoms by solid circles.

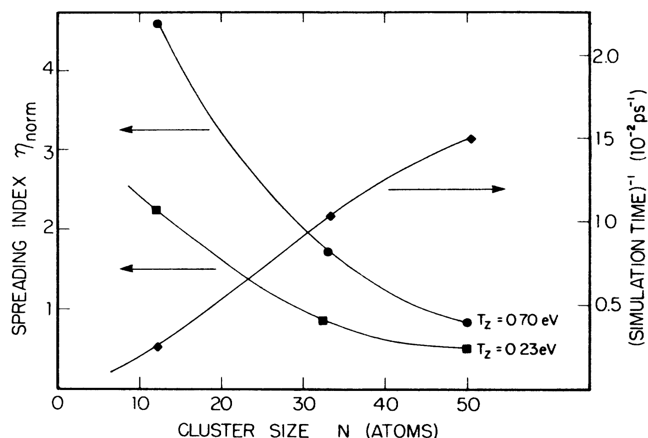

FIG. 15. Normalized spreading index for clusters of various sizes for simulations using two different initial cluster translational energies (T_z). The left-hand axis is the inverse of time needed for depositing a (111) double layer.

We note that the efficiency curve crosses the large spreading curve at a cluster size in the range $N=30$, which may be identified as an optimum cluster size for film-growth simulations.

V. SUMMARY

In summary, we have compared the energy relaxation and dynamics of single-atom and cluster deposition on a Si(111) substrate. We have characterized a set of deposition conditions that lead to high surface diffusion and spreading of the deposited clusters. We find that cluster-deposition simulations can be achieved in substantially less computer time than single-atom deposition. In our Si(111) system we estimate that each (111) double layer can be deposited in 225–300 ps [$(6-9)\times 10^4$ time steps]. This estimate is based on equilibration of each incident 33-atom cluster after adsorption and allowing for surface diffusion on the substrate. In future work we plan to grow films with the cluster-deposition process and study the film growth under various deposition conditions.

Previous silicon-deposition simulations utilized high deposition rates and we infer that they probably observed the crystallization at a solid-liquid interface. These results probably relate more closely to liquid-phase epitaxial growth[26,27] than to molecular-beam epitaxy. We stress that slower deposition rates and allowing for adequate surface diffusion is important in achieving good-quality film growth.

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