

MOLECULAR-DYNAMICS SIMULATION OF THIN-FILM GROWTH

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ABSTRACT

The epitaxial growth of thin films has been studied by molecular-dynamics computer simulation. In these simulations atoms are projected towards a temperature-controlled substrate, and the equations of motion of all atoms are solved for a given interaction potential. The calculations give insight into the microscopic structure of thin films, the dynamics of the adsorption process, and they help answer the way in which substrate temperature, form of the substrate, flux of impinging atoms, and form of the interaction potential, affect epitaxial growth. Simulations were performed for monatomic and binary systems with spherically symmetric atomic interactions, and for systems in which the atoms are interacting via a three-body potential to simulate the epitaxial growth of silicon.

INTRODUCTION

Epitaxial growth from the vapor phase is a subject of much experimental and theoretical interest [1]. The understanding of epitaxial thin-film growth is of importance for the preparation of new materials and novel devices that exhibit unusual physical phenomena; in addition, thin-film growth is already of technological importance for semiconductor and superconducting devices, solar cells, magnetic recording, etc.

The theoretical studies to date have mostly been based on phenomenological, thermodynamic models which rely on a variety of parameters whose significance, quantitative and qualitative, is unknown a-priori [2]. With the advent of supercomputers, it has now become practicable to apply the method of computer simulation to problems of epitaxial growth through the use of realistic models with a sufficiently large number of atoms [3]. We have done what we believe are the first full molecular-dynamics (MD) studies of epitaxial growth; in other words, once the interatomic potential and the procedure for adjusting the substrate temperature are given, the classical equations of motion for all atoms are solved in the usual way without any further approximations.

SIMULATION MODEL

Our molecular-dynamics models consist of an atomic substrate which is placed in the plane $z=0$. The substrate is built of two or three atomic planes stacked properly above each other. Each of the substrate planes contains 224 atoms in a triangular arrangement, thus simulating the (111) surface of the systems studied by us. The atoms in the bottom substrate layers are fixed at their ideal lattice sites, whereas the atoms in the uppermost substrate layer are allowed to move as part of the dynamical system. The rectangular simulation cell is open along the positive z axis, and periodic boundary conditions are applied in the x - y plane which contains the substrate. To simulate the deposition process, atoms with a Gaussian

velocity distribution are introduced periodically at a certain height from the substrate, and the atoms are moving, at the moment of introduction, perpendicularly towards the substrate. The beam temperature is 30-40% higher than the bulk melting temperature of the system being simulated. The temperature of the adsorbate is controlled via the substrate temperature T_S which in turn is adjusted by periodically scaling the velocities of the atoms in the movable substrate layer. The equations of motion are solved numerically with an integration step Δt , and the trajectories of all atoms are followed throughout the simulation as in all standard MD calculations.

RESULTS

In this paragraph, results of growth simulations will be presented for two different types of systems: monatomic systems with spherically symmetric atomic interaction (metal-like), and binary metal-like systems.

Metal-like Systems

In these systems [4] the atoms interact with each other through the Lennard-Jones potential

$$v(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6] . \quad (1)$$

The units of length and of energy are, as usual, taken to be σ and ϵ , respectively. The substrate consists of two close-packed planes representing the (111) surface of an fcc crystal (for the Lennard-Jones potential a close-packed lattice is the stable configuration of atoms).

The calculations show that for spherically symmetric pair potentials, homoepitaxial growth yields well-formed crystallites at all substrate temperatures T_S , including absolute zero. Moreover, the dynamics plays a key role in the growth of these crystals even at the lowest temperatures.

For the case $T_S=0$, the atom density along the z axis (perpendicular to the substrate) after the deposition of 2052 atoms is shown in Fig. 1. It can clearly be seen that the adsorbate consists of quite distinct layers

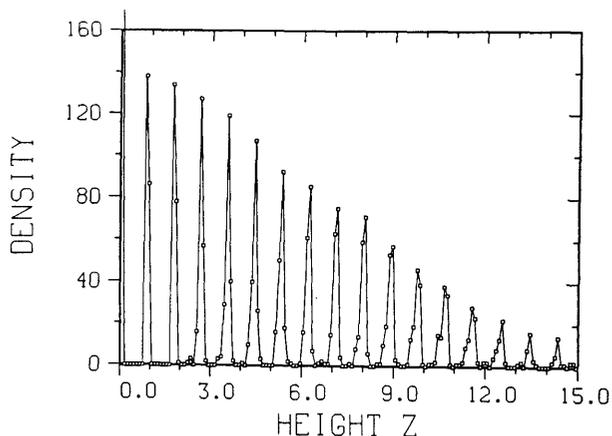


Fig. 1. Histogram of the number of atoms as a function of height z .

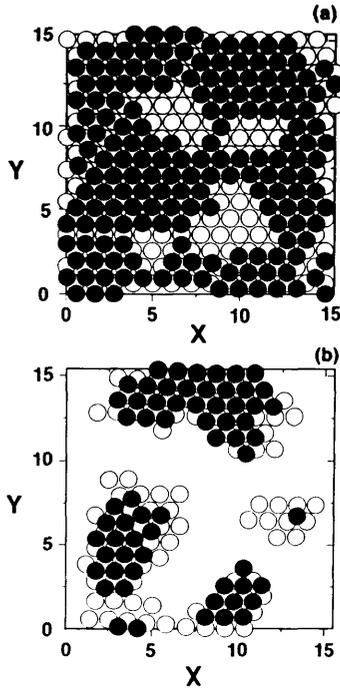


Fig. 2. Arrangements of atoms after the deposition of 680 atoms at $T_S=0$. (a) Atoms in the first deposited layer on top of the movable substrate layer. (b) Atoms in the fifth deposited layer on top of the fourth layer.

with no appreciable disorder in the z direction. Pictures of the arrangement of atoms within the layers (see Fig. 2) show the existence of grain boundaries and voids. The size of the voids increases with the distance from the substrate (compare Fig. 2a and 2b). The atoms are well arranged in triangular patterns with no evidence of in-plane disorder.

At intermediate substrate temperatures (about half the melting temperature), the layers become completely populated. The process of relaxation by which the layers are filled is illustrated by a trajectory plot in Fig. 3. This figure shows the trajectories of the atoms for the last 1500 integration steps of the simulation at a substrate temperature $T_S=0.4$, where $T_m=0.7$ is the melting temperature for the system in reduced units. During the deposition, the high mobility of atoms in the incompletely filled upper layers is responsible for the filling of the close-packed planes further below.

Binary Metal-like Systems

The purpose of these simulations [5] was to study the growth of a mixture of two differently sized Lennard-Jones particles as a function of relative atomic sizes. The results indicate that the ratio of atomic radii is the determining factor for amorphous growth.

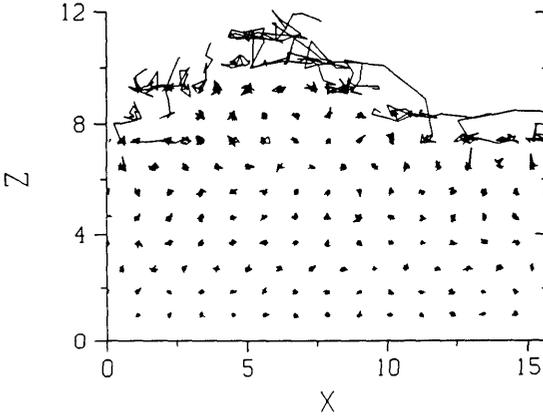


Fig. 3. Particle trajectories at $T_s=0.4$ (vertical cross-section).

There are two types of particles A and B interacting via standard Lennard-Jones potentials

$$v_i(r) = 4\epsilon [(\sigma_i/r)^{12} - (\sigma_i/r)^6] \quad (i = AA, BB, AB) . \quad (2)$$

The unit of length is taken to be σ_{AA} . Here $i=AA, BB, AB$ refer to the interaction between like particles of type A or B or unlike particles A and B. The length parameter σ_{AB} for the unlike particles is given by

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 . \quad (3)$$

This is the natural choice if σ is interpreted as usual as the atomic diameter. The substrate consists of two close-packed planes; each plane contains 224 Lennard-Jones atoms of type A. During deposition the two types of particles are introduced alternately, i.e., in equal numbers. Figure 4 shows the density of particles in the z direction for $\sigma_{BB}/\sigma_{AA}=0.900$ after the deposition of 3052 atoms at $T_s=0.4$. (In the preceding paragraph we have shown that $T_s=0.4$ is the optimum substrate temperature for layer-by-layer epitaxial growth in the monatomic case.) The figure shows that for this ratio of atomic sizes the growth is into well-formed distinct layers with no evidence for amorphous growth. Figure 5 shows the system in a vertical cross-section. The particles are mainly arranged in a lattice corresponding to the bigger atoms.

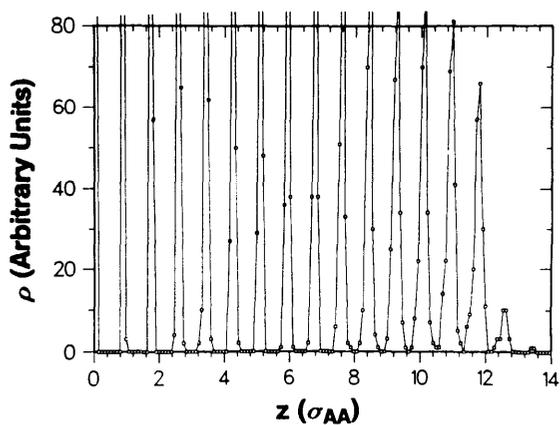


Fig. 4. Particle density versus height z for $T_s=0.4$ and $\sigma_{BB}/\sigma_{AA}=0.900$.

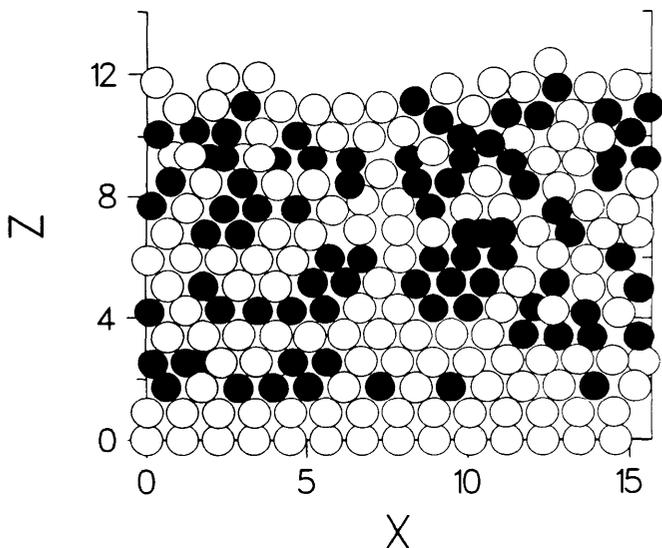


Fig. 5. Arrangement of atoms in a vertical slice, with $\sigma_{BB}/\sigma_{AA}=0.900$. Particles of type A are drawn with open circles, those of the smaller type B with solid circles.

As a function of σ_{BB}/σ_{AA} , a transition from crystalline-layered to a disordered growth occurs at a value of σ_{BB}/σ_{AA} , which is slightly lower than the above value $\sigma_{BB}/\sigma_{AA}=0.900$. Figure 6 shows the atomic density as a function of height z from the substrate for $\sigma_{BB}/\sigma_{AA}=0.875$. After about five atomic layers from the substrate the structure is not layered. Pictures of atomic arrangements show that the structure is quite disordered when compared to the $\sigma_{BB}/\sigma_{AA}=0.900$ case.

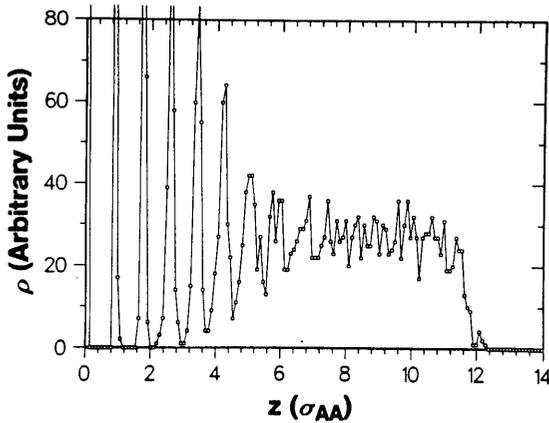


Fig. 6. Particle density versus height z for $T_s=0.4$ and $\sigma_{BB}/\sigma_{AA}=0.875$.

These calculations together with additional calculations for different values of σ_{BB}/σ_{AA} show that a rather abrupt change occurs in the growth mode at a value of $\sigma_{BB}/\sigma_{AA}=0.89 \pm 0.01$. Figure 7 shows the number of distinct layers as a function of σ_{BB}/σ_{AA} ratio. It is interesting that the transition is quite abrupt, almost like in a phase transition. Above $\sigma_{BB}/\sigma_{AA}=0.89$, the growth is into a layered crystalline structure with the lattice parameter determined by the largest of the two components. Below this value the growth is into an unlayered disordered structure after a few monolayers from the substrate. The change in the growth mode is rather abrupt contrary to what one might expect naively.

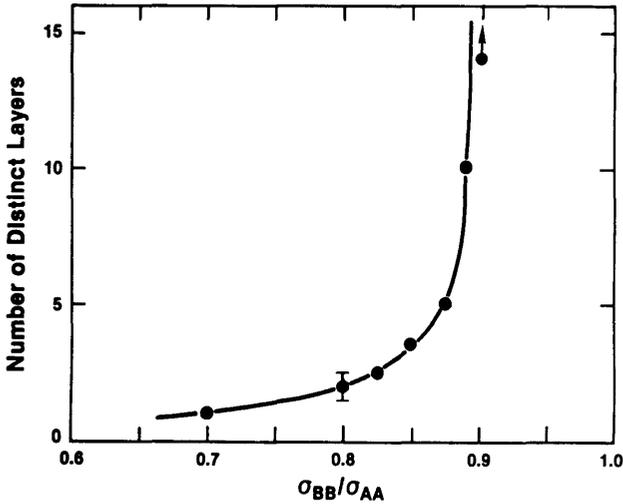


Fig. 7. Number of distinct layers as a function of the ratio σ_{BB}/σ_{AA} (substrate layers are not counted). The arrow indicates that even more layers are expected to form in the case $\sigma_{BB}/\sigma_{AA}=0.9$ (see Fig. 4).

CONCLUSIONS

A comparison of our results with experimental data is quite revealing [1]. It is well known that monatomic metals cannot be grown as amorphous films by using vapor-growth techniques. Metallic elements generally form small crystallites. However, elements that show directional bonding, e.g., Si, Bi, or Ga, can be grown as amorphous films with relative ease. Our results on the monatomic Lennard-Jones system are an indication of the former type of behavior. Since the interatomic force in our case is spherically symmetric, the growth is invariably into well-layered, close-packed structures, similar to what is observed for most metals.

We show that the stabilization of amorphous structures occurs if there are particles of differing sizes in the system. The results on the binary Lennard-Jones system are in good agreement with experimental observations. It is a well known empirical rule that the atomic radii of two metallic elements must differ by more than 10% in order for their binary alloys to form a glass [6]. The value of 10% is in accordance with our critical value for the ratio of atomic radii $\sigma_{BB}/\sigma_{AA}=0.89$.

An interesting and exciting recent development is the growth of silicon using phenomenological models [7]. Our full molecular-dynamics simulations confirm that amorphous structures can be obtained if the interatomic potential exhibits some anisotropy due to directional bonding [8]. In these simulations the atoms interact via a three-body potential developed by Stillinger and Weber [9] to simulate the properties of covalently bonded silicon. At intermediate temperatures the growth is into well-stacked and properly crystallized Si structures. At low temperatures the films grow in an "amorphous-like" structure. This is in accordance with experimental observation [10].

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