Role of Relaxation in Epitaxial Growth: A Molecular-Dynamics Study

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The epitaxial growth of a Lennard-Jones system is studied as a function of substrate temperature T_s and deposition rate. For all substrate temperatures the growth is into well-ordered layers. Layers become fully completed at intermediate T_s. At very low T_s the layers contain defects and voids; however, the atoms are still arranged in close-packed islands within the layers.

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The study of equilibrium or nonequilibrium crystal growth is a subject of much experimental and theoretical interest. The understanding of epitaxial crystal growth is of importance for the preparation of new materials and novel devices that exhibit unusual physical phenomena; in addition, thin-film growth is of technological importance for semiconductor and superconducting devices, solar cells, magnetic recording, etc.

Theoretical studies of epitaxial growth have been limited to phenomenological models[1] or numerical simulations[2–4] that rely on a variety of assumptions. With the advent of supercomputers it has now become practicable to apply the method of computer simulations to problems of epitaxial growth by use of realistic models with a sufficiently large number of atoms. We present here what we believe is the first *full* molecular-dynamics (MD) study of epitaxial growth; in other words, in this simulation once the interatomic potential and the procedure for adjusting the substrate temperature are given, the classical equations of motion for the whole system are solved in the usual way without any further approximations. We find that for spherically symmetric pair potentials, contrary to other results,[4] homoepitaxial growth yields well-formed crystallites at all temperatures. Moreover, the dynamics plays a key role in the growth of these crystals even at the lowest temperatures.

In our calculations the particles interact with each other through the Lennard-Jones potential

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

The units of length and of energy are, as usual, taken to be σ and ϵ, respectively. The potential is truncated at $r=2.5\sigma$. The integration time step is $\Delta t=0.02t_0$ in the usual Lennard-Jones units [$t_0=(m\sigma^2/\epsilon)^{1/2}$, where m is the particle mass]. The rectangular simulation cell is open along the positive z axis. The substrate consists of two close-packed planes which are placed parallel to the x-y plane above each other. (We recall that for a truncated Lennard-Jones potential the fcc lattice is the stable configuration of the crystal.) The atoms in the first layer are kept fixed in the plane $z=0$ at their ideal lattice sites, whereas the atoms in the second layer, placed in the proper stacking on top of the first layer, are allowed to move. Each of these close-packed planes contains 224 atoms. Periodic boundary conditions are applied in the x and y directions parallel to the substrate. In order to simulate the deposition process, particles with a Gaussian velocity distribution corresponding to a beam temperature of 0.9 (melting temperature of a Lennard-Jones crystal ~ 0.7)[5] are introduced every $\nu\Delta t$ in a direction perpendicular to the substrate and moving toward the substrate. The velocities of the atoms in the movable substrate layer are reset periodically to a Maxwellian distribution corresponding to the substrate temperature T_s. The classical equations of motion for all particles are solved simultaneously and the trajectories of all particles are followed throughout the whole simulation.

Figure 1 shows the number of particles in successive horizontal slices versus the number of introduced atoms for an intermediate substrate temperature

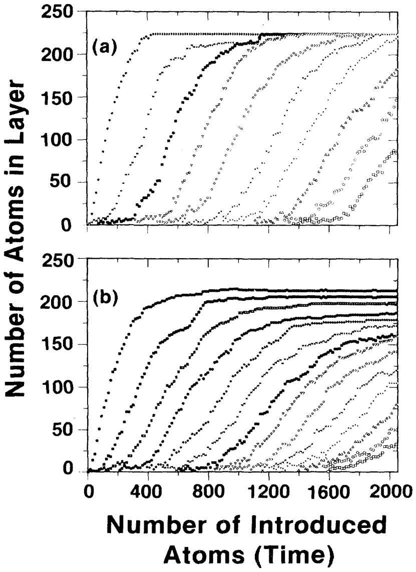

FIG. 1. Number of particles in successive layers (from left to right) vs number of introduced atoms (a) at $T_s=0.4$ and (b) at $T_s=0$; the deposition rate is $\nu=15$. Values on the abscissa are proportional to the simulation time. The dashed line indicates the number of particles in a fully completed close-packed layer.

$T_s = 0.4$ and for a very low substrate temperature $T_s = 0$, both at introduction rate $\nu = 15$. The slices have a thickness equal to the expected plane separation and are centered at z values where layers are expected to be centered for the stacking of close-packed planes. At $T_s = 0.4$ the growth is into fully completed layers, each of them containing 224 atoms as seen in Fig. 1(a). At $T_s = 0$ the number of particles in the various slices is always less than 224 and it decreases with increasing height z [see Fig. 1(b)]; for lower z the number of particles even reaches a saturation value. For the case $T_s = 0$ the particle density along the z axis after the deposition of 2052 atoms is shown in Fig. 2. It can clearly be seen that the adsorbate consists of quite distinct layers with no appreciable disorder in this direction. Pictures of the arrangement of particles within the layers show the existence of grain boundaries and voids, the size of which increases the distance from the substrate (this is seen in Fig. 3).

We made some simulation runs where 680 atoms were deposited at a low introduction rate $\nu = 990$. There is no difference in the qualitative results between the high-rate and the low-rate depositions; the former is shown in Fig. 1(a) for $T_s = 0.4$. At $T_s = 0$ the effect of the low rate of deposition is seen as follows. Because of the long relaxation time between the introduction of atoms, the temperature of the adsorbate comes very close to zero, thus reducing the mobility of the particles; as a consequence of this reduction, voids contained in the adsorbate are larger than those in the case of the higher deposition rate. Nevertheless, there is distinct layering and the particles form islands within the layers. The arrangements of the atoms in the first and fifth layers are shown in Figs. 3(a) and 3(b), respectively. The particles are well arranged in hexagonal patterns with no evidence of in-plane disorder.

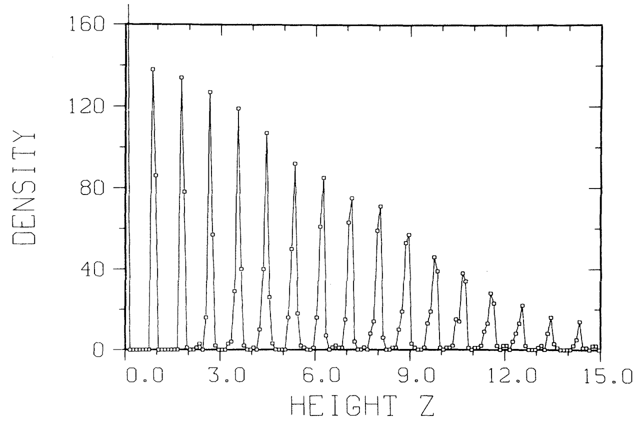

FIG. 2. Histogram of the number of particles as a function of height z after the deposition of 2052 atoms for $T_s = 0$ and deposition rate $\nu = 15$.

The process of relaxation by which the layers get completely populated [as seen in Fig. 1(a)] is shown graphically by a trajectory plot in Fig. 4. This figure shows the trajectories for the last 1500 MD steps for the calculation at $T_s = 0.4$. It is concluded from the figure that during the calculation the high mobility of particles in the incompletely filled upper layers is responsible for the complete filling of the close-packed planes further below; these planes get stacked without a particular stacking sequence. For low T_s one expects the mobility to be lower and, hence, the filling to be incomplete.

To date there have been few computer-simulation studies relating to epitaxial growth. Monte Carlo simulations[1-3] are made with random deposition of particles on a lattice with some rules to simulate condensation, migration, and reevaporation of particles from the substrate. Such Monte Carlo calculations are quite useful to study sizes, shapes, and coalescence of islands as well as adsorption isotherms as a function of temperature and rate. To our knowledge there has been only one study[4] to date using molecular dynamics mainly to investigate the columnar growth in thin films. According to the authors a "strategem" was used to treat the interaction of incident atoms with already condensed particles in order to minimize computational time. In

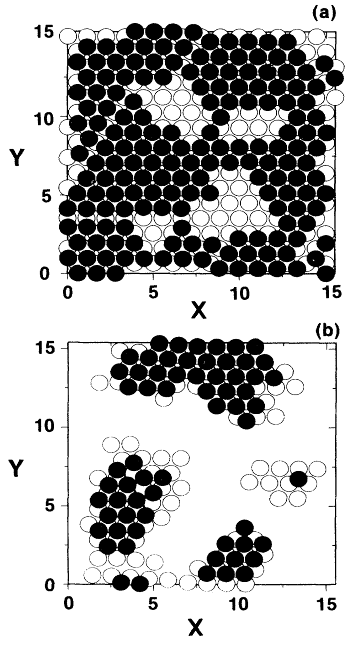

FIG. 3. Arrangements of atoms after the deposition of 680 particles at $T_s = 0$ and deposition rate $\nu = 990$. (a) Atoms in the first deposited layer on top of the movable substrate layer. (b) Atoms in the fifth deposited layer on top of the fourth layer. The close-packed structures contain grain boundaries and voids.

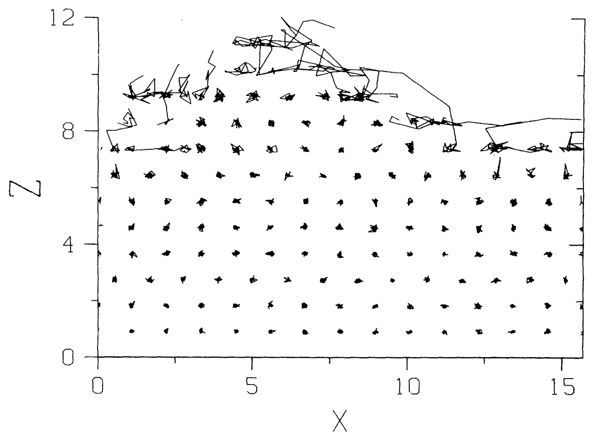

FIG. 4. Particle trajectories for the last 1500 MD steps for the calculation at $T_s = 0.4$ and $\nu = 15$. The particles selected for plotting are those in a slice of thickness 1.0, perpendicular to the y direction. The positions of the atoms were recorded every 75 MD steps and they are connected by straight lines.

this strategem, displacements of atoms within the deposit were not allowed and an amorphous structure was obtained beyond about five atomic planes of the substrate. The relationship of these earlier simulations to our calculations is not clear at present. The main reason is that most of these simulations do not address the question of local atomic rearrangements, i.e., relaxations, which is of major importance for epitaxial studies; an investigation of this question is the main purpose of this work.

A comparison of our results with experimental data is quite revealing.[6] It is well known that monatomic metals cannot be grown as amorphous films using vapor growth techniques. In fact, the usual form of growth of metallic elements is into small crystallites. However, elements that show directional bonding can be grown as amorphous films with relative ease, e.g., Si or Bi[7] and Ga. Our results 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 believe that the stabilization of amorphous structures will occur if the interatomic potential exhibits some anisotropy due to directional bonding or if there are varyingly sized particles in the system.

In summary, we have studied the epitaxial growth of a Lennard-Jones system as a function of substrate temperature using full molecular-dynamics simulation. Our results indicate that for all substrate temperatures the growth is into well-defined layers and in each layer the particles are arranged in well-formed, close-packed structures. These results are in qualitative agreement with general trends observed in the vapor deposition of monatomic metals into thin films.

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