

EPITAXIAL GROWTH OF THIN FILMS STUDIED BY MOLECULAR DYNAMICS SIMULATION

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The epitaxial growth of atomic systems, interacting via the spherically symmetric Lennard-Jones potential is studied as a function of substrate temperature T_S and deposition rate. The calculations reveal the microscopic structure of thin films, and give insight into the dynamics of the adsorption process. For all substrate temperatures the growth is into well ordered layers which 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. It is shown that the films exhibit a pronounced columnar structure if deposited at low T_S .

1. Introduction

Epitaxial growth from the vapor phase is a subject of much current interest.¹ This is motivated by the unique physical phenomena and materials that can be studied using this technique as well as important applications in the fields of semiconductors, magnetism, superconductivity, and optics.

Several theoretical approaches have been used to obtain insight into the microscopic processes of epitaxial growth. In particular, a better understanding of growth processes from an atomistic point of view has been the aim of many of these studies.

Analytical calculations, based on phenomenological, thermodynamic models, can help answer questions on adsorption and formation of clusters in the early stages of growth.²⁻⁶ Problems of this kind have also been studied by Monte Carlo methods.⁷⁻¹⁰ In such calculations, rules for adsorption, migration and desorption of atoms have to be provided; the significance of the various parameters in the calculations is unknown a-priori.

Monte Carlo calculations in continuous space have been performed to simulate the growth of thin films.¹¹ The Monte Carlo method is inherently a simulation method for generating equilibrium configurations of a given system. Since vapor-phase growth is a nonequilibrium process, one might raise questions about the validity of simulations in which the Monte Carlo method is applied to nonequilibrium configurations. Moreover, the Monte Carlo method does not describe the dynamics of a system. It has been found that the molecular-dynamics method, which includes the dynamical motion of atoms, is better suited than the Monte Carlo method to lead a system out of

metastable pockets to configurations with lower potential energies (in particular transformations from disordered to crystalline configurations).¹²

Early molecular-dynamics simulations of thin film growth mainly concentrated on the study of columnar growth in low temperature depositions.¹³ In these simulations the mobility of the deposited atoms was drastically limited by freezing the positions for an impinging atom after some initial relaxation with the adsorbate. Amorphous film structures were found, this being in contrast to full dynamical simulations where crystalline structures are always obtained even at the lowest substrate temperatures.¹⁴ We believe that full dynamical simulations are needed to get a detailed picture of various aspects of epitaxial growth.

In this paper, we present full molecular-dynamics simulations¹⁵ of epitaxial growth. 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. In order to focus on the basic features of epitaxial growth we assume a simple spherical Lennard-Jones interaction between atoms. The effect of substrate temperature T_S and deposition rate on the growth behavior has been studied. The simulations give insight into the dynamics of the growth process, and provide the microscopic structure of the deposited films.

2. Molecular-Dynamics Model

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

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1)$$

The units of length and of energy are, as usual, taken to be σ and ϵ , respectively. The unit of time $t_0 =$

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$(m\sigma^2/\epsilon)^{1/2}$, where m is the atomic mass. The potential is truncated at $r = 2.5\sigma$, a distance slightly larger than the radius of the fifth-nearest neighbor shell in the fcc lattice. The classical equations of motion for the atoms are solved using the Verlet algorithm¹⁶ with an integration time step $\Delta t = 0.02t_0$ (applied to argon, $\Delta t = 4.4 \times 10^{-14}$ s).

The simulations are carried out in a rectangular cell which is open along the positive z axis and periodically extended in x and y directions. The substrate, placed parallel to the plane $z = 0$, is built of two close-packed triangular planes of atoms which represent the (111) surface of a close-packed crystal (fcc or hcp). For the truncated Lennard-Jones potential in our simulations, the fcc lattice is the stable configuration of atoms, and we expect that the close-packed atomic planes of the (111) surface provide optimum growth conditions for homoepitaxial growth.

Each of the two substrate planes contains 224 atoms in a 14×16 triangular array. The x - y dimensions of the simulation cell are adapted to this array; i.e., $14 \mathbf{a} \times 16$

$\sqrt{3}/2 \mathbf{a}$, with \mathbf{a} the nearest neighbor distance. Periodic boundary conditions are applied in x and y directions parallel to the substrate. We include thermal expansion by making \mathbf{a} , and by that the cell dimensions, dependent on the substrate temperature: \mathbf{a} is taken as the nearest neighbor distance in a Lennard-Jones crystal held under zero pressure at a temperature which is equal to the actual substrate temperature.

The atoms in the first substrate layer are fixed in the plane $z = 0$ at their ideal lattice sites; they are not allowed to move. The second substrate layer is properly stacked on top of the first layer, and the atoms in this upper substrate layer are allowed to move as part of the dynamical system.

In this paper, we restrict ourselves to simulations of homoepitaxial growth, i.e., adatoms (A) and substrate atoms (S) are of the same type (potential parameters are the same for interactions between atoms A-A, A-S, and S-S).

In order to simulate the epitaxial growth, atoms are introduced at a certain height from the substrate at random (x, y) positions and moving, at the moment of introduction, perpendicularly toward the substrate. (In Sec. 5, growth with an angle of incidence of 45° is investigated).

Every ν simulation steps Δt , one atom is introduced to the system. In the various simulations presented in this paper, $\nu = 15, 90$ and 990 . The velocities of the incoming atoms are distributed according to a Gaussian distribution with a beam temperature $T_{\text{beam}} = 0.9 \epsilon/k_B$. This temperature is $\sim 30\%$ above the melting temperature of a Lennard-Jones system $T_m = 0.7 \epsilon/k_B$.¹⁶

An important point in simulations of growth processes is the adjustment of the substrate temperature T_s . It is desirable not to intervene in the motion of the adsorbed atoms, and to let energy dissipation take place only at the substrate. In our simulations we adjust the substrate temperature by resetting the velocities of the atoms in the movable substrate layer every $4 - 10 \Delta t$ to a Boltzmann distribution with the desired temperature T_s (see Fig. 1). We found that this procedure provides an effective cooling for the adsorbed atoms and brings the overall adsorbate temperature close to T_s . During the growth simulation

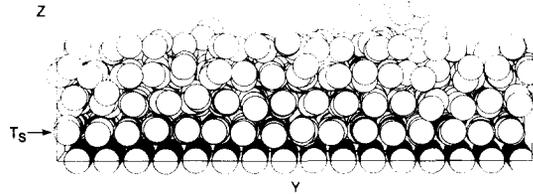


Fig. 1. Sideview after deposition of several hundred atoms showing a well developed layered structure. The atoms in the bottom substrate layer are fixed at their ideal lattice sites. The substrate temperature T_s is adjusted by periodically scaling the velocities of the atoms in the second movable substrate layer.

several thousand atoms are deposited, and the trajectories of all atoms are followed throughout the simulation.

3. Results

In this section results of simulations are presented in which 2052 atoms (more than nine completed monolayers) are deposited at an intermediate ($T_s = 0.4$) and a very low substrate temperature ($T_s = 0$), at a deposition rate $\nu = 15$.

The purpose of these simulations is to investigate the influence of the substrate temperature on the growth behavior. At both T_s , the upper movable substrate layer remains very stable, also during the impingement of the first incoming atoms. One or two atoms might leave the substrate layer, but these vacancies will finally be filled again.

The CPU-time for one of these simulation runs is about 15 h on an IBM S195.

A. Growth at an intermediate $T_s = 0.4$.

The intermediate substrate temperature $T_s = 0.4$ is about half the melting temperature of a Lennard-Jones system, which is close to typical epitaxial growth temperatures in laboratory experiments. During growth the average adsorbate temperature, $\langle T_{\text{ad}} \rangle \sim 0.45$, i.e., somewhat higher than T_s . Except for the uppermost layers, the adsorbate is in the solid state (this can be seen in Fig. 3 below).

Figure 2(a) shows the number of atoms in successive horizontal slices versus the number of introduced atoms, i.e., time. 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. From this we conclude that the growth proceeds in the successive addition of perfect close-packed atomic

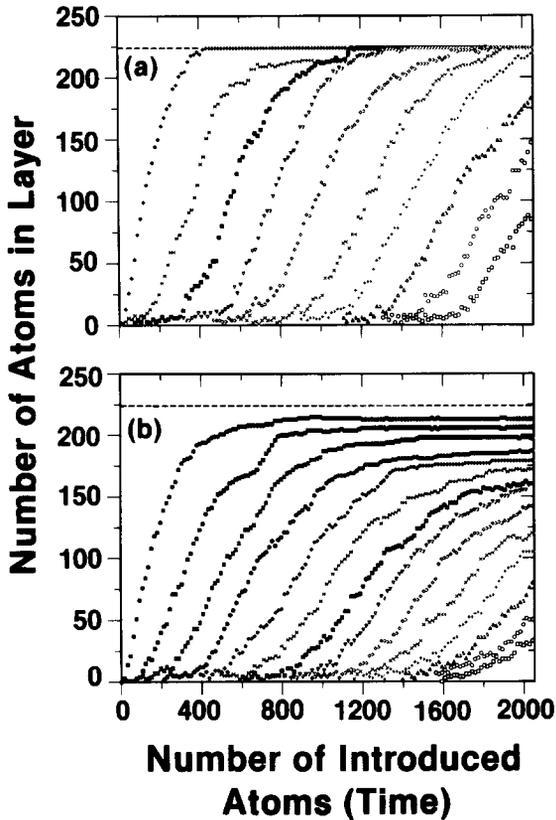


Fig. 2. Number of atoms in successive layers (from left to right) vs number of introduced atoms (a) at $T_s = 0.4$ and (b) at $T_s = 0$; the deposition rate is $\nu = 15$. Values on the abscissa are proportional to the simulation time. The dashed line indicates the number of atoms in a fully completed close-packed layer.

planes without the inclusion of lattice defects. The step-like change in the curves for the second and third deposited layers in Fig. 2(a) can be ascribed to the migration of clusters of atoms from higher to lower layers within the adsorbate.

The process of relaxation by which the layers become completely populated [as seen in Fig. 2(a)] is shown graphically by a trajectory plot in Fig. 3. This figure shows the trajectories for the last 1500 MHD steps for the calculation at $T_s = 0.4$. It is concluded from the figure that during the calculation the high mobility of atoms in the incompletely filled upper layers is responsible for the complete filling of the close-packed planes further below. As shown in the figure these planes are stacked without a particular stacking sequence because the energy difference between the two possibilities of stacking a triangular plane on top of another triangular plane is insignificantly small. We should emphasize, however, that no *in-plane* stacking faults are present at intermediate temperatures (cf.

Fig. 5) which are high enough to heal these in-plane stacking faults, should they exist in initial growth stages of a monolayer.

B. Growth at very low $T_s = 0$.

In these simulations of low-temperature growth, the velocities of the atoms in the second substrate layer are set to zero every four integration steps Δt . During growth the average adsorbate temperature, $\langle T_{ad} \rangle \sim 0.05$; for the uppermost layers the temperature can reach a value $T_{up} = 0.1$.

Figure 2(b), of the number of atoms in successive layers, shows that at $T_s = 0$ the number of atoms in the various slices is always less than 224 and decreases with increasing height z ; even reaching a saturation value for lower z .

The atom density along the z axis after the deposition of 2052 atoms is shown in Fig. 4. It can clearly be seen that the adsorbate consists of quite distinct layers with no appreciable disorder in this direction. The layer separation corresponds exactly to the stacking height for close-packed (111) planes. Therefore, this shows that for the spherically symmetric Lennard-Jones potential the growth of amorphous structures cannot be achieved even at the lowest temperatures.

In Fig. 5(a)-(e) the in-plane structures of five layers are shown. The atoms are mainly arranged in triangular close-packed configurations. However, defects are generated and remain present at these low temperatures. The first deposited layer exhibits boundaries between regions that are stacked in the two possible positions for stacking close-packed planes [Fig. 5(a)]. These in-plane stacking faults continue through the next higher layers [see Fig. 5(b)-(d)].

The lower deposited layers contain vacancies and voids, the size of which increases with the distance z from the substrate. However, even at higher z the atoms are arranged in close-packed islands within the layers. Low-temperature growth is also investigated in Sec. 5.

4. "Low" Deposition Rate

For dynamical atomistic simulations, as are the simulations in this paper, the real time duration is of the order of $10^{-8} - 10^{-9}$ s (applied to argon). We have to choose, for that reason, deposition rates which are *orders of magnitude higher* than the deposition rates usually found in real experiment. Yet, the time between the introduction of atoms in our simulations is comparable to the vibrational time of atoms, and almost all atoms in the beam approach the adsorbate individually. Only few atoms may form clusters in the gas phase.

Since the results of our simulations are in agreement with experimental facts (see Sec. 6, and also refs. 14 and 17), we conclude that the absolute time of the simulations is long enough to include important *short-time* relaxations in the systems. Of course, relaxations on a macroscopic time scale cannot be included in such calculations.

In order to check the influence of the deposition rate we performed 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

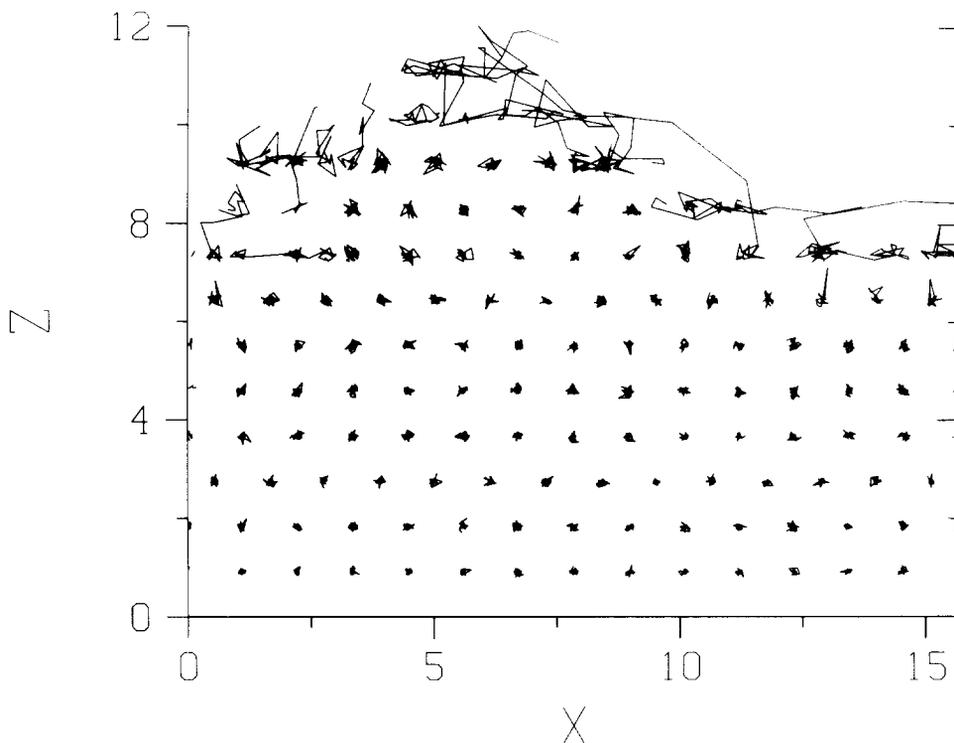


Fig. 3. Trajectories of atoms for the last 1500 MD steps for the calculation at $T_s = 0.4$ and $\nu = 15$. The atoms selected for plotting are those in a slice of thickness 1.0, perpendicular to the y direction. The positions of the atoms were recorded every 75 MD steps and connected by straight lines.

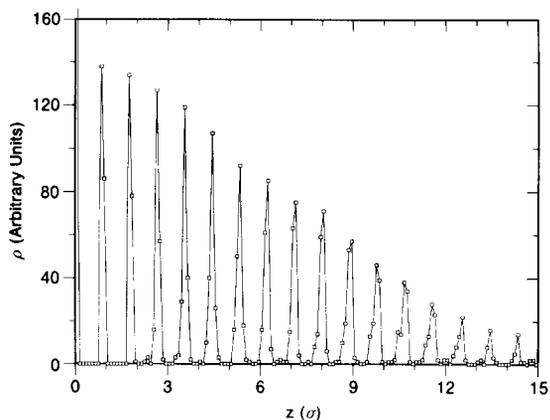


Fig. 4. Histogram of the number of atoms as a function of height z after the deposition of 2052 atoms for $T_s = 0$ and deposition rate $\nu = 15$.

($\nu = 15$ in Sec. 3) and the low-rate depositions.

At $T_s = 0.4$, the films grow, as in the case of the high deposition rate, without the formation of defects; the layers are fully completed as shown for the case $\nu = 15$ in Fig. 2(a). 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 (average adsorbate temperature $\langle T_{ad} \rangle \sim 0.002$), thus reducing the mobility of the atoms. As a consequence of this reduction, the filling of the layers is less complete than in the simulation with $\nu = 15$ [this can be seen from a comparison of Fig. 6 with Fig. 2(b)]; voids contained in the adsorbate are larger than those in the case of the higher deposition rate. Nevertheless, there is distinct layering and the atoms form islands within the layers. The arrangements of the atoms in the first and fifth layers are shown in Fig. 7(a) and 7(b), respectively. The atoms are well arranged in triangular patterns with no evidence of in-plane disorder.

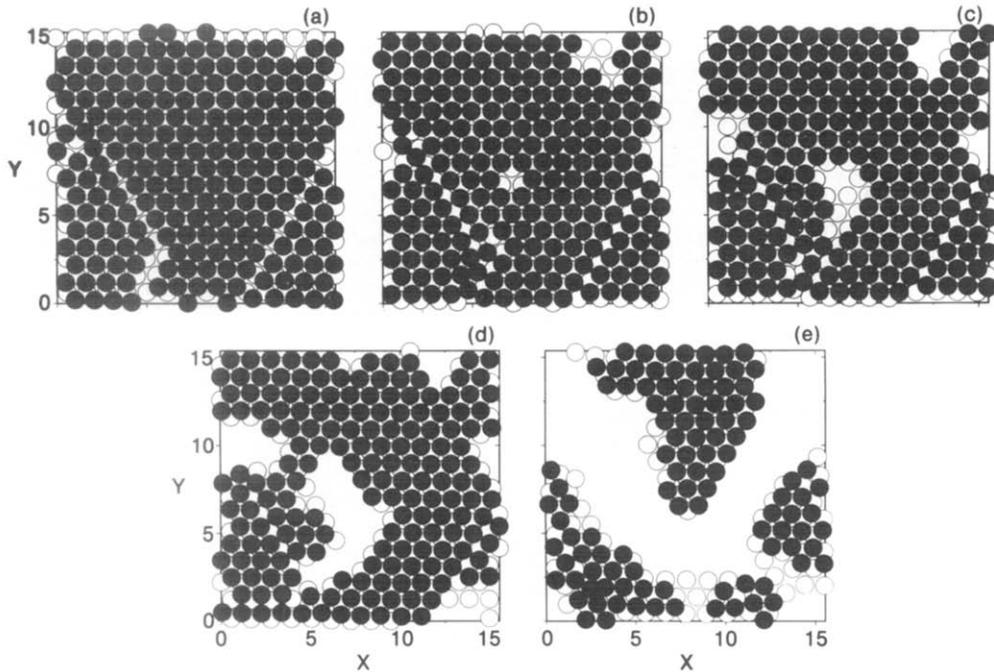


Fig. 5. Arrangement of atoms in various layers for the system (black circles) in Fig. 4. (a) 1st, (b) 2nd, (c) 3rd, (d) 5th, and (e) 11th deposited layer. For each layer the atoms in the next lower layer are drawn with open circles.

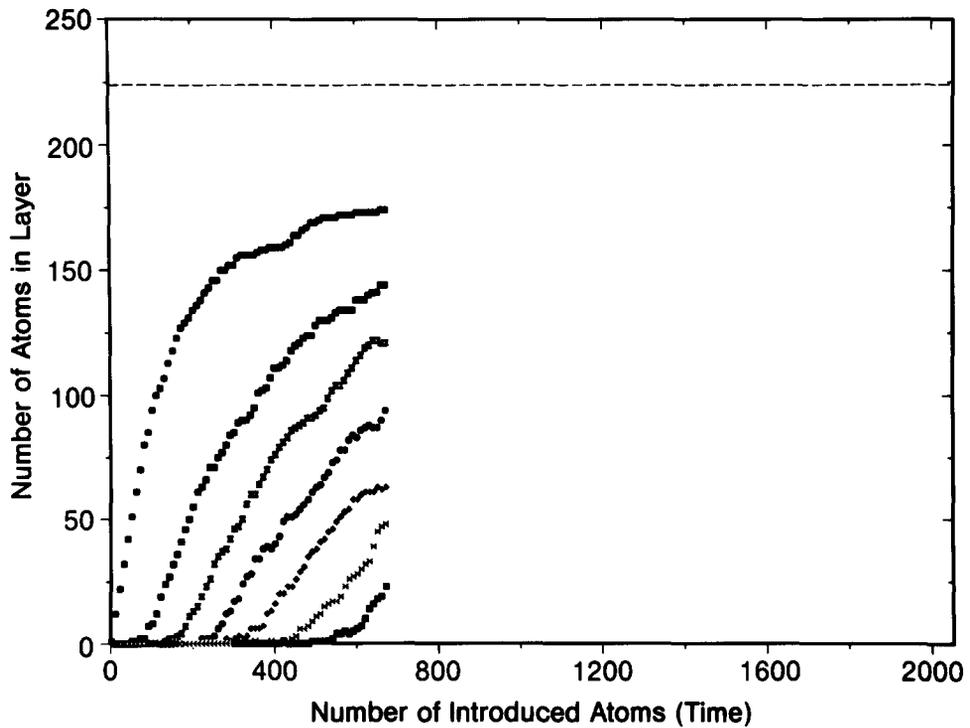


Fig. 6. Number of atoms in successive layers vs number of introduced atoms at $T_s = 0$ and a "low" deposition rate $v = 990$.

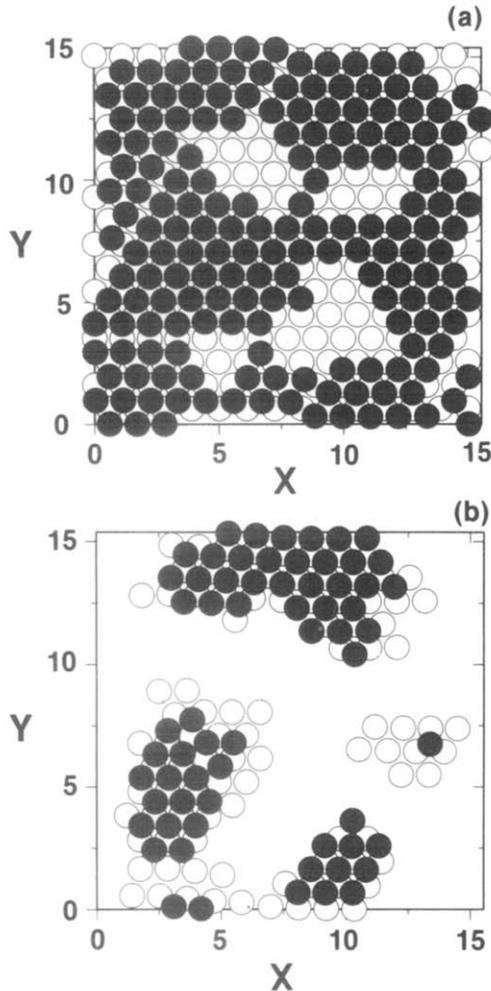


Fig. 7. Arrangement of the atoms after the deposition of 680 atoms at $T_s = 0$ and $v = 990$ for the (a) first and (b) fifth deposited layer (black circles). Open circles show the preceding layer. The atoms are well arranged in triangular patterns.

5. Oblique Incidence At Low T_s

It is known that, under certain growth conditions, vapor-deposited thin films exhibit a structure which is characterized by the formation of micro-columns within the adsorbate.¹³ The formation of this columnar microstructure is favored by a low mobility of the adatoms during deposition, and, hence, can often be found in amorphous films deposited at low temperatures. An oblique incidence of the vapor beam tends to make the columnar structure more pronounced and as a consequence is thought to be the result of self-shadowing effects.¹³

There were several molecular dynamics simulation studies on the growth of columnar

microstructures.^{13,18-19} In these simulations, atoms (in the form of hard spheres,¹⁸⁻¹⁹ or particles interacting via a Lennard-Jones potential¹³) were deposited onto a planar substrate. In order to obtain columnar growth the mobility of the adatoms was limited drastically by applying different strategies. In the case of the hard-sphere depositions atoms were allowed to relax following impingement only to the extent that contact with the nearest triangular pocket formed by three hard spheres was achieved. In the case of Lennard-Jones systems atoms were deposited and the trajectory of each was followed until all but 0.01% of its initial kinetic energy was dissipated in the deposit. Once deposited, atoms within the deposit were not allowed to move. All these simulations exhibit columnar growth, and the films, due to the restricted mobility of atoms, grow into amorphous structures.

In this chapter we will show that even in a fully relaxed system columnar growth can be obtained if the atoms are deposited at a low temperature. We performed a simulation where 7208 Lennard-Jones atoms are deposited onto a substrate consisting of two atomic planes at a substrate temperature $T_s = 0$. Each of the substrate planes contains 896 atoms in a 28×32 triangular array. The atoms are introduced along the positive x - y diagonal at an incident angle $\alpha = 45^\circ$, and a deposition rate $v = 90$. During deposition the average adsorbate temperature $\langle T_{ad} \rangle \sim 0.005$.

All atoms in the adsorbate are allowed to move throughout the simulation, and as a consequence contrary to earlier simulations, the atoms here relax into a crystalline structure. On a CRAY-XMP approximately 100 h CPU-time are needed to complete a simulation run.

Figure 8 shows a vertical cross section along the x - y diagonal after the deposition of 7208 atoms. The atoms are plotted within a slice of thickness $d = 5\sigma$. The deposited film clearly exhibits a pronounced columnar structure. Figure 9 shows that the adsorbate consists of distinct layers; there is no evidence for disorder along the z axis.

The angle β between the orientation of the columns and the z axis is smaller than predicted by the rule

$$\tan \beta = 1/2 \tan \alpha \quad (2)$$

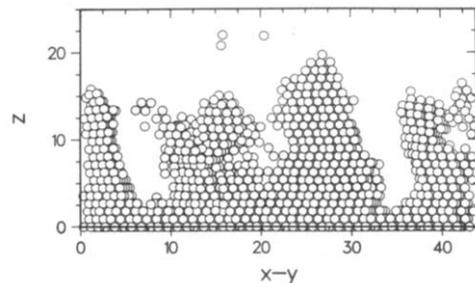


Fig. 8. Vertical cross section in the plane of the x - y diagonal. Atoms are introduced in this plane moving in the positive x - y direction with an angle $\alpha = 45^\circ$. Plotted are atoms that are within a slice of thickness 5.0.

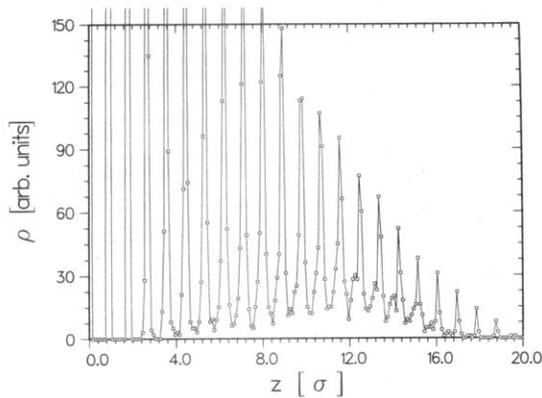


Fig. 9. Histogram of the number of atoms as a function of height z for the system in Fig. 8.

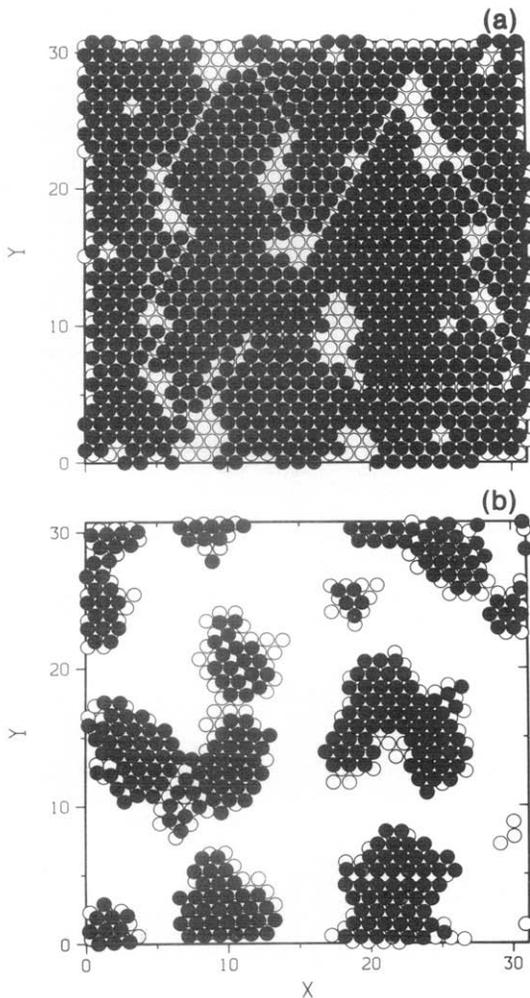


Fig. 10. Arrangement of the atoms in the (a) first and (b) twelfth deposited layer for the system in Fig. 8.

which holds for various experimental cases and for the hard-sphere simulations mentioned earlier.¹³ In our case $\beta \sim 15^\circ$, with an angle of incidence $\alpha = 45^\circ$. Leamy et al.¹³ also using a Lennard-Jones interaction between deposited atoms found somewhat smaller angles β than predicted by Equation (2). In our case, since the atoms are allowed to fully relax and the atomic planes within the columns are parallel to the substrate, one can intuitively understand that the columns are inclined to be oriented towards the substrate normal ($\beta = 0^\circ$).

Figures 10(a) and 10(b) show the in-plane structures of the first and twelfth deposited layers. The first deposited layer contains in-plane stacking faults and voids. The atoms in the twelfth deposited layer [Fig. 10(b)] are arranged within the columns in triangular patterns.

Nothing characteristic can be said about the shape of the columns with respect to the direction the incident beam (we recall that the atoms are introduced along the positive x - y diagonal). Experimentally it has been observed that columns might be elongated in the direction perpendicular to the plane of incidence.¹³ Further studies are needed to address many of these issues.

6. Discussion

To date there have been few computer-simulation studies relating to epitaxial growth. Monte Carlo simulations⁷⁻¹¹ are made with random deposition on a lattice or in continuous space with some rules to simulate condensation, migration, and reevaporation of atoms 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.

As mentioned earlier Monte Carlo is a method for simulating equilibrium systems, and consequently it is not clear how well it describes nonequilibrium processes associated with vapor-phase growth. Also, it has been observed that crystallization of disordered metastable states can occur easier in molecular dynamics than in Monte-Carlo simulations,¹² which might be due to the fact that collective atomic motions are important in the process of crystallization and nucleation. Collective motions, however, can hardly result from the standard Monte Carlo procedure.

In the molecular-dynamics simulations of Leamy et al.¹³ to study columnar growth a stratagem was employed to treat the interaction of incident atoms with already condensed atoms in order to minimize computational time. Displacements of atoms within the deposit were not allowed and an amorphous structure was obtained for all growth simulations carried out by these authors.

In contrast to these studies the films in our simulations invariably grow into crystalline structures. The main reason for this discrepancy is that the earlier simulations do not address the question of local atomic rearrangements, i.e., relaxations, which is of major importance for epitaxial studies. We hence show that the dynamics plays a key role in the growth of thin films even at the lowest temperatures.

In accordance with our findings, molecular-dynamics studies of the crystallization of a Lennard-Jones liquid have shown that even at a low temperature there are no energy barriers which can prevent the system from reaching the

crystalline state.²⁰ Other authors found a similar result from molecular-dynamics simulations on the homogeneous nucleation of a Lennard-Jones system.²¹

A comparison of our results with experimental data is quite revealing.¹ It is well known that monoatomic 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 and Ga.²² 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. The stabilization of amorphous structures will occur if the interatomic potential exhibits some anisotropy due to directional bonding²³ or if there are differently sized atoms in the system.¹⁷

In summary, we have studied the epitaxial growth of a Lennard-Jones system as a function of substrate temperature and deposition rate 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 atoms are arranged in well-formed, close-packed structures. These results are in qualitative agreement with general trends observed in the vapor deposition of monoatomic metals into thin films. We should point out that similar results have been obtained recently regarding the deposition of Lennard-Jones particles by Das-Sarma, Paik, Khor, and Kobayashi.²⁴

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REFERENCES

1. For a review, see for instance, "Epitaxial Growth", edited by J.W. Matthews (Academic, New York, (1975).

2. J.A. Venables, *Vacuum* **33**, 701 (1983), and references cited therein.
3. R. Pandit, M. Schick, and M. Wortis, *Physical Review B* **26**, 5112 (1982).
4. G. Zinsmeister, *Vacuum* **16**, 529 (1966).
5. C.A.B. Ball and J.H. van der Merwe, in "Dislocations in Solids", edited by F.R.N. Nabarro (North Holland, Amsterdam, 1983), Chap. 27.
6. R. Vincent, *Proceedings Royal Society of London A* **321**, 53 (1971).
7. F.F. Abraham and G.M. White, *J. Applied Physics* **41**, 1841 (1970).
8. J. Singh and A. Madhukar, *Journal of Vacuum Science and Technology B* **1**, 305 (1983).
9. A.C. Adams and K.A. Jackson, *Journal of Crystal Growth* **13/14**, 144 (1972).
10. T.J. Coultts and B. Hopewell, *Thin Solid Films* **2**, 37 (1971).
11. B.W. Dodson and P.A. Taylor, *Physical Review B* **34**, 2112 (1986).
12. M. Schneider, *Zeitschrift fur Physik B* **55**, 199 (1984), and references cited therein.
13. H.J. Leamy, G.H. Gilmer, and A.G. Dirks, in "Current Topics in Materials Science", edited by E. Kaldis (North-Holland, Amsterdam, 1980), Vol. 6, p. 309.
14. M. Schneider, A. Rahman, and I.K. Schuller, *Physical Review Letters* **55**, 604 (1985).
15. A. Rahman, *Physical Review* **136**, A405 (1964).
16. L. Verlet, *Physical Review* **152**, 98 (1967).
17. M. Schneider, A. Rahman, and I.K. Schuller, *Physical Review B* **34**, 1802 (1986).
18. S. Kim, D.J. Henderson, and P. Chaudhari, *Thin Solid Films* **47**, 155 (1977).
19. K.-H. Muller, *Journal of Applied Physical* **58**, 2573 (1985).
20. J.Q. Broughton, G.H. Gilmer, and K.A. Jackson, *Physical Review Letters* **49**, 1496 (1982).
21. C.S. Hsu and A. Rahman, *Journal of Chemical Physics* **70**, 5234 (1979); **71**, 4974 (1979).
22. W. Buckel and R. Hilsch, *Zeitschrift fur Physik* **138**, 109 (1954).
23. M. Schneider, I.K. Schuller, and A. Rahman, *Physical Review B* **36**, 1340 (1987).
24. S. Das-Sarma, S.M. Paik, K.E. Khor, and A. Kobayashi, *Journal of Vacuum Science and Technology B* **5**, 1179 (1987).