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# Vapor-phase growth of amorphous materials: A molecular-dynamics study

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We have studied the vapor-phase growth of a mixture of two differently sized Lennard-Jones particles as a function of relative atomic size and substrate temperature, and we investigated what influence the substrate has on the growth. As a function of relative atomic size there is an abrupt change from well-layered crystalline growth to a nonlayered disordered growth. This transition is not affected in a substantial way by temperature or size of the substrate atoms or by the periodic boundary conditions used in the calculations.

The growth and study of amorphous materials is a problem of current scientific and technological interest. One of the most commonly used methods for the preparation of amorphous materials in thin-film form is vapor-phase deposition on a substrate.[1,2] Much experimental work[3–5] has been done on the structure and physical properties of amorphous thin films. The theoretical approach available to date has been restricted to phenomenological models,[1] and we know only of a few numerical calculations[6] related to vapor-phase growth of amorphous materials. We present here a molecular-dynamics simulation[7] of amorphous growth on a substrate from the vapor phase. In particular, we have studied the growth of a mixture of two differently sized Lennard-Jones particles as a function of relative atomic sizes, substrate temperature, and size of the substrate atoms. The results indicate that the ratio of atomic radii is the determining factor for amorphous growth because for spherical atomic interactions, relaxation plays an important role in vapor-phase growth.

In these simulations there are two types of particles $A$ and $B$ interacting via standard Lennard-Jones potentials

$$v_i(r)=4\varepsilon[(\sigma_i/r)^{12}-(\sigma_i/r)^6] \quad (i=AA,BB,AB) . \tag{1}$$

The units of length and of energy are taken to be $\sigma_{AA}$ and $\varepsilon$, respectively. The potential is truncated at $r=2.5\sigma_{AA}$. Here $i=AA,BB,AB$ refer to the interaction between like particles of type $A$ or $B$ or unlike particles $A$ and $B$. For simplicity, the parameter $\varepsilon$ is taken to be the same for like and unlike particles. The length parameter $\sigma_{AB}$ for the unlike particles is given by

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

This is the natural choice if $\sigma$ is interpreted as usual as the atomic diameter. The integration step $\Delta t=0.01t_0$ in the usual Lennard-Jones units [$t_0=(m\sigma_{AA}^2/\varepsilon)^{1/2}$, where $m$ is the particle mass taken to be the same for both particles].

The substrate consists of two close-packed planes which are placed parallel to the $x$-$y$ plane above each other. Each plane contains 224 Lennard-Jones particles of type $A$. The atoms in the first layer are kept fixed in the plane $z=0$ at ideal lattice sites. The atoms in the second layer are properly stacked on the $z=0$ plane of atoms and are allowed to move. The lattice constant is adapted to the actual substrate temperature by taking the value for a Lennard-Jones crystal of atoms of type $A$ held at the same temperature under zero pressure. Periodic boundary conditions are applied in the $x$ and $y$ directions parallel to the substrate. The rectangular simulation cell is open along the positive $z$ axis.

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 $\sim 0.7$) are introduced periodically every $30\Delta t$ in a direction perpendicular to the substrate and moving toward the substrate. The two types of particles are introduced alternately, i.e., in equal numbers. The velocities of the atoms in the movable substrate layer are reset periodically to a Maxwellian distribution corresponding to the substrate temperature $T_s$. During deposition the average temperature $T$ of the adsorbate lies slightly above the actual substrate temperature $T_s$, i.e., $T=T_s+\Delta T$. $\Delta T$ is largely independent of $T_s$ and its value $\Delta T\sim 0.05$ is about 7% of the melting temperature. The classical equations of motion for all particles are solved simultaneously and the trajectories of all particles are followed throughout the whole simulation. At this point we would like to stress that once the interatomic potential is given no additional assumptions are made in these calculations. Therefore, insofar as the conclusions do not depend on the choice of potential, the qualitative conclusions obtained here probably apply to real systems.

Figure 1(a) shows the density of particles in the $z$ direction for $\sigma_{BB}/\sigma_{AA}=0.900$ and $T_s=0.4$ after the deposition of 3052 atoms. (We have shown earlier[8] that $T_s=0.4$ is the optimum substrate temperature for layer-by-layer epitaxial growth in the monatomic case.) In order to eliminate the effect of thermal motion, the system was cooled after the end of the deposition process to a low temperature by switching the substrate temperature to $T_s=0$. The density of this low-temperature state is shown in Fig. 1(b). Figures 1(a) and 1(b) show that for this ratio of atomic sizes the growth is into well-formed distinct layers with no evidence for amorphous growth. It is an interest-

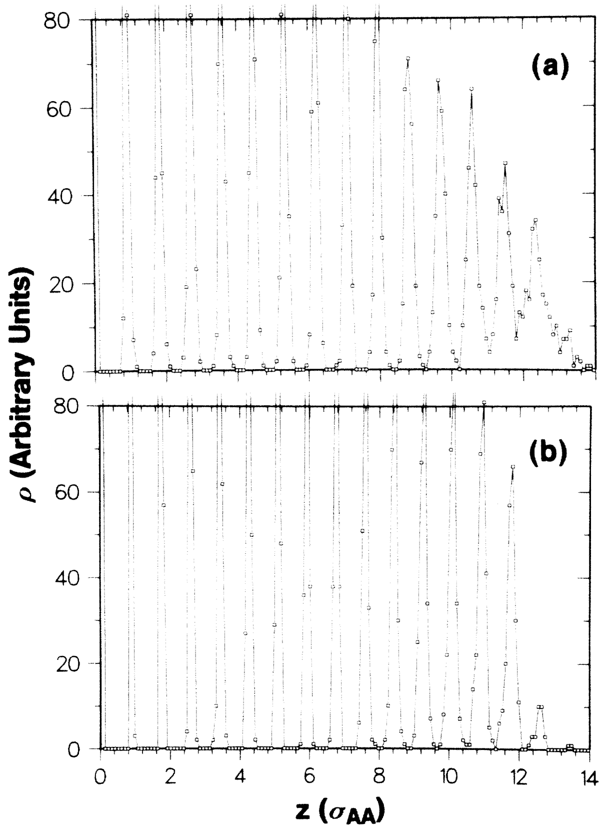

FIG. 1. Histogram of the number of particles as a function of height $z$ after the deposition of 3052 atoms for $\sigma_{BB}/\sigma_{AA}=0.900$. (a) System immediately after the end of the deposition process at $T_s=0.4$. (b) Same system after it was cooled to a low temperature by switching the substrate temperature to $T_s=0$. During cooling, no further particles are deposited.

ing observation that the first deposited layer contains exactly 224 atoms, which is the number of atoms in the substrate layers. The perfect hexagonal structure of this layer is shown in Fig. 2(a). Each of the following nine layers contains either 232 or 233 particles. The configuration of the 233 atoms in the second deposited layer is shown in Fig. 2(b). The particles are mainly arranged in a lattice corresponding to the bigger atoms. This fact will be mentioned again when we discuss the case $\sigma_{BB}>\sigma_{AA}$. In some regions the smaller particles allow for a slightly denser packing which leads to the formation of lattice defects. Figure 3 shows the system in a vertical cross section. We would like to emphasize that the dynamics plays an important role in the development of the crystalline order even at the lowest temperature. This is due to the fact that the atoms impinge with sufficient energy to allow the displacements necessary to crystallize into the hexagonal structure.

As a function of $\sigma_{BB}/\sigma_{AA}$, a transition from crystalline-layered to a disordered growth occurs at a value of $\sigma_{BB}/\sigma_{AA}$, which is slightly lower than the value $\sigma_{BB}/\sigma_{AA}=0.900$ in the preceding paragraph. Figures 4(a) and 4(b) show the atomic density (as described above) 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. A picture of the actual atomic positions in a slice parallel to the $x$-$y$ plane is shown (Fig. 5). It is clear that at this value of

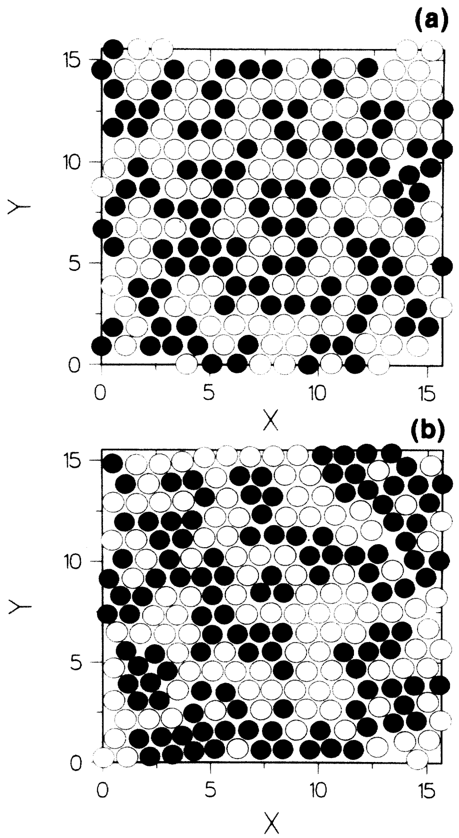

FIG. 2. Arrangement of atoms within layers for the system shown in Fig. 1(b), with $\sigma_{BB}/\sigma_{AA}=0.900$. (a) First deposited layer with 224 atoms. (b) Second deposited layer with 233 atoms. Particles of type $A$ are drawn with open circles, those of type $B$ with solid circles.

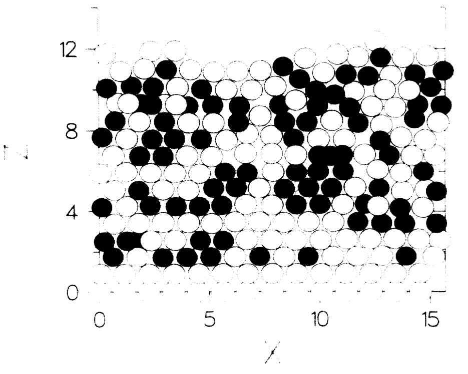

FIG. 3. Arrangement of atoms in a vertical slice of thickness 1.0 for the system shown in Fig. 1(b), with $\sigma_{BB}/\sigma_{AA}=0.900$.

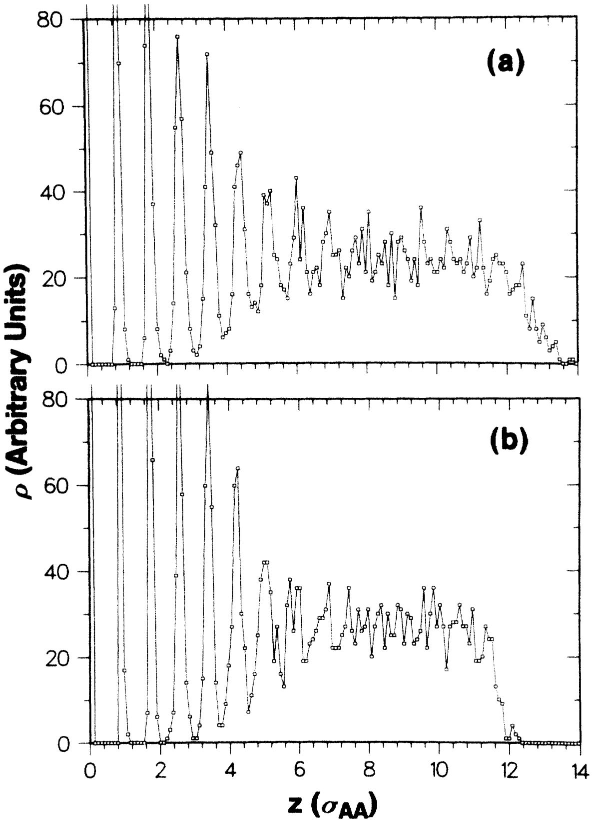

FIG. 4. Particle density as a function of height $z$ after the deposition of 3052 atoms for $\sigma_{BB}/\sigma_{AA}=0.875$. (a) and (b) as described for Fig. 1.

$\sigma_{BB}/\sigma_{AA}=0.875$ the structure is quite disordered when compared to the $\sigma_{BB}/\sigma_{AA}=0.900$ case.

When for the case $\sigma_{BB}/\sigma_{AA}=0.9$ the deposition takes place at a very low substrate temperature $T_s=0$, the adsorbate exhibits some degree of disorder. The density along the $z$ axis after the deposition of 2052 atoms at $T_s=0$ is shown in Fig. 6. It can be seen that at higher $z$, a slight disorder is superimposed upon the layered structure because of the lower atomic mobility during the deposition process. We should stress that in the monatomic case the layers are quite distinct even when deposited at $T_s=0$.[8]

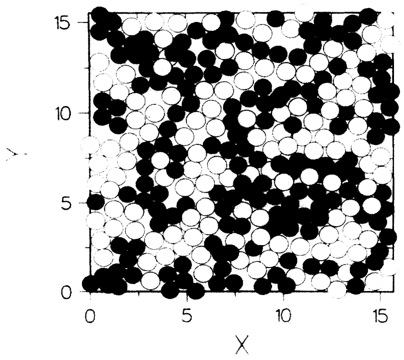

FIG. 5. Arrangement of atoms in a horizontal slice of thickness 1.0, centered at $z=9.8$, for the system shown in Fig. 4(b), with $\sigma_{BB}/\sigma_{AA}=0.875$.

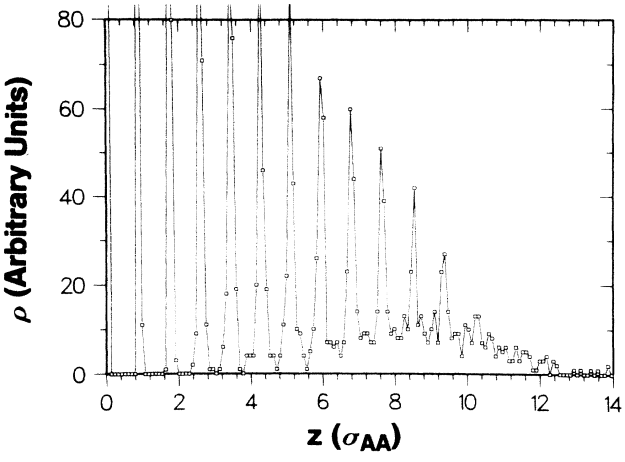

FIG. 6. Particle density versus height $z$ after the deposition of 2052 atoms at a substrate temperature $T_s=0$, with $\sigma_{BB}/\sigma_{AA}=0.9$.

In order to check the role of the substrate we have also performed calculations at $\sigma_{BB}/\sigma_{AA}>1$, and the results show the same type of behavior indicating that the transition from layered-crystalline to nonlayered-disordered growth is not affected substantially by the substrate (we recall that all substrate particles are of type $A$). In particular, the adsorbate has a crystalline layered structure for $\sigma_{BB}/\sigma_{AA}=1.1$, now the lattice spacing being determined by the larger particles $B$. We thus observe that it is the large atom which determines the manner of crystal growth in spite of leaving the substrate layers always of type $A$.

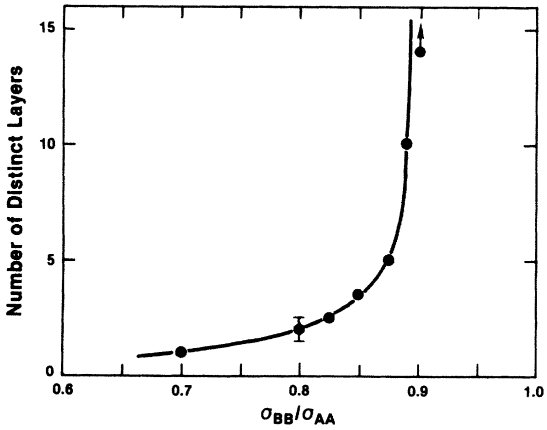

FIG. 7. Number of distinct layers as a function of the ratio $\sigma_{BB}/\sigma_{AA}$. The substrate layers are not counted. The arrow indicates that even more layers are expected to form in the case $\sigma_{BB}/\sigma_{AA}=0.9$ [see Fig. 1(b)].

To check the role, if any, of the periodic boundaries, additional runs were also performed without using periodic boundary conditions but depositing the overlayer inside a finite rectangle on an extended substrate. Moreover, a large number of runs were also performed as a function of $\sigma_{BB}/\sigma_{AA}$, especially in the range $\sigma_{BB}/\sigma_{AA} < 1$.

All calculations show that a rather abrupt change occurs in the growth mode at a value of $\sigma_{BB}/\sigma_{AA} = 0.89 \pm 0.01$ at the optimum epitaxy temperature of $T_s = 0.4$. Figure 7 shows the number of distinct layers as a function of $\sigma_{BB}/\sigma_{AA}$ 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.

In summary, we have studied the vapor-phase growth of a mixture of two types of Lennard-Jones particles on a crystalline substrate. We find that for equal numbers of both species deposited there is an abrupt change from layered-crystalline to nonlayered-disordered ("amorphous"-like) structure as a function of ratio of atomic radii. This transition does not depend in a significant way on the size of the substrate atoms or on the periodic boundary conditions used in the calculations.

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