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Surface kinetics and roughness on microstructure formation in thin films

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Formation of columnar structures in a thin-film grown by direct deposition was studied with a full molecular-dynamics simulation. The effects of substrate temperature, beam energy, and surface roughness on columnar structure formation were investigated. Small surface perturbations evolve into a columnar structure with the column orientations exhibiting the empirical tangent relationship. These microstructures are formed only at low substrate temperatures (below half the melting temperature). The columnar growth mechanism is found to be rather insensitive to the beam energy, except that the column width becomes thicker with increasing beam temperature.

Microstructure formation in thin films is an important technical and basic research problem which has recently received much attention. The vapor deposition of thin films on substrates held at temperatures below the bulk melting temperature occurs under highly nonequilibrium conditions, in contrast to the solidification of bulk materials near equilibrium conditions. As a consequence of this nonequilibrium process, a wide-spread excess volume is almost universally observed in vapor-deposited thin films.[1,2] The physical properties of thin films are strongly influenced by such microstructures, causing anisotropic electrical and magnetic properties,[3] enhanced adsorption of gases,[4] optical effects,[5] retardation of epitaxial crystallization,[6] etc.

Microstructure formation in a vapor-deposited thin film depends sensitively on deposition conditions such as substrate temperature, deposition rate, incident beam angle, and ambient pressure. For high deposition rates [typically (1×10^2)-(5×10^3) Å/sec], experimental studies have identified three different temperature regions (referred to as "zone I, II, and III") in which morphologically distinct microstructures are formed.[7]

In zone I (below $0.3T_m$ for metals, where T_m is the material melting temperature), the microstructure is porous and contains many interconnected voids around *columnar structures*. Columnar structure formation was found to be insensitive to the nature of the atomic interactions, atomic ordering (crystalline or amorphous), and the presence of impurities. Columnar structure is observed most clearly for oblique deposition, with the columns generally inclined toward the perpendicular to the substrate plane at an angle β which is smaller than the incident beam angle α. The relationship between the inclination angle β and the incident angle α (referred to as the tangent rule),

$$\tan\beta = \tfrac{1}{2}\tan\alpha , \tag{1}$$

was found first experimentally for crystalline Al films by Nieuwenhuizen and Haanstra.[8]

Several models[2,9-13] have been proposed to study columnar growth. For instance, phenomenological model calculations[11] predict that surface perturbations larger than a critical wavelength can grow and lead to columnar structure at very low substrate temperature. Earlier numerical simulations[2,9] employed either a "freezing" mechanism, in which the impinged particles are stopped at the position of impact without allowing any relaxation, or a "quenching" mechanism in which a large, artificial dissipation force reduces the surface mobility of the particles. Although these simulations provide an instructive demonstration of the self-shadowing mechanisms, it is not possible to study the role of dynamical parameters such as substrate temperature, which is one of the most important parameters in columnar growth.[11] The film density obtained in these simulations is much lower than those found experimentally; moreover, an amorphous structure is generally obtained which is not the case in monoatomic metallic thin films.[14] For this reason, it is desirable to study thin-film growth using a full dynamical calculation in order to understand microstructure formation within a well-defined microscopic model.

In this paper, we simulate columnar structure formation in a *crystalline* thin film using a full molecular-dynamics (MD) simulation technique. In this type of simulation, once the interatomic potential is given no additional assumptions are made regarding the growth mechanism. The aim of this paper is to investigate the effect of a small perturbation (of a size typically of the order of surface fluctuation during film growth) on columnar structure. We studied columnar structure formation under various growth conditions including incident angle, beam energy, substrate temperature, and surface irregularities. We find that small surface perturbation lead to columnar structures. The columns, produced by oblique impingement, are tilted toward the perpendicular to the substrate plane with a smaller angle than the incident-beam angle. Columnar structure is observed only at *low substrate temperatures* [below half the two-dimensional (2D) melting temperature, T_m]. However, this structure is observed over a wide range of beam energies ($\sim0.2T_m$ to higher than $2T_m$), although the column thickness increases with beam energy. Since these columnar structures are metastable, they will transform into an array of void after the deposition is completed due to migration of the deposited atoms. Lifetime calculations of columnar

structure require accurate estimates of parameters and computing power that are beyond limits of any current simulation. For comparison, we also performed a stochastic Monte Carlo (MC) simulation on a square lattice.

In order to minimize computing time, we consider a single component two-dimensional system with atoms interacting via the Lennard-Jones (LJ) interatomic potential:

$$V(\mathbf{r}_i,\mathbf{r}_j) = -4\varepsilon\left[\left(\frac{\sigma}{|\mathbf{r}_i-\mathbf{r}_j|}\right)^6 - \left(\frac{\sigma}{|\mathbf{r}_i-\mathbf{r}_j|}\right)^{12}\right], \qquad (2)$$

truncated above $|\mathbf{r}_i-\mathbf{r}_j|=2.5\sigma$, with standard LJ units in which σ, ε, ε/k_B, and $t_0=(m\sigma^2/\varepsilon)^{1/2}$ are the length, energy, temperature, and time units, respectively, with m and k_B being the mass of each atom and the Boltzmann constant. The 2D system employed here has the certain disadvantage that it contains many constraints due to the restricted phase space and might be oversimplified to describe real systems. Nevertheless, we believe that the essential features, to be discussed below, reflect many of the full 3D descriptions.[2,10] The substrate consists of three movable layers containing fifty atoms each and an underlying rigid substrate. Initially the substrate atoms are placed at their exact lattice sites, and then their velocities are assigned randomly according to the classical Maxwell-Boltzmann distribution. The movable substrate atoms are equilibrated to a substrate temperature T_s by successive velocity scaling at every 100 MD time steps (one MD time step represents $0.02t_0$). After the equilibration process, an incident atom is injected at a random lateral position, at a height sufficiently far from the deposit, to assure that it is not within range of a particle in the growing film. The incident atom velocity impinging with an angle α, is chosen according to the classical Maxwell-Boltzmann velocity distribution scaled to a given temperature T_b. Incident atoms impinge upon the substrate every 100 MD time steps. Manifestly, the impingement rate is much higher than any realistic deposition rate. This usually high rate together with small system size may prevent us from extracting quantitative conclusions. However, we believe that qualitative features or geometrical effects, such as the shadowing effect (the origin of tangent rule) will still be valid. In fact, almost the same film morphology is found even at an order of magnitude slower impingement rate (one atom every 1000 time steps) except that the column width increases slightly at the slow rate.

The usual periodic boundary conditions are not well suited for this simulation, especially for large α, because the columns grow inclined and may eventually cross the boundary. Thus, we employ a dynamic boundary condition in which a growth front outside the boundary, grows at the same rate as the front neighboring the inside region of the boundary. The inside region of the boundary is sampled periodically to determine the position of the growth front. When the inside neighboring positions to the boundary (within 3σ) are occupied or sampled by hopping atoms, an external horizontal front is constructed *ad hoc* at the same height. This consists of three movable and 17 stationary atoms. As the growth front advances, the horizontal location of the boundary moves dynamically according to the growth pattern (i.e., the region of interest is always in the center of the system), while the lateral system size is kept at a constant. Considering the fact that: (1) the growth front of a LJ system is fairly smooth with uniform deposition[15] (i.e., no shadowing effects are expected from regions outside the boundary region), (2) the interaction range is 2.5σ (i.e., no direct interaction between atoms inside of the system and atoms beyond the buffer region), no artifacts are expected due to this boundary condition. This was checked by performing simulation with various system sizes.

Figure 1 shows snap-shot pictures of a two-dimensional

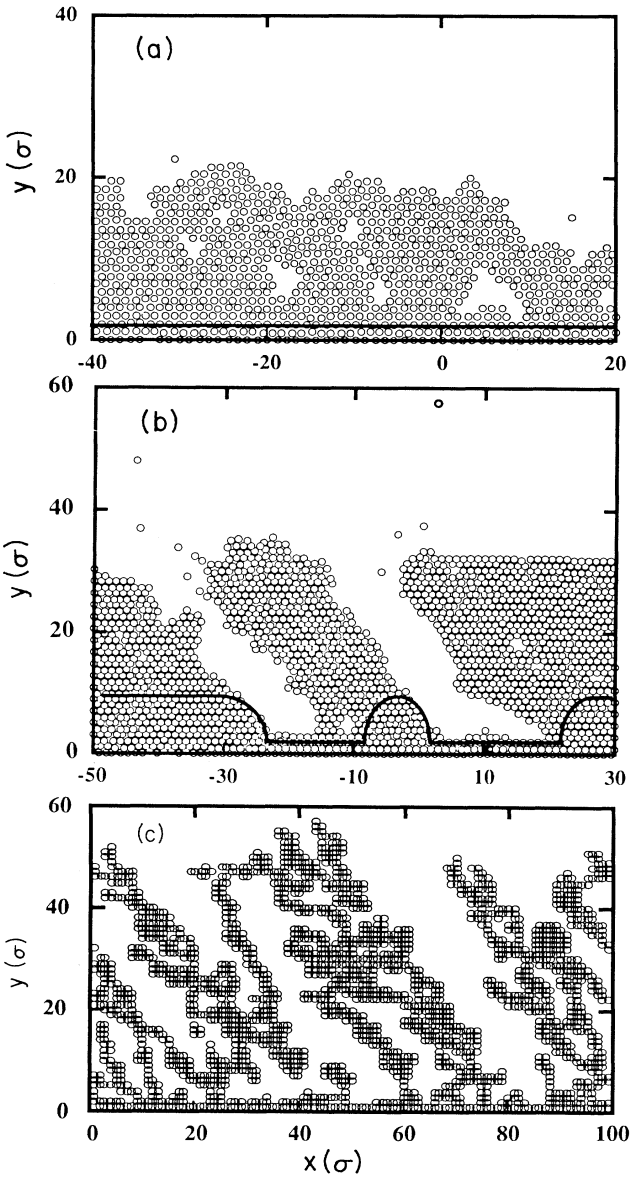

FIG. 1. Particle configurations of 2D LJ thin films grown by the molecular-dynamics simulation at a substrate temperature $T_s=0.1$ and beam temperature $T_b=0.6$ impinged on (a) a flat substrate; (b) steps. The incident beam angle $\alpha=60°$. The solid curve represents the initial surface configuration. (c) Monte Carlo simulation results allowing only nearest-neighbor hopping at $T=0.5$. x and y are plotted in units of σ.

thin film grown at a substrate temperature $T_s=0.1$ (the bulk melting temperature of the 2D LJ system is $T_m=0.415$),[16] (a) on a flat surface and (b) on a substrate with small surface perturbation (marked with thick solid lines) at an incident angle $\alpha=60°$ and a beam energy $T_b=0.6$. The size of the surface perturbation (about ten atoms in height and width) is chosen from typical surface fluctuation length scale found in earlier molecular-dynamics simulation of the LJ system.[10,15] Unlike limited surface mobility simulations[2,9,10] at this temperature the growth on the flat surface [Fig. 1(a)] does not develop a columnar structure.[17] The atomic corrugation alone cannot initiate the columnar structure. However, when the surface perturbation is present [Fig. 1(b)], a well-defined columnar structure is developed. This structure was found to be insensitive to the geometrical shape of the steps, however their size and relative distance affect the column structure. The columns are oriented toward the vertical with smaller inclination angle than the incident beam. This result shows that small surface irregularities caused by surface impurities, nucleation or other dynamical factors can evolve and are needed for the evolution of columnar structure. The local structure of the columns is a close-packed crystal structure (as expected)[15] with vacancies. Two-dimensional films are expected to develop a crystalline structure due to topological constrains and detailed MD studies of the 3D systems have shown that atoms interacting with monatomic spherically symmetric potentials always grow into a crystalline structure. Unlike 3D simulation where many stacking faults have been observed,[15] we find almost no stacking faults in this 2D simulation. The present studies, therefore, show that the local atomic structure does not play an important role in the details of the columnar growth.

For comparison, a stochastic Monte Carlo simulation [Fig. 1(c)] on a lattice gas model with nearest-neighbor hopping at (even higher temperature) $T_s=0.15$ resembles other limited surface mobility simulation[2,9,10] and evolves to a columnar structure even on a flat surface. The temperature of the two simulations is calibrated by comparing single atom hopping times on a flat surface assuming the same impingement rate (i.e., an MC time step set to be equal to 100 MD time steps). We note, however, that the MC dynamics may not represent a real system because of the restricted 2D phase space of the MC simulation and the assumption of nearest-neighbor hopping.

The effect of substrate temperature is illustrated in Fig. 2. At $T_s=0.2$ and beam energy $T_b=0.6$ [Fig. 2(a)], the structure of the film resembles the low-temperature result ($T_s=0.1$ and $T_b=0.6$) [Fig. 1(b)]. The column widths and inclination angles are virtually the same in both cases. At even higher substrate temperature $T_s=0.3$ [Fig. 2(b)], the perturbatin smooths out, and no evidence of column formation is found. This transition corresponds to the zone I and zone II transition of metallic thin film found in experiments[7] and phenomenological theory.[11] However, the transition temperature obtained in our 2D LJ simulations is higher than found experimentally.[7]

The formation of columnar structures is insensitive to the beam energy, however generally the column width thickens with increasing beam energy. The average inclination angle does not depend significantly on beam energy, and columnar structures are observed even at beam energies higher than $2.5T_m$.

Figure 3 shows the average column angles as a function of the incident angle. The dashed line represents the tangent rule [Eq. (1)] and the solid line the $\beta=\alpha$ relationship. The column orientations follows the tangent rule with slight discrepancies observed at incident angles $\alpha \leq 30°$ and $\alpha > 60°$.

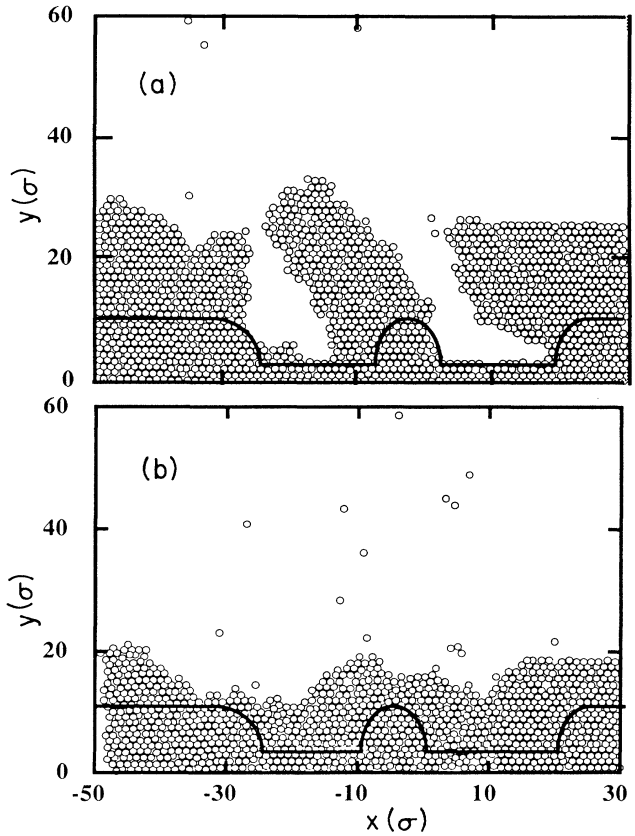

FIG. 2. Particle configuration, as in Fig. 3, impinged upon a substrate with initial steps on it at temperatures (a) $T_s=0.2$, $T_b=0.6$; (b) $T_s=0.3$, $T_b=0.6$.

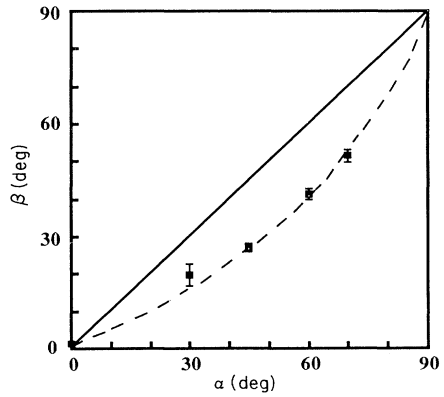

FIG. 3. Column orientation as a function of incident angle α. The solid line represents the $\beta=\alpha$ line and the dashed curve is obtained from Eq. (1).

The film density is plotted, in Fig. 4, as a function of the incident-beam angle. The results are obtained by taking the ratio between the area of the center column and the average area of a void, assuming that the columns are uniformly distributed over the system. The film density decreases monotonically with increasing α, in good agreement with experimental observations.[18] The void width is proportional to $A\tan\beta$, where A is the shadowing step height, and column thickness is of the order of the diffusion length scale. Using the tangent rule, the film density as a function of α can be written as

$$\rho=\frac{\rho_0}{1+a\tan\alpha}, \tag{3}$$

where ρ_0 is the film density at $\alpha=0°$ and the constant a is proportional to the ratio of the shadowing step height to the column thickness. The numerical results (open squares) are well fitted to Eq. (3) (solid line in Fig. 4) with $a=0.26$ and $\rho_0=0.9$. This results are in general agreement with earlier simulations.[2,10]

As is the case with all molecular-dynamics simulations, there are two major weakness of this method: (a) the knowledge of an "exact" potential for a specific material and (b) the short simulation time scale. Because of this, the conclusions obtained from these calculations must be of a qualitative nature. The results show that the tangent rule and the column density is independent of specifics of the potential. These results are valid for spherically symmetric potentials, and are a direct consequence of shadowing and not long-time kinetics.

In conclusion, we simulated the formation of 2D crystalline columnar structures using a full molecular-dynamics simulation technique. These simulations show that small surface fluctuation initiate and are important for the development of columnar formation. The columns

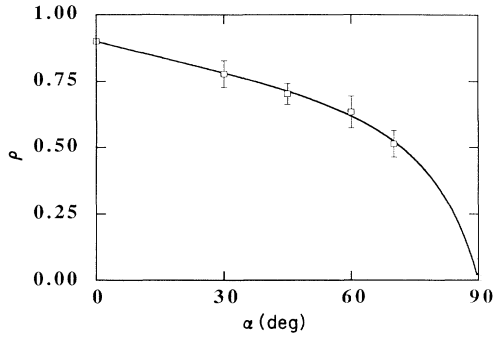

FIG. 4. Density of a 2D LJ film as a function of incident beam angle α at temperatures $T_s=0.1$ and $T_b=0.6$. The solid curve represents Eq. (3). Here, unit ρ is the number of atoms per unit area (atoms/σ^2).

are observed at substrate temperatures below half the 2D melting temperature. After an optimum column height is achieved, the subsequent columnar growth is insensitive to beam temperature except that the column width becomes thicker (i.e., density of the film becomes higher) with increasing beam temperature. Even in these full dynamical simulations, the dependence of the inclination angle on the incident angle is in good agreement with the empirical tangent rule. The film density decreases as the incident-beam angle increases in accordance with a simple geometrical consideration.

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