

Molecular-dynamics study of diffraction-intensity oscillations during epitaxial growth

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Diffraction-intensity oscillations have been observed using molecular-dynamics simulations of vapor deposition. Atoms interacting via modified Lennard-Jones potentials were deposited onto fcc(111) and fcc(100) surfaces with periodic boundary conditions and the diffraction was calculated during growth. The oscillations increased in amplitude with increasing temperature and, in some cases, with reduced deposition rate. Larger oscillations were observed on the fcc(100) surface than the fcc(111) surface. Strong reentrant oscillations, observed earlier experimentally, were not observed.

Surface-sensitive diffraction during epitaxial growth has been studied for many years because it contains information about the structure of the growing film. Oscillations observed during vapor deposition in the intensities of reflection high-energy electron-diffraction (RHEED) (Refs. 1 and 2) and thermal energy atom scattering (TEAS) of helium atoms^{3,4} are thought to be correlated with layer-by-layer growth. Experimental studies have investigated the relationship between diffraction-intensity oscillations and layer-by-layer growth,⁵ while numerical simulations have been used to help interpret experiments and provide insight into growth mechanisms.⁶⁻¹⁵ In the present work we have used molecular dynamics to simulate diffraction-intensity oscillations. We find a strong dependence on temperature and crystallographic orientation and the absence of the experimentally observed reentrant oscillations.

Simple diffraction theory does not predict oscillations for randomly deposited atoms without downward mobility,¹⁶ implying that downward atomic transport during growth is necessary if oscillations are present. Several mechanisms to produce this have been explored. Oscillations that increase at high temperature are typically attributed to increasing atomic mobility.⁷ However, this idea fails to explain the experimental observation of oscillations at low temperatures. In fact, for Pt growth on Pt(111) surfaces, oscillations have been reported which increase as the temperature is lowered below 400 K.¹⁶

Marmorkos and Das Sarma used Monte Carlo simulations to demonstrate that increased substrate temperature increased the tendency of atoms to diffuse to and over steps to reach lower levels.⁶ However, the observation of low-temperature oscillations in some systems led to speculation that the condensation energy of an atom could cause a transient mobility large enough to cause oscillations.¹⁷ Evans has reported on a different kind of transient mobility denoted as "funneling," which refers to the tendency of atoms deposited onto sides of islands or onto isolated atoms to come to rest at lower levels, thereby improving the layer-by-layer growth.⁷ Evans concluded that even when lateral diffusion across flat surfaces is

ignored, funneling would cause oscillations for growth on fcc(100) surfaces and for single domain growth on fcc(111) surfaces.

Molecular dynamics is a useful simulation technique for such problems because thermal effects can be realistically included by controlling the velocities of the atoms in the substrate crystal. In addition, complex multiatomic behavior occurs automatically in these simulations without further input. Studies using Lennard-Jones potentials found crystalline growth and enhanced layer-by-layer growth at intermediate temperatures ($T_{\text{substrate}}/T_{\text{melting}} \approx 0.6$).^{8,9} Molecular-dynamics simulations of growth indicate that the resulting transient mobility across flat surfaces is small, suggesting that another mechanism may be responsible for the low-temperature oscillations.¹⁰ Gilmore and Sprague, using an embedded-atom-method Ag potential, observed a variation in growth mechanisms on the fcc(111) surface when the incoming atom velocity was varied.¹¹

The main disadvantage of molecular dynamics for the study of these problems is that computer technology limits the range of growth rates and system sizes that can be investigated. Due to the immense computational needs of these studies, typical growth rates that can be simulated are on the order of 10^9 atomic layers per second or faster. Since these growth rates are much faster than experimental rates, atomic diffusion over long periods cannot be simulated realistically. However, atomic behavior just after deposition, such as diffusion due to condensation energy,¹⁷ substrate atom displacement,^{11,12} and funneling due to rough surfaces,⁷ is presumably represented in molecular-dynamics simulations.

We have simulated the growth of atoms onto the fcc(100) and fcc(111) surfaces using the modified Lennard-Jones potential described by Broughton and Gilmer, and chose the lattice constant for the substrate according to the formula for thermal lattice expansion that they developed.¹⁸ The time interval per simulation step was 0.02 in reduced time units. For Pt atoms this corresponds to $0.02(m\sigma^2/\epsilon)^{1/2} \approx 1.5 \times 10^{-14}$ s where m , σ , and ϵ are the atomic mass, atomic diameter, and an ener-

gy value which determines the strength of the interaction, respectively. We determined ϵ for Pt atoms by comparing the zero pressure melting temperature of the modified Lennard-Jones system and the atmospheric pressure melting temperature of Pt, assuming it to be identical to the zero pressure melting temperature. We used the Broughton and Gilmer potential melting temperature $t_m = k_B T_m / \epsilon = 0.61$, which is smaller than the Lennard-Jones value of $t_m = 0.68$.¹⁹ Here $t = k_B T / \epsilon$ is the reduced temperature and k_B is the Boltzmann constant.

Simulations started with a flat substrate consisting of one static and two movable atomic layers. The substrate was allowed to relax for 2000 steps before deposition, which was enough time for the diffraction values to stabilize except at the highest temperatures where surface roughening took place.

The temperature of the system was controlled by adjusting the velocities of the atoms in the lowest movable atomic layer. This method has the advantage of allowing the motions of surface atoms to be determined only through interactions with other atoms. However, the cooling was found to be insufficient to cool the entire system if the deposition rate was faster than about one layer per 1000 simulation steps. For all cases discussed below, the cooling was effective in keeping the temperature uniform throughout the system. The incoming atoms were deposited at normal incidence and had identical velocities corresponding to a reduced temperature of $t = 0.9$.

In diffraction investigations of growth, the most studied diffraction condition has been the situation where two adjacent layers interfere destructively. In this situation, known as the anti-Bragg or out-of-phase condition, the diffraction intensity should be most sensitive to the flatness of the surface.²⁰ As a check on our results, two different methods, identified here as the lattice method and the continuum method, were used to calculate the out-of-phase diffraction intensity. Both methods calculate the single-scattering diffraction formula using only the top atoms:

$$I(\mathbf{q}) = [\sum_j \exp(i\mathbf{q} \cdot \mathbf{r}_j)]^2 / N^2, \quad (1)$$

where $\mathbf{q}$ is the scattering vector, N is the number of atoms in a complete layer, and $\{\mathbf{r}_j\}$ are the positions of the top atoms. The intensity is normalized to the intensity from a flat surface at zero temperature.

In the continuum method the exact positions of the top atoms are used to calculate Eq. (1) using $\mathbf{q}_{\text{out-of-phase}} = (0, 0, \pi/\Delta z)$, where Δz is the vertical separation between layers. The top atoms were chosen by dividing the two-dimensional surface into appropriate bins which include exactly one atom from every complete layer. The highest atom in each bin was chosen as a top atom. Using this method checks were made at other $\mathbf{q}$ values including the in-phase diffraction condition $\mathbf{q}_{\text{in-phase}} = (0, 0, 2\pi/\Delta z)$.

The lattice method is a simplification of Eq. (1), in which all atoms are treated as if they occupied exact lattice sites. For the out-of-phase condition only the numbers of atoms in each layer enters into the formula:

$$I_{\text{out-of-phase}} = [\sum_m (-1)^m (N_{m+1} - N_m)]^2 / N^2, \quad (2)$$

where N_m is the number of atoms in layer m .

Figure 1 shows the time dependence of the out-of-phase diffraction intensity calculated using the lattice and the continuum methods. As expected, the continuum method gives slightly smaller intensities since the atoms are off the lattice sites, and this difference is larger for higher temperatures. The in-phase diffraction is roughly independent of deposition time since for this diffraction condition all atoms on lattice sites interfere constructively.

Figure 2 shows the amplitude of the first oscillation as a function of rate for an fcc(100) surface with 72 atoms/layer at $t_{\text{substrate}} = 0.4$. The oscillation amplitudes in Figs. 2 and 3 are obtained by averaging the lattice method diffraction results of four independent runs. The large increase with longer relaxation times between deposited atoms shows that the atoms are filling in the lower layer vacancies thus improving the layer-by-layer growth. Similar results have been observed in Monte Carlo simulations by Das Sarma and Tamborenea.¹³

Figure 3 shows the first oscillation amplitude vs substrate temperature for deposition onto fcc(100) and fcc(111) surfaces with similar sizes and deposition rates. The increases at high temperatures are presumably due to higher thermal mobility as found in previous Monte Carlo simulations.^{6,13} We attribute the oscillation amplitude decrease at the highest temperatures to the thermal instability of the surfaces, since the out-of-phase diffraction values before growth were quite low for these cases.

The presence of low-temperature oscillations for the fcc(100) surface indicate that downward atomic motion exists in these simulations even at low temperatures. However the amplitude of the fcc(100) oscillations is

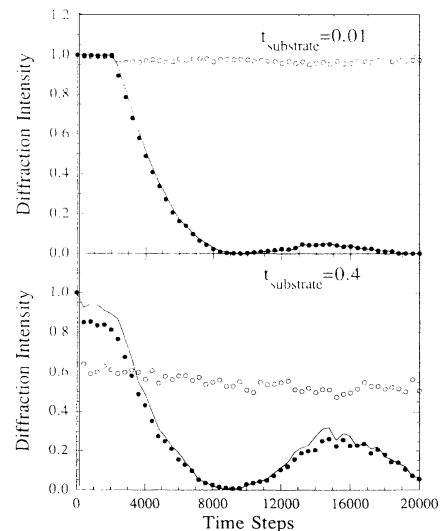


FIG. 1. Diffraction intensity vs time for deposition onto an fcc(100) surface with 128 atoms/layer and a deposition rate of 12 800 steps/layer: (—) out-of-phase, lattice method; (●) out-of-phase, continuum method; and (○) in-phase, continuum method. One time step $\approx 1.5 \times 10^{-14}$ s if scaled for Pt atoms. Debye-Waller motion and slight thermal surface roughening have lowered the initial intensities for the higher-temperature case.

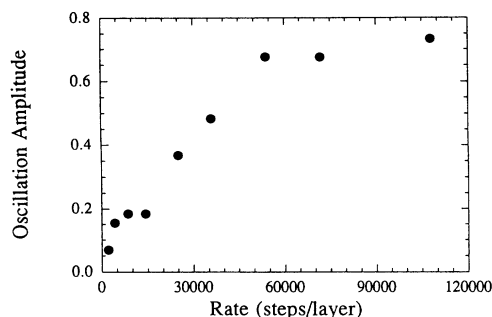


FIG. 2. Oscillation amplitude vs deposition rate for an fcc(100) surface with 72 atoms per layer and $t_{\text{substrate}} = 0.4$.

smaller than Evans's predicted value of ≈ 0.15 for the simple downward funneling model.⁷

Kunkel *et al.* reported that Pt on Pt(111) growth showed TEAS oscillations which were strong at low and high temperature but absent at intermediate temperature ($T_{\text{substrate}} \approx 400$ K) and therefore denoted them as "reentrant" oscillations.¹⁶ Since increasing thermal mobility could only explain the high-temperature oscillations, they proposed a different model to explain the low-temperature oscillations. Briefly, reduced clustering due to low mobility at low temperatures could increase the probability of downward transport, possibly through a decreased diffusion barrier. A small oscillation increase may be present in our simulations at low temperature (Fig. 3), but the data is inconclusive. Note that since the simulated deposition rate is much larger than experimental rates, the amount of thermal diffusion present in the simulations will be much less than in experimental situations. This suppression of thermal diffusion may be responsible for the lack of strong reentrant oscillations in our data.

In all cases the fcc(100) surface shows markedly higher oscillations amplitudes than the fcc(111). This might be caused by different funneling properties of the two surfaces. For instance, it may occur that for the fcc(100) surface an atom requires four nearest neighbors in the supporting layer to remain stable, while for the fcc(111) surface only three are required. Due to simple statistical

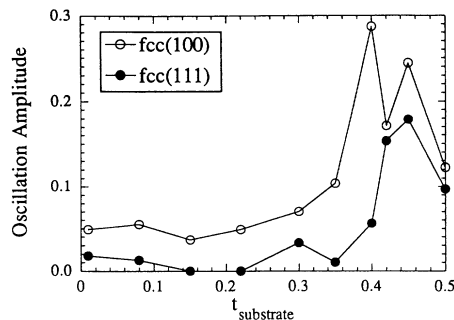


FIG. 3. Oscillation amplitude vs. $t_{\text{substrate}}$ for (○) fcc(100) surface with 128 atoms/layer and a deposition rate of 12 800 steps/layer; (●) fcc(111) surface with 140 atoms/layer and a deposition rate of 12 600 steps/layer.

reasons the formation of three nearest neighbors is higher than that of four. Therefore, in the absence of other factors the fcc(111) surface will then be able to support more atoms in upper layers, causing smaller diffraction oscillations.

Runs on fcc(100) systems with larger box sizes (512 atoms/layer) show similar trends. However, we cannot rule out the possibility that much larger box sizes are needed to adequately simulate diffraction, since it is known that at least in some cases the coherently scattering region for RHEED is larger than $1000 \text{ \AA}$.²¹

In conclusion, we have simulated diffraction oscillations during growth using molecular dynamics and have observed stronger oscillations for the fcc(100) surface than the fcc(111) surface. Increases in oscillations were observed for higher temperatures for both surfaces. Strong reentrant oscillations were not observed.

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