Reflection High-Energy Electron Diffraction (RHEED) Oscillations at 77 K

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Strong intensity oscillations have been found in RHEED during epitaxial growth at 77 K. This temperature is too low for thermally activated diffusion and establishes that the deposited atom uses its latent heat of condensation to skip across the surface, preferentially coming to rest at growing island edges, to achieve quasi-layer-by-layer growth. This growth mechanism implies that RHEED oscillations should be observable at 0 K. The data also provide insight into the basic principles governing RHEED oscillations.

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Since their discovery a few years ago,[1] the oscillations which occur in the reflection high-energy electron diffraction RHEED specular intensity during epitaxial growth have been the subject of intensive investigation both experimentally[2] and theoretically.[3] The motivation for this activity is clearly that an improved understanding of the varied characteristics of these oscillations is likely to provide a deeper understanding of (and better control over) the microscopic processes involved in epitaxial growth. The present study of very-low-temperature epitaxy of metals on metals provides an improved understanding both of the role of coherent elastic scattering in RHEED oscillations and of the microscopic mechanisms of epitaxy. With this improved understanding, it is found that better control over epitaxy can indeed be gained and growth modes can be achieved that are not thermodynamically favored.

In most cases, RHEED oscillations have a period corresponding to the deposition of 1 monolayer (ML).[2] The oscillations are thought to occur only under conditions which produce layer-by-layer growth via the nucleation of 2D islands on a flat terrace, gradual merger of the islands into a flat terrace, and renewed nucleation, in a cyclical process.[1-3] The nucleation and growth of the islands are thought to be mediated by thermal diffusion of deposited atoms to the edges of growing 2D islands.[1-3] However, in recent work, RHEED oscillations have been observed for growth on substrates at room temperature,[4] and even well below room temperature.[5] These observations raise the question of whether thermal diffusion can actually be the sole mediating mechanism.

Motivated by this question, the present study was undertaken to find out if RHEED oscillations can occur at 77 K, a temperature low enough to ensure that thermally activated surface diffusion is effectively suppressed[6] (in hindsight, we can say that it was also probably suppressed in some of the work in Ref. 5, although this point was not discussed). Indeed, strong oscillations have been found at 77 K for all systems studied to date, including Cu and Fe on Cu(100) and Ag, Cu, Fe, and Mn on Ag(100). Figure 1 presents typical data for Cu and Fe on Ag(100). The strength and duration of the oscillations suggest that the growth must be at least quasi layer by layer.[3,7,8] Theoretical work has established that if the deposited atoms condense into the lattice site on which they land, layer growth at each site follows a Poisson distribution and essentially no oscillations are observed.[6,8,9]

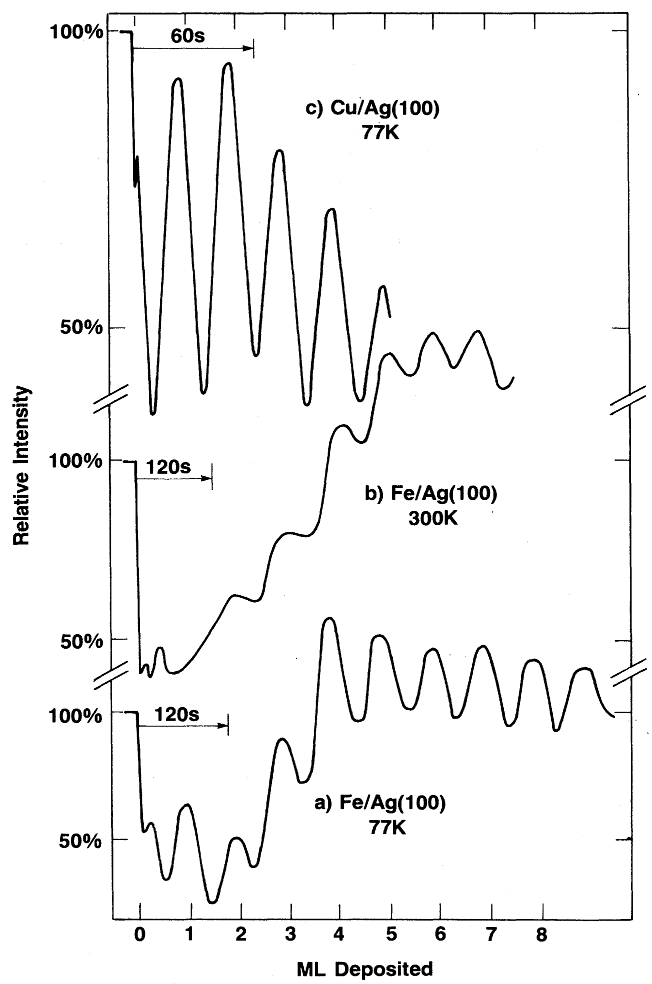

FIG. 1. The RHEED specular intensity for (a) Fe on Ag(100) at 77 K; (b) Fe on Ag(100) at 300 K; and (c) Cu on Ag(100) at 77 K. The incident angle is 1.4°, the beam energy is 5 keV, and the azimuth is ⟨001⟩.

Since this is clearly not the case in Figs. 1(a) and 1(c), the deposited atoms must be using their latent heat of condensation (≈ 3 eV), in lieu of thermally activated diffusion, to overcome the energy barrier to surface diffusion (≈ 0.4 eV)[7] and skip along the surface.[10] However, one would not expect more than several such lattice-site hops to be possible before the deposited atom came to rest since, by momentum conservation, each collision with an underlying atom of equal mass should have the deposited atom losing a large fraction of its kinetic energy. Indeed, the low-energy electron diffraction (LEED) spot intensity profiles of all the epitaxial films grown in this study are greatly enlarged at beam voltages set for destructive interference between different level terraces (even after depositing an integral number of monolayers). The width of these profiles [Δk (FWHM) $\approx 10\%$ of a $\langle 01 \rangle$ reciprocal-lattice vector] suggests that the average terrace size is roughly of the order of ten atoms across.[11] This would appear to require a large number of hops for the deposited atom if the directions of the hops were uncorrelated (e.g., 100 hops to move away ten sites). This suggests that the deposited atom tends to move in one direction and can do so for on the order of ten hops but has a strong preference for stopping when it encounters a step at the edge of an island. At LEED beam voltages corresponding to constructive interferences between terraces, the spots are nearly as sharp as the initial substrate spots indicating that even at 77 K nearly all the atoms occupy lattice sites. Thus, the epitaxial film is neither laterally nor vertically disordered, but does contain a degree of randomness in the occupancy of lattice sites in the top layer or two of atoms. [Note: Fe and Cu on Ag(100) are bcc, Fe on Cu(100) is fcc, and Mn on Ag(100)) is intermediate between fcc and bcc, as verified by x-ray photoelectron (XPS) forward scattering.]

Figure 1(b), for Fe deposited on Ag(100) at 300 K, provides additional insight into the growth mechanisms. The oscillation at 1 ML is always missing at 300 K since the Fe tends to agglomerate by thermal diffusion. This agglomeration is driven by surface and interface free energies and its occurrence has been verified by XPS forward scattering.[12] As the Ag(100) substrate becomes buried by Fe, Fe on Fe begins to grow layer by layer, and oscillations develop. Thus, this combination of RHEED oscillations, LEED spot profiles, and XPS provides a better understanding of the processes involved in low-temperature epitaxy and shows how growth modes can differ with temperature. In particular, a quasi-layer-by-layer growth mode may be achieved, by suppressing thermally activated diffusion, even when such a growth mode is not thermodynamically favored (as is typical for a high surface-free-energy metal grown on a low surface-free-energy substrate[13]).

In light of the many discussions in the literature on the optimum temperature for observing RHEED oscillations, an additional point may be of interest. Since thermally activated diffusion is absent at 77 K, the present observations strongly suggest that for these systems good RHEED oscillations should be observable even at 0 K.

The present data on RHEED oscillations at 77 K have also made it possible to gain a deeper understanding of the electron scattering processes involved in the RHEED oscillations themselves. This is possible, in part, because it is clear from the preceding discussion that below a thickness of about 0.1 ML, the atoms deposited at 77 K will tend to reside as isolated adatoms on the surface. Therefore, the initial transient in the RHEED specular intensity will be due to scattering of the electron wave by these isolated adatoms. As illustrated in Fig. 2, these transients can go in either direction depending on incident angle and beam energy, and they often have a very steep slope. The initial transients in Fig. 2 reach 50% of their full extent at a coverage of only 0.08 ML.

It appears that the incident wave field undergoes strong elastic scattering by the adatoms and that, depending on incident angle and energy, the phase of this scattered wave may be either constructive or destructive with respect to the wave scattered from the flat surface. Support for this interpretation comes from a variety of other observations made with Cu on Cu(100) at 77 K and beam energies from 2.5 to 30 keV.

First, after depositing several ML, a sufficient number of steps and adatoms are present so that the first- and second-order Bragg spots of the transmission-electron-diffraction pattern are clearly observable (this is also observed for the metals other than Cu). The sharpest upward and downward initial transients correspond to angles of incidence that put the specular reflection near the center of the first-order Bragg spot and near the anti-Bragg position (between the first- and second-order Bragg spots), respectively. In Fig. 2 the insets illustrate

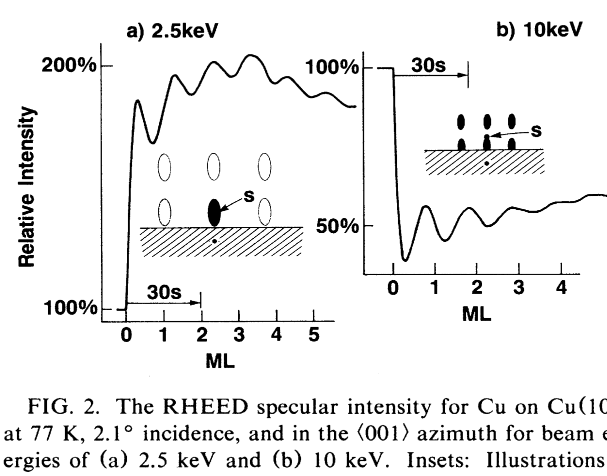

FIG. 2. The RHEED specular intensity for Cu on Cu(100) at 77 K, 2.1° incidence, and in the $\langle 001 \rangle$ azimuth for beam energies of (a) 2.5 keV and (b) 10 keV. Insets: Illustrations of the crystal shadow edge, the Bragg spots, and the specular (s) position.

where the specular beam is located with respect to the Bragg spots and the shadow edge of the crystal.[14] The Bragg spots are elongated since $k_\perp$ is not well conserved. Since the steepest initial transients occur just below the center of the Bragg and anti-Bragg positions, the isolated adatoms may give a somewhat different phase shift for the scattered wave than do small 2D islands that generate the Bragg spots.

Second, at low coverage these adatoms will appear, to a grazing-incidence electron wave, as protruding out into the vacuum, and can scatter amplitude into the specular direction more efficiently, because of reduced elastic and inelastic attenuation, than can a flat surface.[15]

Third, the azimuthal angle of incidence seems to be of less importance than the polar angle in determining the direction of the initial transient (up or down). At 1.4° incidence and 5 keV (the specular and Bragg conditions coincide here), upward initial RHEED transients for Cu on Cu(100) are observed along the ⟨001⟩ and ⟨013⟩ azimuths, as illustrated in Figs. 3(a) and 3(b), and also at 6° off the ⟨011⟩ azimuth. Since the phase shift of the incident wave specularly scattered by adatoms is probably only weakly dependent on azimuth, these data suggest that the phase shift of the wave scattered by the flat terrace areas of the surface is also only weakly dependent on azimuth. However, until more complete azimuthal data are available, we must hold open the possibility that certain azimuths may give different results due to such phase-shift effects. Nevertheless, the important point is that these data allow us to rule out surface-wave resonances as a primary factor governing the initial transients and the phase of the oscillations. These Kikuchi-related effects are subject to existence conditions that are highly azimuth dependent.[16] At incident conditions that do excite surface-wave resonances (not illustrated in Figs. 1–3), the specular intensity is higher, but nothing unusual was observed in the RHEED oscillations.

Fourth, to test whether specular scattering plays a critical role, attempts were made to observe oscillations

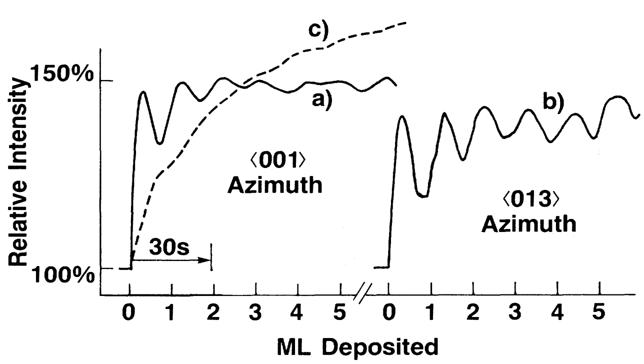

FIG. 3. The RHEED specular intensity for Cu on Cu(100) at 77 K at 1.4° incidence and 5 keV, along (a) the ⟨001⟩ and (b) the ⟨013⟩ azimuths. The intensity at the second-order Bragg spot for the conditions of (a) is shown in (c).

in the nonspecular Bragg spots. In general, it was extremely difficult to identify any such oscillations. They were always at least an order of magnitude weaker than the oscillations in the specular beam and were superimposed on a monotonically changing background. Figure 3(c) illustrates a typical result, recorded for 1.4° incidence and 5 keV in the ⟨001⟩ azimuth where the specular and first-order Bragg spots coincide. However, the intensity was collected at the second-order Bragg spot immediately above the specular beam. This rather featureless curve indicates that amplitude scattered into the specular beam (where all equivalent atoms in a given layer contribute in phase) is crucial for both sudden initial transients and strong oscillations.

Fifth, to test whether diffuse, incoherent scattering (or horizontal Kikuchi lines) plays a significant role, several attempts were made to observe oscillations in the background between the specular and Bragg positions. No oscillations were observed and only the weakest of rises in intensity was found. Therefore, diffuse incoherent scattering appears largely irrelevant. However, bulk channeling of the incident beam into the time-reversal states of horizontal Kikuchi bands could be involved if the roughened surface enhances such channeling. In the usual two-beam dynamical theory, if the specular spot is just above the center of the Bragg spot, a type-1 wave is set up (amplitude between atoms giving anomalous transmission down into the bulk[17]) and the specularly reflected intensity could drop as the surface roughens, as in Fig. 2(b). If the specular spot is below the Bragg spot, a type-2 wave (amplitude on the atoms[17]) is set up and the specular intensity could increase as the surface roughens, as in Fig. 2(a), because of increased elastic backscatter (as in the electron channeling patterns of scanning electron microscopy[17]).

Clearly, steep initial transients and strong oscillations are critically dependent on having coherent, elastically scattered amplitude from different scatterers being either in or out of phase. However, it is important to point out that unresolved complexities remain. The data of Figs. 1–3 might suggest that the initial transient determines the phase of the oscillations [a near 180° reversal occurs between 2(a) and 2(b)]. In fact, the situation is more complex. In general, the phase of the oscillations changes somewhat more slowly with incident energy or incident angle than does the initial transient. This means that, experimentally, in moving the specular beam off the Bragg spot, the initial transient changes direction more rapidly than the phase of the oscillations changes. Perhaps this is because the absolute phase shift between the adatom-scattered wave and the flat-terrace-scattered wave is greater than that between 2D-island-scattered wave and the flat-terrace-scattered wave. Note that the 2D island is an intermediate case in that the wave can enter or exit through a step (like the adatom case) or can enter or exit through the top of the island (like the flat-terrace case). In any event, an important issue for future theoretical work will be comparison of the phase shift of the specularly scattered wave from a flat terrace, an isolated atom, a 2D island of progressively increasing size, and the dynamical interaction among them. With such an analysis it should be possible to extract the structural information concerning film growth that is expressed in the relative changes between the initial transient and the oscillation phase for the case of the specular spot being intermediate between Bragg and anti-Bragg conditions.

In conclusion, RHEED oscillations at 77 K provide a better understanding of low-temperature epitaxial-growth processes for metals on metals, suggest a method for achieving quasi-layer-by-layer growth even when it is thermodynamically unfavorable, and provide an improved understanding of the coherent elastic scattering processes governing RHEED oscillations.

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