Reentrant Layer-by-Layer Growth during Molecular-Beam Epitaxy of Metal-on-Metal Substrates

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The discovery of a reentrant layer-by-layer growth during molecular-beam epitaxy of Pt on Pt(111) is reported. Explanations of the reentrant behavior based on previous field-ion-microscopy observations are proposed.

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Intensity oscillations in reflection high-energy electron diffraction[1] (RHEED) and in thermal-energy atom scattering[2] (TEAS) during epitaxial growth and ion sputtering are unique evidence for layer-by-layer growth and removal processes, respectively. The first RHEED experiments were performed with semiconductors. Later on, clear oscillations during growth of metal-on-metal substrates were seen in TEAS[3] above room temperature and then at 100 K in RHEED.[4] The very low temperatures at which metals appear to grow layer by layer caused most of the excitement for both practical and theoretical reasons. This opens the way to grow successive overlayers of different materials by reducing interdiffusion. On the other hand, because layer-by-layer growth requires a certain degree of adatom mobility, it should be expected to fail at low enough temperatures. However, in view of its persistence, even at 77 K, an interesting suggestion has been made:[5] "the deposited atom uses its latent heat of condensation to skip across the surface, preferentially coming to rest at growing island edges." This would imply the exciting perspective that layer-by-layer growth should be observable down to 0 K.

Surprisingly, an apparently basic contradiction in the temperature behavior of the TEAS and RHEED oscillations has not been recognized so far. While in both TEAS and RHEED measurements an upper temperature limit for the existence of oscillations has been observed and explained by similar arguments (steady-state distribution of steps,[4] growth taking place from step edges,[5] i.e., step propagation[6]), RHEED oscillations are still present down to the lowest temperature reported so far,[5] in contrast to the TEAS oscillations which disappear when descending just below room temperature.[3] The discrepancy is obviously not related to the nature of the system: The Cu/Cu(001) system has been investigated in both cases. Because there is no *a priori* reason why TEAS should not exhibit oscillations under conditions where layer-by-layer growth is inferred from RHEED oscillations,[7] we concluded that there must be a deeper physical reason. This has triggered the present TEAS investigation of the growth of Pt on Pt(111) over an extended temperature range (100–900 K).

The main result is the discovery of what we call reentrant layer-by-layer growth.[8] This is demonstrated in Fig. 1 by three curves for He antiphase specular intensity versus deposition time, measured at different temperatures; the other parameters, including the deposition rate, confined between 1/40.6 and 1/36 ML/s (where ML denotes monolayer), have been kept identical. (The data in Fig. 1 are representative of an extended series of reproducible experimental data taken in the temperature

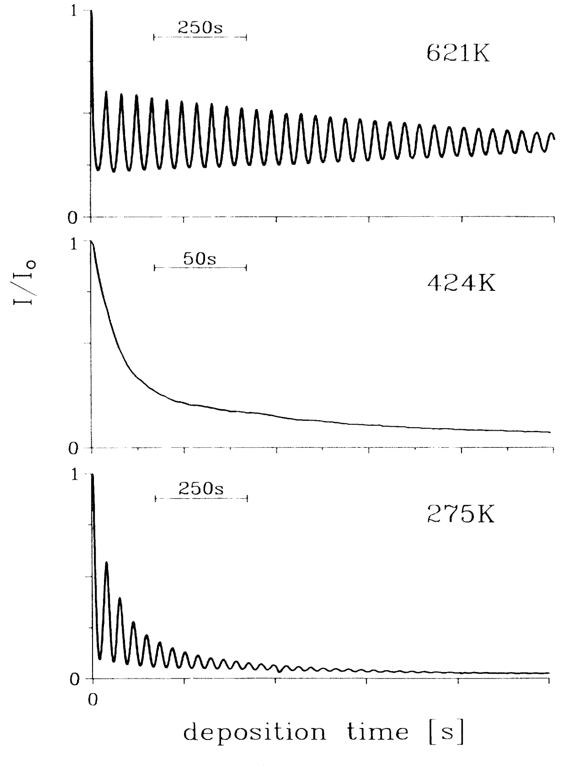

FIG. 1. The normalized He specular peak height vs Pt on Pt(111) deposition time measured at three different surface temperatures. All other parameters including the deposition rate (confined between 1/40.6 and 1/36 ML/s) are identical. The oscillatory behavior at high and low temperature is evidence for layer-by-layer growth (denoted in the text by $2D_h$ and $2D_l$ growth, respectively); the monotonic decrease in the intermediate region indicates 3D growth.

range 100–800 K showing a gradual transition from the oscillatory to the nonoscillatory and eventually to the reentrant oscillatory behavior. Extensive and careful control experiments demonstrate that the effects observed, including those shown in Fig. 2, are not due to contamination.) Obviously the layer-by-layer growth is—at least for Pt/Pt(111)—reentrant. This provides a physical explanation for the apparent contradiction between the TEAS and RHEED data pointed out above. In addition, it suggests that the explanations for the dramatic damping at the upper temperature limit of the low-temperature oscillations (steady-state step distribution,[4] step propagation[6]) and for the low-temperature limit of the high-temperature oscillations (loss of adatom mobility[3]) are probably not appropriate for the respective cases.

Before proposing a qualitative explanation for the behavior evidenced by the TEAS plots in Fig. 1, which might provide a better understanding of the growth process, we will discuss the various growth modes and their relation with the TEAS plots and will give a few experimental details.

In the ideal layer-by-layer growth mode, a new layer starts to be formed only *after* the preceding layer (underneath) is completed; thus the growth is two dimensional (2D) and fractions belonging to at most two consecutive layers are simultaneously uncovered. This type of growth leads to strong and, in the ideal case, undamped oscillations of both the in-phase and antiphase coherent TEAS intensities. The coherent intensities (here the specular beam) oscillate because defects and, in particular, step edges have a large cross section for diffusively scattering the thermal He beam (e.g., a band 12 Å wide along step edges scatters diffusively). Thus when a layer is complete (minimum density of steps), the surface reflects optimally and the specular intensity reaches a maximum. In contrast, when a new layer is about half filled the number of defects (in particular, the step-edge length confining the islands) reaches a maximum and thus the reflectivity exhibits a minimum. The oscillations of the antiphase peak height are more pronounced (deeper minima) because just when the new layer is half filled the destructive interference between the He waves scattered from the now equal uncovered areas of the two layers is theoretically perfect (for a detailed discussion see, e.g., Ref. 7).

An almost ideal 2D behavior has been observed under optimal experimental conditions (base pressure 10^{-11} mbar, a well prepared Pt surface, a thoroughly cleaned Pt atom source, negligible impurities in the He beam, etc.) in the high-temperature region, $2D_h$. Over 150 periods could be clearly seen. It could be demonstrated that most of the observed slight damping of the oscillation amplitude is due to minute inhomogeneities of the Pt deposition rate over the macroscopic spot area of the monitoring He beam;[9] this is essentially not a departure from the ideal 2D growth but a slowly increasing difference between the phases of the growth process on widely separated regions of the probed area. In contrast, the oscillation amplitudes in the low-temperature region ($2D_l$ in Fig. 1) are more strongly damped and the coherent intensity eventually drops to low values (both effects become stronger with decreasing temperature). This means that, in spite of the quasi-layer-by-layer growth, the defect density increases with deposition time due to the reduced mobility. The initial damping is more pronounced in TEAS than in RHEED due to the very large cross section of the defects for thermal He diffuse scattering.[7] Nevertheless, up to about thirty periods are still observable at $T_s = 295$ K.

In contrast to the 2D growth, in the three-dimensional (3D) growth a new layer starts to be formed well *before* the preceding ones are completed. As a consequence, the defect density (in particular, the total step-edge length) increases monotonically, leading to a likewise monotonic decrease of the coherent intensity (in-phase and antiphase). The monotonic decrease observed in the temperature region in between the low- and high-temperature regions of 2D growth in Fig. 1 is evidence of 3D growth.

In order to obtain insight into the growth mechanism in its simplest form, we have investigated here a homoepitaxial system. We have chosen Pt(111) as a substrate to avoid delicate "mobility" assumptions:[5] Pt atoms are known to be mobile on Pt(111) down to 70 K.[10] The Pt(111) surface with a step atom density of about 0.5% has been first cleaned by extended oxidation-sputtering cycles until no impurities could be detected by Auger-electron spectroscopy and TEAS. Before each growth measurement, the previously deposited layers were removed by sputtering and the sample was annealed at 1000 K. This and occasional prolonged annealing at 1300 K ensured reproducible results even in the particularly sensitive $2D_h$ region. A detailed description of the UHV He scattering apparatus and of the TEAS measuring procedure can be found in Ref. 7.

We return now to the explanation of the reentrant 2D growth; the explanation, admittedly somewhat speculative, is qualitatively supported by the available data. When the temperature and the deposition rate are such that the deposited adatoms are mobile and supersaturation exists (both conditions are fulfilled in the whole range of the present experiment), the adatoms will form islands.[11] According to the definitions above, in the 3D growth region, new islands nucleate on top of the lower-level islands *well before* these coalesce into a complete layer; in contrast, in the *ideal* 2D growth, new islands nucleate openly on a completed layer. In the real experiment, islands do of course nucleate on top of islands of the preceding layer, when the latter is close to completion, while the growth process still retains the essential features of the 2D growth. This may occur, e.g., on the largest islands formed by coalescence towards layer completion.

Let us analyze first the island-formation process in some detail. When the deposition starts, the adatoms are first dispersed and their lattice-gas 2D spreading pressure steadily increases. At sufficiently high spreading pressure local-density fluctuations lead to adatom clustering (islands). When these islands exceed a critical size they are stable during a long enough time to incorporate a newly arriving adatom before falling apart. As seen by field-ion microscopy (FIM) the incorporation of adatoms at *ascending* steps occurs on impact.[12] Thus, once formed, the supercritical islands grow rapidly. Their step-edge perimeter representing a sink for the adatoms on the lower layer, the adatom density on this lower layer soon ceases to increase and eventually starts to decrease; so does the probability for the creation of new supercritical nuclei. The number of islands growing on the lower layer is thus essentially the number of supercritical nuclei created in the initial stage. This number decreases with increasing temperature and decreasing deposition rate:[13] At higher temperatures and/or lower deposition rates less and thus larger islands will grow.

Decisive for 3D or 2D growth is whether or not supercritical nuclei are formed on the top of growing islands. If the adatoms present on the islands can jump onto the lower layer without having to overcome a barrier larger than the diffusional barrier on the surface itself, the adatom density on the growing islands will be equal to that on the lower layer. Because, as shown above, in the presence of islands the latter is too low for the formation of supercritical nuclei, no islands are formed on the top of the growing ones either: Thus, 2D growth takes place. However, again FIM studies[14] have shown that on the dense W(110) surface adatoms are reflected from descending steps. (More recently the corresponding barrier has been found to be about 200 meV.[15]) If, in fact, a similar barrier exists also at the descending steps of the Pt(111) islands, we have a plausible explanation for the transition around 500 K between the $2D_h$ and the 3D behavior: Above 500 K the thermal energy of the adatoms is large enough so that they jump easily onto the layer below and there is no nucleation until layer completion ($2D_h$ growth). In contrast, with the temperature decreasing below 500 K the number of attempts for a successful jump becomes larger and so does the Pt adatom density on the islands; thus supercritical nuclei are formed on top of the islands, resulting in 3D growth.

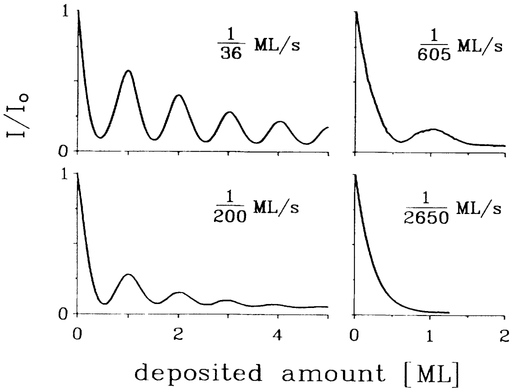

FIG. 2. The normalized He specular peak height vs Pt on Pt(111) deposited amount measured at the same temperature (273 ± 2 K), but at different deposition rates. All other parameters are identical. By decreasing the deposition rate the growth process changes gradually from $2D_l$ (upper left curve—identical with the bottom curve in Fig. 1) to 3D behavior (bottom right curve).

A possible cause of the reentrant $2D_l$ growth when the temperature is decreased further can be found in the reduced island size and/or their less regular shape, both due to the reduced adatom mobility at lower temperature. Indeed, detailed FIM measurements on W(211) islands have shown that at the edges of small islands and at the energetically less favorable steps bordering larger islands, the retention of adatoms is small or even negligible:[16,17] The adatoms may jump easily onto the lower level. By assuming a similar behavior of Pt adatoms on the Pt(111) islands, we may infer that on the small islands with irregular shapes growing at low temperatures the Pt adatom density stays low, practically equal to that on the lower-layer level. Thus no supercritical nuclei can be formed on the top of these islands and $2D_l$ growth occurs.

This certainly speculative explanation of the reentrant $2D_l$ growth is strongly supported by the curves in Fig. 2 in which the size and the shape of the islands are manipulated by varying the deposition rate over 2 orders of magnitude. The curves represent plots similar to those shown in Fig. 1, in this case measured at the same temperature $T = 273 \pm 2$ K but with different deposition rates. They demonstrate clearly that by decreasing the deposition rate the system moves from $2D_l$ into the 3D-growth region. Based on simple intuition the result is at least surprising: By giving the system more time to build larger and more regular structures, the clear periodic signal disappears. In the frame of our explanation, however, the reason is straightforward: With decreasing deposition rate the islands become larger and more regular; a high adatom density leading to critical nucleation can then build up on top of the islands.[18]

We report the discovery of reentrant layer-by-layer growth during molecular-beam epitaxy of Pt on Pt(111). This solves an apparent contradiction between RHEED and TEAS results reported previously on other systems. A qualitative explanation for the reentrant behavior is proposed. Experiments to clarify details of the phenomena are in progress.

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[8] The term *reentrant* is in current use in a similar sense in connection with the wetting of surfaces by nonmetallic adsorbates. In the present context, it has the additional advantage that it is not directional; i.e., people accustomed to layer-by-layer growth at low temperatures disappearing above a certain temperature will now have to expect that above a certain temperature interval this type of growth (and thus the oscillations) will reappear; conversely, the others which have observed the oscillations at high temperatures which faded below a certain limit will expect the reappearance of the oscillations when cooling the sample below another limit.

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[11] To simplify the argument we will neglect here the fixation of the adatoms at preexisting step edges, which at $T > 850$ K, where it becomes preponderant, leads to the "step propagation." This is not a restriction of the generality because we are focusing here on the processes taking place below 650 K.

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[13] At higher temperatures the critical size for islands to be stable is larger; at lower deposition rates they have to be stable for a longer time before a new adatom arrives and is incorporated.

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[18] If confirmed, the mechanism of leakage through irregular descending steps might also represent an alternative explanation for the upper 3D-2D$_h$ transition. Indeed, from simple scaling the roughening of step edges on a Pt(111) surface is expected to occur between 600 and 700 K. As the proliferation of kinks—the main characteristic of this roughening—will start certainly somewhat earlier, this might explain the 3D-2D$_h$ transition, and would predict that this transition temperature is largely independent of deposition rate.