Atomic Processes in Low Temperature Pt-Dendrite Growth on Pt(111)

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Shape and branch thickness of dendritic Pt-adatom islands on Pt(111) are compared with the results of kinetic Monte Carlo simulations. Atoms attached to just one atom of an island were found to have an asymmetric jump probability towards higher coordinated sites. This asymmetry, which results from nonequivalent hopping paths, gives rise to preferential growth directions at low temperatures.

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Fractal and dendritic two-dimensional adatom islands may be grown at low temperatures by homoepitaxial or heteroepitaxial deposition on fcc (111) or hcp (0001) surfaces [1–6]. Since compactness and step-edge roughness of islands are two main factors determining the transport between atomic layers, the importance of this pattern formation process for thin film growth was readily realized [2,7]. However, considerable discrepancies still exist concerning diffusion processes on the atomic level which determine the formation and appearance of the experimentally observed dendritic and fractal islands. Fractal Au dendrites on Ru(0001) [1] and Pt dendrites on Pt(111) [3] were considered as physical realizations of a two-dimensional hit-and-stick model [8], whereas the difference of step-edge diffusion along the two types of close-packed steps was suggested to be decisive in the growth of Ag dendrites on Ag(111) and Pt(111) [4,5].

Here, by an interactive approach of experiments and simulations, a new mechanism is identified, which determines the anisotropy of growth of Pt on Pt(111) at low temperatures. Experimentally, the analysis is based on the temperature dependence of the island shapes and branch thicknesses of Pt dendrites grown on Pt(111) in the range from 150 to 285 K as obtained from scanning tunneling microscopy (STM) topographs. The ability of kinetic Monte Carlo (MC) simulations to reproduce the branch thicknesses and the island shapes derived from the experiments turns out to be a stringent test for assumptions on the growth processes of the Pt dendrites.

The experiments were performed in a UHV chamber with a variable low temperature STM [9]. In each experiment $(9.4 \pm 0.5)\%$ of a monolayer (ML) Pt was deposited at a fixed temperature T_s between 150 and 285 K with a deposition rate of 6.7×10^{-4} ML s^{-1} from a thoroughly cleaned, electron beam heated Pt foil onto a Pt(111) surface with a terrace width of 1000–4000 Å. After deposition the sample was quenched to 20 K and imaged by STM in order to rule out diffusional changes subsequent to deposition.

Figure 1 exhibits two representative STM topographs obtained after deposition at 180 (a) and 245 K (b). The islands have a dendritic-branched structure with apparent average branch thicknesses of 13 (a) and 23 Å (b). The shape of the islands and the orientation of their branches are anisotropic. This is most pronounced at 245 K, where the branches grow preferentially in the three $\langle \bar{1}\,\bar{1}2 \rangle$ directions of the (111) terrace, giving rise to islands with triangular envelopes.

In order to get a measure of the island structure suitable for comparison with MC simulations, we determined first from the average apparent branch thickness, d_{app}, the true one, d_{true}, at each growth temperature. The average apparent branch thickness was determined from grey scale topographs like those in Figs. 1(a) or 1(b). This quantity is plotted as a function of temperature in Fig. 1(c). Any measure value d_{app} results from a widening w of the true branch thickness d_{true} by the STM tip: $d_{\mathrm{app}} = d_{\mathrm{true}} + 2w$ [10]. Since the STM-tip-dependent widening w cannot be obtained directly, we proceeded as follows: The total apparent coverage Θ_{app} was determined for each of the

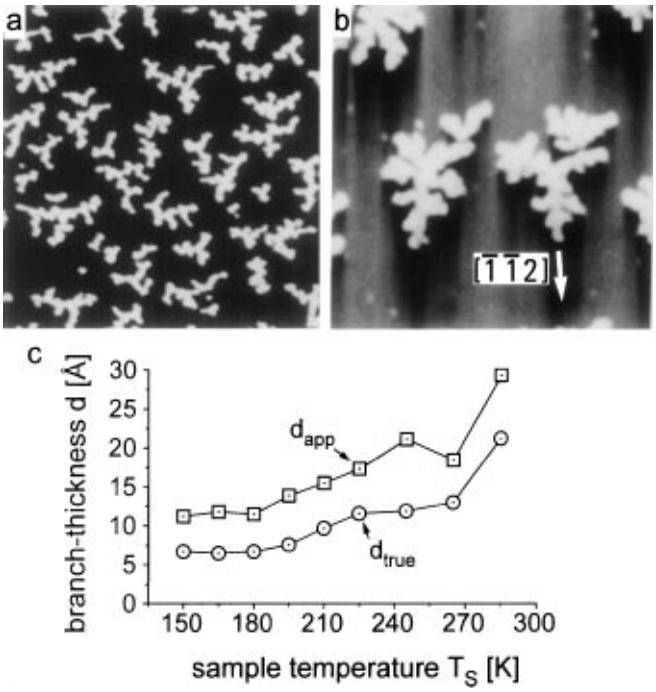

FIG. 1. STM topographs of 600 Å × 600 Å size obtained after deposition of 9.4% ML at $T_s = 180$ (a) and 245 K (b). (c) Temperature dependence of the average apparent branch thickness d_{app} of the Pt dendrites and of the corrected values d_{true} (see text).

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images. While the true coverage was in all case $\Theta_{\text{true}} = (9.4 \pm 0.5)\%$ ML [11], Θ_{app} ranged typically from 13% to 17% of a ML. Since the branch thickness of the dendrites investigated here is much smaller than the branch length, $d_{\text{true}} = d_{\text{app}}\Theta_{\text{true}}/\Theta_{\text{app}}$. The widening $w = \frac{1}{2}(d_{\text{app}} - d_{\text{true}}) = \frac{1}{2}d_{\text{app}}(1 - \Theta_{\text{true}}/\Theta_{\text{app}})$ caused by the STM tip ranges in the present experiments from 2 to 5 Å, being consistent with Ref. [10]. Using the procedure described above, d_{true} is plotted in Fig. 1(c). The true branch thickness appears to stay nearly constant around 6.5 Å between 150 and 180 K, then increases, reaching a small plateau of about 12 Å between 225 and 265 K before a final rapid increase sets in.

The average *in-plane* coordination number C of atoms in the aggregate is a direct output of the MC simulations. Accordingly, the corrected branch thicknesses d_{true} have been transformed into experimental average in-plane coordination numbers C_{exp}. One obtains an upper bound for C_{exp} [curve "exp-up" in Fig. 2(a)] by assuming that the edges of the branches are atomically flat. A better approximation for C_{exp} is obtained by assuming that every fifth edge atom contributes to branch roughness (i.e., to be only twofold coordinated), which gives rise to the curve exp in Fig. 2(a). The task of the MC simulation is now to reproduce the island shapes qualitatively and the curve exp quantitatively.

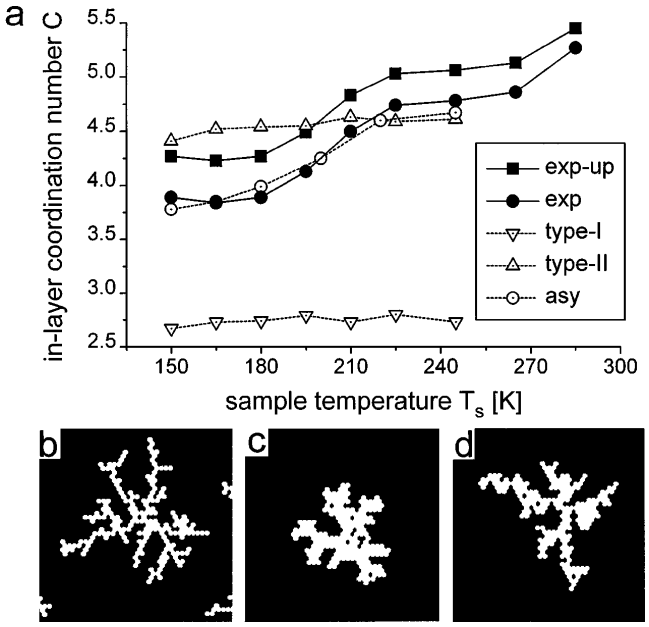

FIG. 2. (a) Temperature dependence of average in-plane coordination number C of atoms in Pt dendrites. Full symbols result from transformation of d_{true} under the assumption of atomically smooth branches (exp-up) and of every fifth edge atom contributing to branch roughness (exp). Open symbols result from MC simulations assuming hit-and-stick growth (type I), immobile bonding only in twofold coordinated sites (type II), and temperature dependent asymmetry in jump probability from onefold to twofold coordinated sites (asy) (see also text). Simulated island shapes at 180 K of type I (b), type II (c), and with the asymmetry assumption (d).

In the kinetic MC code used, Pt atoms are deposited at random in space and time with the deposition rate of 6.7×10^{-4} ML s^{-1} onto a hexagonal grid with periodic boundary conditions containing 3×10^4 fcc sites until a coverage of 10% ML is reached. For Pt-adatom migration an activation energy 0.26 eV and an attempt frequency 5×10^{12} Hz are used, which were determined in independent experiments [12]. The value of the activation energy agrees with a previous determination by field ion microscopy (FIM) [13]. Other processes and energies used in the simulation will be introduced below, chosen to be as simple as possible while still consistent with FIM observations. In the two-dimensional MC simulation, funneling [14] is included, and the few atoms deposited directly onto aggregates ($<0.3\%$ ML) are incorporated into the step edge at the nearest available sites.

The simplest assumption for the growth of the Pt dendrites is that the only thermally activated diffusion mechanism allowed is adatom migration. An adatom arriving at an aggregate sticks and stays immobile at the impact site, even if it is only onefold coordinated to the aggregate (the lightly shaded atoms in Fig. 3). This gives rise to the growth of islands of fractal type I (in the terminology of Ref. [15]). The simulated island shape at 180 K shown in Fig. 2(b), which is strongly branched and isotropic, is obviously different from the experimentally observed one [(Fig. 1(a)]. Moreover, the resulting coordination number plotted as curve "type I" in Fig. 2(a) is by far too low and almost independent of temperature.

In order to increase the coordination number one may assume that each atom attaching to an island in an only onefold coordinated site is mobile and jumps to a twofold

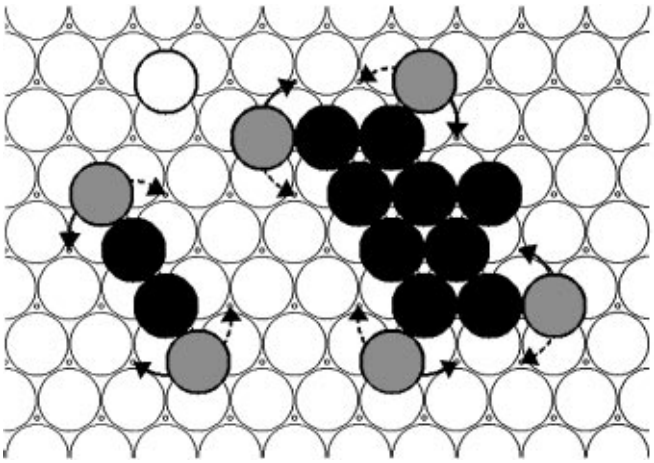

FIG. 3. Ball model of small agglomerates on Pt(111). The lightly shaded atoms are only onefold coordinated in plane. Dashed and full arrows indicate diffusional jumps into twofold coordinated sites via atop positions ad via bridge positions, respectively.

coordinated site before its initial position is stabilized by another arriving atom (fractal type II [15]). The island shape simulated with this assumption at 180 K, shown in Fig. 2(c), is almost compact, and the overall shape is also isotropic, as can be seen from the analysis of many islands. This differs again from the experimentally observed shape [Fig. 1(a)]. The corresponding simulated coordination number plotted as curve "type II" in Fig. 2(a) is almost temperature independent in contrast to the experimental curve. The failure of curve type II to describe the experiment adequately is also obvious from the fact that below 200 K it exhibits a higher coordination number than curve exp-up, which is an upper bound for the experimental coordination number. Including step-edge diffusion along close-packed steps would shift the type-II curve to even higher coordination numbers and thus can definitely by ruled out below 200 K.

In conclusion, neither island shape nor the temperature dependence of the coordination number of the experimental observed Pt dendrites on Pt(111) above 150 K can be explained by a hit-and-stick mechanism (fractals type I) as suggested previously by four of the present authors [3] or by other assumptions suggested for similar systems [1,4,5,15]. In particular, there exists a new anisotropic growth regime between 150 and 180 K which has an average coordination number lying between those of type-I and type-II fractal growth regimes as defined in a previous theoretical study [15].

To get a physical basis for more complicated assumptions to be used in the MC simulation a closer inspection of Fig. 3 is helpful. For each of the lightly shaded onefold coordinated atoms two different diffusion paths to adjacent sites are indicated: An atom moving along the full row is able to remain in a higher coordination with respect to the substrate (moving via hcp and bridge positions) than an atom moving along the dashed arrow (via an atop position [16]). Thus it appears reasonable to assume that jumps from onefold to higher coordinated sites via bridge positions have a lower onset temperature than via atop ones [17]. Defining the onset temperature as the temperature at which the jump frequency is 1 Hz, we chose for the onset temperatures of the two types of jumps 130 and 200 K, respectively. The temperature dependence of the coordination number simulated with these assumptions [curve "asy" in Fig. 2(a)] reproduces quantitatively the experimental data. Also the branched structure and the tendency towards anisotropy at 180 K are similar in simulation [Fig. 2(d)] and experiment [Fig. 1(a)]. This similarity is strikingly confirmed also at higher temperatures as seen in Fig. 4, where the shapes of islands grown at 245 K in experiment (a) and simulation (b) are compared. In both cases islands with triangular envelopes and preferential branch growth in the $\langle\bar{1}\,\bar{1}2\rangle$ directions are visible, as well as less regular shaped islands. The agreement between simulation and experiment is remarkable and gives strong evidence for the correctness of the asymmetry assumption. The further increase in branch thickness observed above 245 K has to be attributed to the onset of an additional diffusion mechanism which involves the motion of atoms which are more than onefold coordinated. This is probably the motion of atoms along close-packed steps [18].

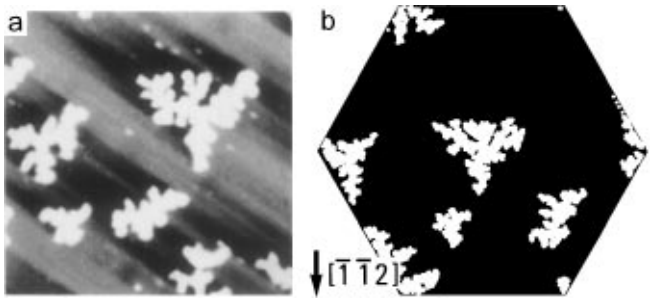

FIG. 4. (a) Experimental (500 Å × 500 Å) and (b) simulated (482 Å × 556 Å) islands shapes at 245 K. In order to facilitate the comparison a widening of 2 Å has been added to the branches of the simulated islands.

We note that, in view of the above results, the presence of step-edge diffusion is improbable for the growth of Ag dendrites on Pt(111) at 110 K [4,5], where a branch thickness of 2.5 atoms (~6.5 Å) [6] similar to that measured here below 180 K has been observed. Instead, since the Ag dendrites on Pt(111) exhibit also a triangular envelope oriented identically to that of Pt dendrites on Pt(111) the same mechanism as found here is likely to be operative. We also note that in the MC results in Ref. [15] this asymmetry is absent, because there only in-plane interaction of the adatoms were considered. In recent MC simulations for Pt on Pt(111) growth at 255 K, Pt islands with the opposite orientation of the triangular envelope were obtained [19] (triangle corners pointing into the $\langle 11\bar{2}\rangle$ directions). Such an orientation, which is at variance with the experimental one, can be obtained in our simulations only by reversing the asymmetry, i.e., by using a lower onset temperature for the jump via atop positions than via bridge ones, and thus can be traced back to the asymmetry as derived from EMT calculations of diffusion barriers.

Strong support for the asymmetry assumption is provided by the nature of the aggregation of Pt adatoms at the two types of close-packed $\langle 110\rangle$ steps preexistent on Pt(111). The two types of steps with different structure as obvious from the ball model in Fig. 5(a) have been defined as *A*- and *B*-type steps in Ref. [20]. The STM image in Fig. 5(b) shows that while the *A*-type step grows very rough with strong asperities, the *B*-type one remains relatively smooth. The MC simulation performed at the same temperature of 180 K with the correct asymmetry assumption shows the same difference between the appearance of the two types of steps upon growth. The reason for this behavior can be easily recognized from Fig. 5(a). Decisive for the degree of roughness of the growing steps is the fate of the atoms (lightly shaded), which are onefold

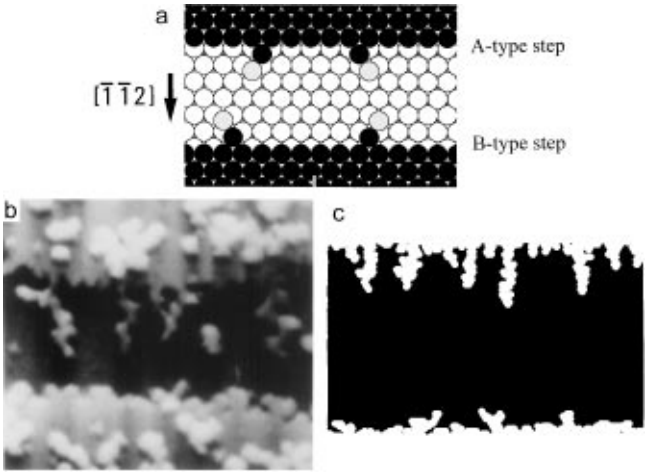

FIG. 5. (a) Diffusional jump towards step edge via bridge positions is possible for the onefold coordinated atoms attached to step adatoms at the *B*-type step (via bridge positions), whereas no such easy path exists for those attached to step adatoms at the *A*-type step (only via atop positions). In experiment (b) and simulation (c) at 180 K asperity growth is observed at *A*-type step edges, while the *B*-type step edges remain relatively smooth.

coordinated at step adatoms: while those near the *B*-type step can reach the step by an easy jump via bridge positions, the onefold coordinated atoms near the *A*-type step can reach this step only via the unfavorable atop sites. Accordingly, the latter will have a correspondingly higher chance to be stabilized by an arriving atom. Thus the *B*-type step stays relatively smooth, while on the *A*-type step strong asperities are present as obvious from experiment [Fig. 5(b)] and simulation [Fig. 5(c)].

In conclusion, the asymmetry in the jump probability for atoms attached onefold to Pt islands towards twofold coordinated sites at the island edge plays the decisive role for the temperature dependence of branch thickness and for Pt-dendrite shape on Pt(111) from 150 up to 250 K as well as for the shape of the aggregation at the different types of close-packed step edges. This process is likely to introduce anisotropy in the low temperature growth also on other surfaces with hexagonal symmetry.

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