

How Sensitive is Epitaxial Growth to Adsorbates?

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(Received 5 May 1998)

CO coverages as low as 10^{-3} monolayers—which may result from background partial pressures in the low 10^{-11} mbar range—are found to affect island shapes, island densities, step-edge barriers for adatoms and film roughness during homoepitaxial growth on Pt(111). The effects are traced to preferential adsorption of CO molecules on low coordinated Pt atoms. [S0031-9007(98)06823-9]

PACS numbers: 68.35.Bs, 68.55.Jk, 68.55.Ln, 82.65.My

Long before surfactants became fashionable it was known that adsorbed species from the residual gas may influence the morphology of films grown by vapor deposition (e.g., [1]). For “clean” growth, not only carefully cleaned substrates are necessary, but also the rate of impingement of the residual gases—especially of the reactive ones—must be minimized. As an example, the presence of atomic hydrogen in the residual gas during low-temperature silicon growth on Si(001) contributes to the loss of epitaxy at some critical thickness [2]. Technically, the impingement rate cannot be reduced infinitely. Therefore a microscopic understanding of the mechanisms by which minute amounts of foreign atoms may influence the growth process is essential. As an additional problem, the influence of residual gases has so far been mostly studied during deposition of many monolayers (ML) (e.g., [2,3]). As many impurities tend to float at the growth front, their concentration increases continuously. Here, we present experiments in which we focused on an atomic-scale understanding of the influence of minute amounts of CO on the submonolayer homoepitaxial growth on Pt(111).

The experiments were performed in a variable temperature STM apparatus. The Pt(111) sample was prepared by prolonged bombardment with a mass selected 1 keV Xe^+ ion beam at 700 °C, and annealing to 950 °C. The Pt-wire used for evaporation was cleaned by heating at 1000 °C for several days in an oxygen atmosphere of about 5×10^{-4} mbar in a separate vacuum chamber. Pressure measurements were performed with an ionization gauge down to 1×10^{-10} mbar and with a quadrupole mass spectrometer for lower pressures. They were calibrated and corrected for the ionization sensitivities for pure CO, H_2 , and Xe and found to behave linearly with respect to each other in the pressure range from 1×10^{-10} to 1×10^{-8} mbar. A prerequisite for the present experiments was an efficient reduction of the residual gas pressure during growth, especially of the CO partial pressure. This was achieved by (i) an overall reduction of the chamber base pressure and (ii) by replacing the electron bombardment Pt evaporator by a resistively heated Pt wire mounted on a watercooled support. (ii) was necessary, because accelerated electrons (e.g., from hot filaments) lead

in well outgassed vacuum chambers to a significant rise in CO partial pressure by electron stimulated desorption and/or processes following ionization events in the background gas [4]. (We verified that the onset of electron bombardment in our previous evaporator gave rise to significant CO partial pressures of a few 10^{-10} mbar). As a consequence of the two improvements, the total pressure during deposition remained below 2×10^{-11} mbar and the CO partial pressure below 5×10^{-12} mbar, to which the evaporator pressure rise contributed 7×10^{-12} and 2×10^{-12} mbar, respectively. Finally, we note that the flux of background gas particles impinging on the sample surface during deposition is usually larger than expected from the background pressure measurement. Because of the nearby evaporator the local pressure rise at the sample is higher than at the distant pressure measurement device. Purposely admitting CO during growth as in the experiments described below allowed us to estimate a factor of about 3 between measured and actual pressure rise at the sample, for our previous deposition experiments with an electron bombardment evaporator.

The key experiment discussed in this paper is shown in Fig. 1. Five STM topographs are compared corresponding to deposition of 0.15 ML Pt at 400 K at a rate of 5×10^{-3} ML/s with different CO partial pressures. The CO pressure was set 100 s before deposition started and maintained during the 30 s deposition time. The Pt islands resulting from clean deposition in Fig. 1a are triangular consisting of $\langle 110 \rangle / \{111\}$ steps ($\{111\}$ -microfaceted steps oriented along $\langle 110 \rangle$, briefly *B* steps) with a certain number of kinks. One triangle vertex of each island points to the right. A CO partial pressure of 1.0×10^{-10} mbar causes drastic changes in the island shapes (Fig. 1b). The islands are more compact and contain also segments of $\langle 110 \rangle / \{100\}$ —or *A* steps. In Fig. 1c at a CO pressure of 4.7×10^{-10} mbar the island edges are already dominated by *A* steps and start to develop a triangular shape, now with one triangle vertex pointing to the left. At CO pressures of 9.5×10^{-10} mbar (Fig. 1d) and 1.9×10^{-9} mbar (Fig. 1e) fully triangular islands consisting almost exclusively of *A* steps result from growth. Most of the islands in Figs. 1d and 1e already support a second-layer island, in contrast to those grown at lower CO

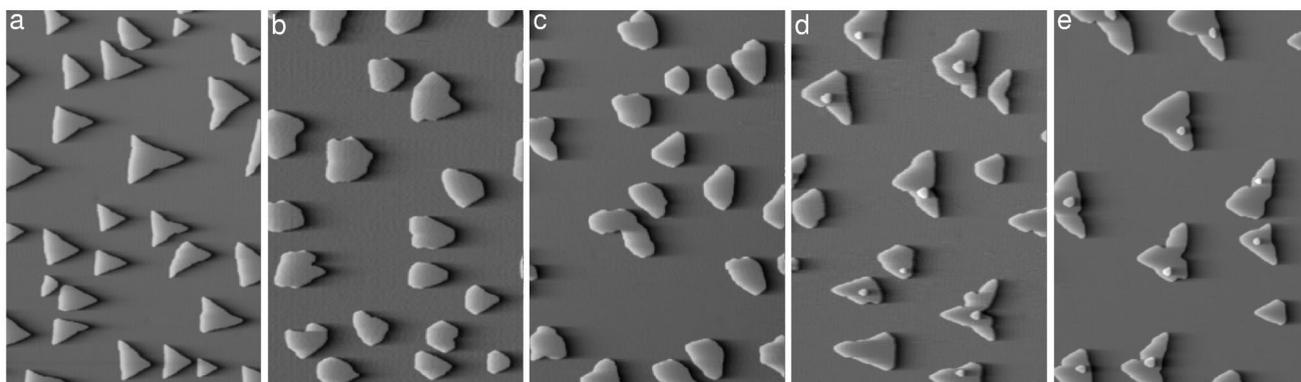


FIG. 1. STM topographs after deposition of 0.15 ML Pt on Pt(111) at 400 K with a deposition rate of 5×10^{-3} ML/s and with different CO partial pressures during growth. (a) $p_{\text{CO}} < 5 \times 10^{-12}$ mbar ("clean"); (b) $p_{\text{CO}} = 1 \times 10^{-10}$ mbar; (c) $p_{\text{CO}} = 4.7 \times 10^{-10}$ mbar; (d) $p_{\text{CO}} = 9.5 \times 10^{-10}$ mbar; (e) $p_{\text{CO}} = 1.9 \times 10^{-9}$ mbar. CO was admitted 100 s prior deposition. Scan size 1700×2500 Å.

pressures. This aspect has been quantified by determining for each CO partial pressure the average island area, for which the probability of finding a second layer nucleus is 0.5. This island area is converted to a critical diameter d_c of a circular island of identical area and plotted in Fig. 2 (left axis). As pointed out by Tersoff *et al.* [5], a decreasing d_c is uniquely related to an increasing height of the step edge (Ehrlich-Schwoebel) barrier E_{ES} for adatoms to descend from an island. Also plotted in Fig. 2 is the dependence of E_{ES} on p_{CO} as obtained from the values of d_c by the formula given by Tersoff *et al.* [5] (right axis). We note that other approaches exist [6], which give a qualitatively similar behavior but different values for E_{ES} . The topographs in Figs. 3b and 3d obtained after deposition of 5 ML at 300 or 400 K with $p_{\text{CO}} = 9.5 \times 10^{-10}$ mbar show not only differences in edge orientation and island compactness but also a drastically higher roughness compared to the clean growth in Figs. 3a and 3c. The interface width increases due to the presence of CO at 300 K from 1.5 Å (Fig. 3a)

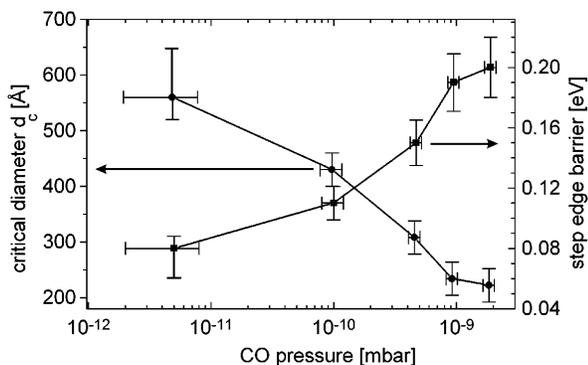


FIG. 2. Critical diameter d_c for nucleation on top of an island (left axis and full circles) and associated step edge barrier height according to Ref. [5] (right axis and full squares). Lines are to guide the eye.

to 3.1 Å (Fig. 3b) and at 400 K from 2.5 Å (Fig. 3c) to 4.1 Å (Fig. 3d). Similar increases in interface width due to the presence of CO are observed for other growth temperatures below 470 K. Finally, in Fig. 4 the island density after deposition of 0.15 ML in dependence of p_{CO} is plotted. Apparently the presence of CO on the surface causes a *decrease* in island density by about a factor of 2 in the analyzed pressure range. In conclusion, the presence of CO in the background pressure during deposition changes all aspects of homoepitaxial growth on Pt(111) at about 400 K.

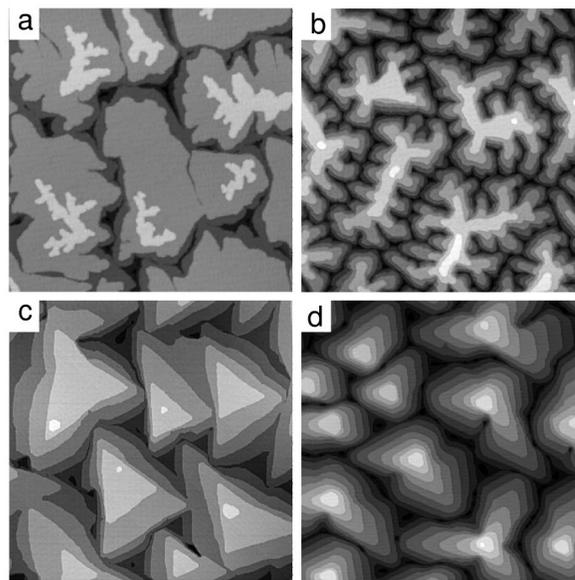


FIG. 3. Surface morphology after deposition of 5 ML with a rate of 5×10^{-3} ML/s at 300 K for (a), (b) and at 400 K for (c), (d). CO partial pressures during growth were $p_{\text{CO}} < 5 \times 10^{-12}$ mbar (clean) in (a), (c) and $p_{\text{CO}} = 9.5 \times 10^{-10}$ mbar in (b), (d). Scan sizes are 1070×1070 Å in (a), (b) and 2130×2130 Å in (c), (d).

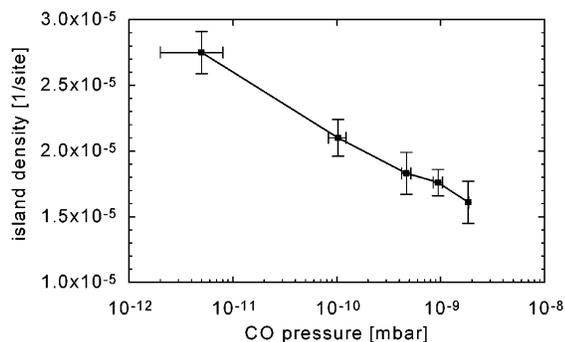


FIG. 4. Island density versus CO pressure for the experiments illustrated in Fig. 1.

How is it possible that small amounts of CO—to be specified below—bring such drastic changes about? To answer this question it is useful to recall the well-known adsorption behavior of CO on Pt(111) [7]: CO adsorbs on Pt(111) preferentially on-top. In the limit of low coverage the bond strength is ≈ 1.4 eV on the terrace and ≈ 1.7 eV at step edges. For kinked steps even higher binding energies are found. The CO-Pt bond appears to be the stronger the lower the Pt-atom coordination. At the temperatures considered here CO is highly mobile. It rapidly exchanges between terrace and step edge sites but prefers the step-edge sites by far. The saturation coverage of steps is 1 CO molecule per step atom (e.g., Collins and Spicer, Henderson *et al.* [7]).

For the effect of CO on the island density when sub-monolayer amounts of Pt are deposited, two possible explanations are given here, both relying on the preferential binding of CO to low coordinated Pt atoms. (i) A CO molecule that binds atop a Pt adatom weakens the bonds between the adatom and the terrace. This may lead to reduced corrugation of the potential energy surface of the adatom and thereby to an enhanced diffusion coefficient compared to a clean adatom. Such a “skyhook” mechanism has been proposed theoretically by Stumpf for H on a Be adatom on Be(0001) [8]. (ii) CO molecules binding atop a small Pt cluster, e.g., a Pt dimer, may weaken the cluster bonds and thereby promote cluster dissociation. According to standard nucleation theory [9] enhanced adatom diffusion (i) as well as reduced cluster stability (ii) decrease the resulting island density.

The changes in island shape, step-edge barrier, and film roughness are probably caused by CO adsorbed at step edges. As CO adsorbs preferentially at steps, this assumption implies that these effects should already saturate for a small amount of adsorbed CO, i.e., as soon as the step atoms are CO saturated. Saturation of the island-shape effect is reached somewhere between Figs. 1c and 1d (there is no more shape change between Figs. 1d and 1e). An inspection of Fig. 2 gives a similar estimate for the saturation effect on d_c . Upper bounds for the CO coverages involved in Figs. 1c and 1d are

obtained assuming a CO-sticking coefficient of 0.79 (the value at 300 K as determined by Steininger *et al.* [7]) and infinite lifetime of the adsorbed molecules. The resulting values are 9×10^{-3} and 1.8×10^{-2} ML, respectively. The step atom to terrace atom ratio after deposition of 0.15 ML in the exposure range of interest here is 9×10^{-3} . The upper bound coverages result in a CO concentration of 1–2 CO molecules per step atom, in qualitative agreement with our assumption [10]. Note that the dramatic effects seen already in Fig. 1b correspond only to 0.2 CO molecules per step atom. Deviations from the clean growth behavior are observed for CO concentrations of only 0.1 CO molecules per step atom, which, e.g., may be realized by several 100 s CO exposure with a partial pressure in the low 10^{-11} mbar range. After prolonged growth (e.g., 100 ML deposited) we find clear shape effects due to CO accumulation at step edges even for our best growth conditions with $p_{\text{CO}} < 5 \times 10^{-12}$ mbar.

Up to now, one of the most obstinate problems in understanding homoepitaxy on Pt(111) was a growth-temperature-induced switch from a triangular growth shape bounded by A steps to one bounded by B steps at 455 K [11]. This switch has been analyzed by a number of theoretical groups [12], but no mechanism has been agreed on, so far. This situation is somewhat reassuring, since the data of Fig. 1 clearly show that the switch from A- to B-step triangular islands in the previous experiments is not a direct temperature effect at all (as claimed before by us [11]), but rather, is mediated by CO. CO adsorption on step atoms is significant below 455 K leading to A-step triangles; the decrease in CO molecule lifetime on Pt(111) is what switches the island shape to the clean B-step triangles above 455 K. Clean growth experiments show only triangular B-step bounded islands in the entire temperature range from about 350–650 K. But how does CO cause the switch in island shape? A speculative explanation is based on the link between step free energy and binding of step adatoms to steps. Conceptually, in order to obtain a triangular island from an initially hexagonal island, a flux of step adatoms is necessary along the island edge to the growth facets which will grow out and disappear. For Ir(111) it has been shown experimentally (and explained on the basis of a simple model), that the lower step free energy of B steps is associated with a stronger binding of step adatoms to A steps [13]. Assuming the same relation to hold for Pt(111), due to the lower step free energy of B steps in clean growth a flux of step adatoms from B steps to A steps would result and, consequently, lead to the observed B-step bounded islands. Following this idea of a link between step adatom binding and step free energy, it is possible that the CO-induced switch in island shape to A-step bounded islands is brought about by a minute change in step energetics attributable to the adsorption. If CO passivates A-step atoms more effectively, step adatoms at A steps should bind less well. The differences

in peak desorption temperatures between terrace- and step-CO for vicinals of Pt(111) with *B* steps or *A* steps indeed indicate a stronger binding of CO to *A* steps [7]. STM topographs obtained after quenching the sample after small CO exposure prove the preferential binding of CO to step edges, but they do not allow so far to discriminate between the binding behavior at the two different dense packed steps.

For the height of the step edge barriers on Pt(111) there exists an apparent contradiction between recent *ab initio* calculations of Feibelman [14] and our previous measurements [15]. The calculations of Feibelman give for the descent of an adatom at a straight *A* step via an exchange mechanism a negligible barrier of only 0.02 eV, a barrier far too low to sustain 3D growth. Our previous experiments showed pyramids (3D growth) at 400 K, composed of triangular islands bounded by *A* steps (Fig. 2 of Ref. [15]). The contradiction is only apparent, however, since Feibelman's calculations were for clean steps, whereas the *A* steps in Ref. [15] were decorated with CO, leading to a strong increase in the step edge barrier height. Indeed the morphology of Fig. 2 in Ref. [15] is almost indistinguishable from the one in Fig. 3d obtained with $p_{\text{CO}} = 9.5 \times 10^{-10}$ mbar. In a number of experiments we established that the mere presence of segments of straight or slightly misoriented *A* steps for growth temperatures below 470 K already indicates their decoration by CO. The surfactant action of O in the previous experiments [15] by precovering Pt(111) prior to growth was demonstrated to be largely due to a reduction of the edge barrier during growth. While this conclusion still holds, the reduction is caused by the fact that O preadsorption prevented CO adsorption on step edges. It is not due to lowering of the edge barrier by O, as we stated previously [15]. With the present findings one can explain the roughness evolution in the homoepitaxy of Pt(111) on the basis of island shapes, both under clean conditions and in the presence of residual CO. This will be shown in a further extended publication.

In conclusion, we have demonstrated that all aspects of homoepitaxial growth on Pt(111) are influenced by minute amounts of adsorbed CO. The sensitivity to adsorbates is due to the preferential adsorption of CO on step atoms, i.e., at those places where growth proceeds. In clean growth on Pt(111) only one triangular growth shape is present, which is bounded by *B* steps. The presence of *A* steps at temperatures below 470 K always indicates the presence of CO. The consequences of this finding are in agreement with recent *ab initio* calculations [14], which predict a negligible edge barrier at *A* steps in clean growth on Pt(111). The experiments presented indicate also that in order to obtain results representative for a clean growth system, deposit atom to impurity atom impingement rates of 10^{-4} or below may be necessary. This is substantially less than previously anticipated.

We thank J.K. Fremerey and Peter Feibelman for useful discussions, the latter also for comments on the manuscript and communicating the results of his *ab initio* calculations prior to publication. Th.M. acknowledges support by the Deutsche Forschungsgemeinschaft.

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