It is well known that surfactants, including residual gas molecules adsorbed on substrate surfaces, in many cases decisively change the type of thin-film growth.\textsuperscript{1,2} The morphology of submonolayer islands influenced by these surfactants is important for further growth of the next layers and also allows to gain more insight into the influence of adsorbates on growth.

The most important effect of surfactants is switching the growth mode from three to two dimensional (2D). Generally speaking, surfactants can influence growth in two ways. They can either affect surface and interface energies, i.e., modify the thermodynamic equilibrium state, or they can modify the growth kinetics by modifying diffusion barriers, availability of low-energy diffusion pathways, etc. An example for the first mechanism is the growth of Pt on TiO\textsubscript{2} (110) under the influence of CO. It was found that the presence of CO leads to a higher fraction of the surface covered by Pt islands. The authors explain this by the increase of the number of Pt surface atoms providing adsorption sites for CO.\textsuperscript{3} On the other hand, in multilayer growth of Co on Pt(111) it was argued that CO acts as a surfactant by modifying growth kinetics. There, CO at saturation coverage leads to more irregular island shapes, providing more sites for easy interlayer diffusion and therefore leads to 2D growth at coverages where 3D growth takes place without surfactants.\textsuperscript{4} An example of direct modification of the diffusion rate by gas adsorption was demonstrated for the case of Pt self-diffusion on Pt(110). There, the diffusion rate of adatoms can be increased by adsorbed hydrogen. The explanation for this effect is a reduced barrier for the direct diffusion pathway,\textsuperscript{5} which may be related to the weaker bonding between metal atoms caused by the presence of hydrogen (“skyhook” effect).

Adsorption of small amounts of CO can also have an effect opposite to that of “usual” surfactants, converting 2D growth into 3D growth.\textsuperscript{6} It was argued that the sensitivity of homoepitaxial growth of Pt on Pt(111) to minute amounts of CO is due to the preferential adsorption of the CO molecules on step atoms, where interlayer diffusion is affected. Furthermore, the presence of CO changes the shape of deposited Pt islands from one orientation of the triangles over hexagonal shape to the oppositely oriented triangles. This effect was explained by the influence of CO on adatom binding at the different steps, thereby modifying the diffusion barriers at the island edge.\textsuperscript{7}

In this contribution we will focus on the change of island density of Co atoms deposited on Pt(111) at room temperature at a coverage of 0.2 ML with and without CO molecules on the surface. This interface is interesting not only from a basic research point of view, but also for the reason that Co-Pt multilayer systems can be used as components for high-density magnetic and magneto-optical storage media.\textsuperscript{8} Whereas growth of Co on Pt(111) is complicated by the formation of dendrites,\textsuperscript{9,10} this growth system has the great advantages that the substrate is fairly easy to prepare in a clean state (important for avoiding heterogeneous nucleation at impurities), that CO adsorbs at room temperature, but CO dissociation does not occur, and also that deposition of Co can be accomplished with reasonably high rates at much lower background pressure than, e.g., deposition of Pt.\textsuperscript{3,6}

The processes during submonolayer epitaxy are governed by kinetics, i.e., they occur far from thermodynamic equilibrium. Restricting ourselves to the case of complete condensation (deposited atoms do not reevaporate again) and growth of two-dimensional islands we can find the following processes on the surface: adatoms deposited randomly on the flat substrate diffuse on the surface and can either encounter another adatom or a defect on the substrate or a group of adatoms. A large amount of theoretical effort has been made to precisely describe these processes during the initial stages of deposition (see, e.g., Refs. 11–17). After a certain (usually low) coverage, the number of islands reaches saturation due to the predominance of adatom-islend merge over nucleation. In this stage the total island density $N$ (number of islands divided by the number of available adatom sites per area) depends on the diffusion coefficient $D$ (in units of sites, i.e., surface unit-cell areas, per second), $D = \frac{1}{2} v_0 \exp(-E_d/kT)$, with the attempt frequency $v_0$ and the surface diffusion barrier $E_d$. $N$ also depends on the deposition rate $F$ (in units of monolayers per second), the scaling exponent $\chi$, which is equal to $i/(i+2)$ (for two-dimensional islands and isotropic diffusion),\textsuperscript{11} and the binding energy of the critical cluster $E_c$. Here, $i$ denotes the critical cluster size (number of monomers that, after aggregation of one more, form a stable cluster).
The island density also weakly depends on the capture number \( \sigma \) describing how efficiently the islands compete for available monomers. This quantity depends on the potential decrease in the vicinity of islands. Although it is not straightforward to determine the value of \( \sigma \) precisely, for the first approach this is a slowly varying quantity between 2 and 4 for critical clusters and 5–10 for stable clusters.\(^{11}\) With the assumptions made, the island density can be expressed as\(^{12,16}\)

\[
N = \eta \left( \frac{D_i}{F} \right)^{-x} \exp \left( \frac{E_i}{(i+2)kT} \right).
\]

The constant \( \eta \) has a typical value 0.25 for a critical cluster size \( i = 1 \) and is only slightly smaller for \( i = 2 \) or 3 (Refs. 11,16). The diffusion coefficient or the diffusion barrier of monomers on the substrate can therefore be determined from the island density \( N \):

\[
E_d = -\frac{E_i}{i} + kT \left( \frac{i+2}{i} \ln(N/\eta) - \ln(4F/\nu_0) \right).
\]

Further details of the growth process can be determined from the island size distribution \( n(s) \), i.e., the number of islands with size \( s \). If we express \( n(s) \) as a function of the relative island size \( s/s_0 \), with \( s_0 \) being the average island size, and in the coverage range under consideration, \( n(s) \) is almost independent of the coverage and mainly depends on the critical cluster size \( i \). Using the scaling law found by Amar and Family,\(^{13}\)

\[
n(s) \propto (s/s_0)^{i} \exp[-ia_i(s/s_0)^{1/a_i}],
\]

we can find the value of \( i \) from the experimentally measured island size distribution. The constants \( a_i \) depend on the critical nucleus size \( i \) [\( a_i \approx 0.2715, 0.2976, \) and 0.3086 for \( i = 1, 2 \) and 3, respectively; values are from solving Eq. (2b) in Ref. 13]. Equations (2) and (3) will allow us to make a quantitative comparison of the Co diffusion barrier on the clean Pt surface and the Pt surface with adsorbed Co molecules.

The Pt substrate was cleaned in an ultrahigh vacuum (UHV) preparation chamber with a base pressure below \( 1 \times 10^{-10} \) mbar by sputtering with 2-keV Ar\(^+\) ions followed by annealing at 1150 K. Co was deposited from an electron-beam evaporator with a deposition rate of \( F \approx 0.5 \) ML/min with the sample at room temperature (310 K). A retarding voltage was applied to the end of the evaporator to avoid bombardment of the sample by fast ions. To ensure optimum vacuum conditions, the evaporator was cooled with liquid nitrogen when depositing without CO, while it was water cooled in the experiments with CO. The coverage was calculated from the deposition rate measured by a quartz crystal microbalance prior to deposition on the Pt substrate. The cleanliness of the Pt(111) substrate and the Co-covered surfaces was checked by Auger electron spectroscopy (AES). The surface morphology was studied by a scanning tunneling microscope (STM) operated in constant current mode at room temperature. The tips were prepared from a tungsten wire by electrochemical etching. Both AES and STM measurements were performed in a UHV chamber with a base pressure below \( 5 \times 10^{-11} \) mbar.

Figure 1 shows STM images of 0.2 ML of Co deposited on Pt(111) at room temperature (a) without CO and (b) at saturation coverage of CO. For Fig. 1(b), the Pt surface was exposed to a CO pressure of \( 1 \times 10^{-7} \) mbar for 150 s prior to deposition to obtain saturation coverage of adsorbed CO. A CO pressure of \( 5 \times 10^{-8} \) was kept during the deposition process. Taking the different image sizes into account, it becomes immediately clear that there is a significant difference of island densities between the two preparations.

In Fig. 1(a) one can also observe many dendrites, which appear as long and ramified islands and are caused by the Co-induced “double-line” reconstruction of Pt(111).\(^{9,10}\) The dendrites are absent in the preparation with CO [Fig. 1(b)], which is not astonishing since CO is expected to suppress the formation of this surface stress-driven reconstruction.\(^{18}\) Obviously, the presence of the dendrites is a phenomenon not considered in the nucleation theory presented above. There are several reasons, however, which assure us that the dendrites do not lead to a significant change of island density.

(i) In the initial stage of growth, where nucleation occurs and the island density is determined, there is a lack of material for growing extended structures such as dendrites. The dendrites therefore grow only during the late stages of the deposition and thereafter.

(ii) It has been observed experimentally\(^{9}\) that the dendrites continue growing even long after deposition is finished, again showing that dendrite growth is mainly a postdeposition phenomenon.

(iii) From the STM images it can be seen that no island is nucleated at a dendrite, on the other hand, all dendrites start growing from an island edge along the double-line reconstruction.
FIG. 2. Comparison of the experimental island size distribution with CO [histogram; 118 islands in Fig. 1(b)] with the scaling law (Ref. 13) for critical cluster sizes of $i = 1$ (solid line), $i = 2$ (dotted line), and $i = 3$ (dot-dashed line). Distributions for $i > 3$ are even narrower than that of $i = 3$. $s_0$ is the average island size.

(iv) The existence of large free areas between the dendrites demonstrates that the mean island distance is much larger than in Fig. 1(b), also in places clearly unaffected by the dendrites. We should also mention that due to their small width of only $\approx 3$ nm, roughly equal to the pixel size in Fig. 1(a), the dendrites contain less material (about 0.05 ML) than one might estimate at first glance. As a first approximation we can therefore neglect the change of island density caused by the dendrites and count only the compact islands in Fig. 1(a).

For the two sample preparations, we obtain island densities of $5.3 \times 10^{-6}$ islands/site without CO [from Fig. 1(a)] and $6.6 \times 10^{-5}$ islands/site with CO [from Fig. 1(b)]. In both cases the islands (when ignoring the dendrites) have a compact shape. Islands prepared without adsorbed CO on the Pt surface are more triangular whereas those prepared with CO on the substrate have a more hexagonal shape. The island size distribution determined from the STM image in Fig. 1(b) (i.e., under influence of CO) is shown in Fig. 2. In spite of some statistical scatter of the data the best fit is clearly found for a critical cluster size of $i = 2$ and confirmed by a statistical analysis which excludes $i = 1$ by more than 4 standard deviations.

A reliable island size distribution for deposition on the clean surface [corresponding to Fig. 1(a)] could not be obtained due to the presence of the dendrites. We can nevertheless use nucleation theory to explore possible values of $i$. Although noninteger effective critical nucleus sizes have been discussed in the literature, we will limit ourselves to integer values of $i$, and keep in mind that the cases discussed might be a simplification of the actual situation. A simple evaluation of Eq. (1) shows that we can exclude the possibility of a critical cluster size of $i = 1$, since this would imply an extremely high diffusion coefficient of $6 \times 10^{11}$ s$^{-1}$, in other words a very low diffusion barrier, well below 0.1 eV (assuming a prefactor $v_0 \approx 10^{13}$ s$^{-1}$). Comparing this to the diffusion barrier of 0.26 eV ($v_0 = 5 \times 10^{12}$ s$^{-1}$) for Pt on Pt(111), we consider such a low value for Co on Pt(111) highly improbable. With the additional criterion that the critical nucleus size $i$ must lead to the lowest island density of all values of $i$ (Ref. 11), and assuming that the binding energy of the adatom clusters is proportional to the number of bonds between cluster atoms, we find that the $i = 2$ regime covers a range of binding energies of the Co adatom dimer of $\approx 0.19 \ldots 0.52$ eV (assuming a prefactor of $10^{12}$ s$^{-1}$) and diffusion barriers up to 0.16 eV. In this type of model for layers with hexagonal packing the next value of $i$ is 6 (Ref. 12), related to a Co bond energy between 0.12 and 0.19 eV and diffusion barriers between 0.17 and 0.28 eV. We consider lower values of the Co-Co bond energy unrealistic, but both $i = 2$ and 6 are in the range of physically meaningful values.

There are four possible explanations how adsorbed CO molecules could modify the island density: CO molecules change (a) the capture number of the islands or (b) the critical cluster size, (c) the binding energy of the critical cluster or (d) the diffusion coefficient of the deposited Co atoms.

The first possibility (a) can be excluded immediately. The capture number is connected to the potential decrease in the vicinity of the island step edges. This decrease is usually a matter of a few interatomic distances. Thus, and also according to its slow variations and weak influence on the island density mentioned above, the big effect observed experimentally cannot be caused by the changes of the capture number. Possibility (b) would require a decrease of the critical cluster size in the presence of CO, from $i > 2$ (i.e., $i = 6$) without CO to the value observed in the presence of CO, $i = 2$ (stable trimer). Since we could not determine the critical nucleus size for deposition on the clean surface, we cannot exclude such a possibility. Nevertheless, we consider it highly improbable since adsorbates (including CO) usually weaken the intermetallic bonds and thus should rather lead to an increase of $i$ and, hence, a lower island density, in contrast with what we observe. The same argument also holds for (c) a CO-induced strengthening of the critical cluster at fixed size (increase of $E_2$).

What remains is possibility (d), a change of the diffusion coefficient. Assuming the same size $i = 2$ and binding energy of the critical cluster, we find a CO-induced reduction of $D$ by a factor of $\approx 150$. With the additional assumption of a constant prefactor $v_0$, this translates into an increase of the diffusion barrier by 0.13 eV, irrespective of the value of $E_2$ (Eq. 2). As mentioned above, one would expect the Co-Co binding energy $E_2$ to decrease rather than increase in the presence of CO, thus the reduction of the diffusion constant may be even stronger.

Let us finally discuss the mechanism how CO can reduce the diffusion constant. The effect observed by us is opposite to the increase of diffusivity by adsorbed hydrogen and also cannot be explained by the so-called skyhook mechanism, where an adsorbate bound to an adatom weakens its binding to the substrate, thereby increasing its diffusion rate. In contrast with Ref. 5, we are working at saturation coverage of the adsorbate. The saturation structure of CO on Pt(111) at room temperature is a $c(2 \times 4)$ superstructure with a coverage of 0.5. In this structure, some threefold hollow sites (adatom sites for Co) are neighbored by a CO molecule in the directly adjacent bridge site, some hollow sites have their nearest CO neighbor in an on-top site. Whatever the exact configuration of the CO molecules surrounding a Co adatom looks like, displacing the Co atom will lead to a new con-
configuration of the molecules. Such a rearrangement of the CO molecules will obviously hinder diffusion. Even in a case where the configuration of CO molecules remains the same after the diffusion step, it is easy to envision that the adatom will have to squeeze itself through the gap between two CO molecules during its jump, resulting in a higher diffusion barrier. In any case, the situation could be loosely described as a surface so much crowded with CO molecules that it is difficult for a metal adatom to get through.

In summary, we have studied the nucleation of Co on Pt(111) with and without preadsorbed CO. STM images show a significant increase of the island density (by almost a factor of 10) when the surface is covered by CO molecules during deposition. Whereas the critical cluster size could not be unambiguously determined for Co grown on the clean Pt(111) surface, the island size distribution in the case of growth on the CO-saturated surface yields a critical cluster size of \( i = 2 \). The most likely reason for the increase of the island density with CO is a decrease of the diffusion constant by more than two orders of magnitude. We have argued that diffusion jumps of the Co adatoms require a displacement or rearrangement of the surrounding CO molecules in the final state and/or the transition state, both hindering the diffusion of the deposited atoms.

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