Interlayer Diffusion of Adatoms: A Scanning-Tunneling Microscopy Study

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Low coverages of Co are deposited at room temperature on a Pt(111) surface with vacancy islands providing a high density of steps. Scanning-tunneling microscopy images with chemical contrast show that Co atoms do not descend Pt steps by diffusing over the step, but descend from the upper terrace to the lower by an exchange diffusion process with the Pt atoms at the step edge. The Co atoms descend a Pt step edge by this process neither at straight *A* nor at *B* steps, but rather at the corners or kinks of the vacancy islands. [S0031-9007(99)09409-0]

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The need for understanding the growth of thin metal films on metal substrates has been in the center of intense research the last decade [1]. In general, the aim of this effort has been to produce smooth films with sharp interfaces. It has been realized that adatom interactions with lattice steps are crucial for the understanding of the growth [2]: Layer-by-layer growth can occur only if adatoms can descend steps and thereby fill up the lower terraces. An adatom approaching a descending step may descend the step in two ways (see Fig. 1): (i) by diffusion *over* the step or (ii) by pushing a substrate atom at the step edge farther onto the lower terrace, replacing the substrate atom (*exchange process*). On fcc(111) surfaces two different kinds of straight steps exists, the so-called *A* and *B* steps, with (100) and (111) microfacets, respectively; corners and kinks may provide further diffusion paths and complicate the situation.

For homoepitaxial growth of Pt on Pt(111), *ab initio* calculations show that the lowest-barrier interlayer transport mechanism is an exchange process with a barrier height of only 0.31 eV at the *A* step and 0.64 eV at the *B* step. The barrier heights for diffusion over the steps are significantly larger (0.53 and 0.80 eV, respectively) [3]. The lowest barrier of 0.31 eV is in rough agreement with a barrier of 0.36 eV determined by field ion microscopy (FIM) [4], though neither the site nor the mechanism of the process has been determined in Ref. [4]. The fact that the lowest barrier is close to the activation barrier for self-diffusion E_D on the terrace (theoretical and experimental values of E_D are 0.29 eV [3,5] and 0.26 eV [4,6,7], respectively), indicates that Pt on Pt(111) should grow layer-by-layer (2D) if *A* steps are present on the surface.

However, it has also been found that homoepitaxy of Pt on Pt(111) is 2D at high and low temperatures, but three dimensional (3D) at intermediate temperatures (*reentrant* layer-by-layer growth, Refs. [8,9]). Recent scanning-tunneling microscopy (STM) investigations [10,11] demonstrated that mainly *B* steps are present during growth at intermediate temperatures, explaining the observed 3D growth. At lower temperatures, one explanation for the so-called reentrant 2D growth is an irregular island shape [8,9], with an enhanced density of kinks or concave corners, where descent of adatoms should be facilitated [12,13]. Indeed, a very recent STM investigation of the homoepitaxial growth of Pt on Pt(111) [11] indicates a change in the coarsening at different Pt coverages which is attributed to a change of the kink density at the step edges, supporting the above notion of the importance of kinks at step edges for the growth.

For heteroepitaxial systems, the interlayer diffusion process can be determined by field ion microscopy, probing the site of an atom after it has descended the step. In contrast to Pt/Pt(111) [3], both W and Re atoms on Ir(111) diffuse over *A* steps and undergo exchange at *B* steps, except for very small islands (12 atoms) [14,15]. Also in contrast to [3], step descent of Ir on Ir(111) was found to be easier at *B* than at *A* steps [14]. Unfortunately, FIM is restricted to the study of adatoms on rather small islands and does not allow one to study concave corners of steps, which would be desirable for understanding phenomena such as reentrant layer-by-layer growth. Finally, it should be noted that in the case of Al/Al(111) [16], *ab initio* calculations found a preference for interlayer transport via an exchange process, but a negligible energy barrier difference between this process occurring at an *A* or a *B* step (0.04 and 0.06 eV, respectively).

A heteroepitaxial system which is of particular interest is the Co/Pt interface, due to the unusual magnetic properties these systems exhibit. The perpendicular anisotropy and large magneto-optical signals discovered in these films [17] are features necessary in magneto-optical recording media. The interfacial magnetic anisotropy has been shown to depend on a combination of structural and

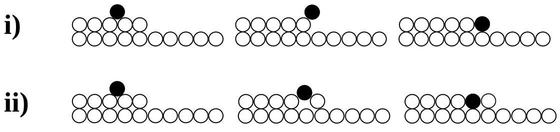

FIG. 1. Schematic side view of an adatom descending a step. (i) Adatom diffusion over the step. (ii) Adatom exchanging place with substrate atom at the step.

morphological parameters of the film [18–22]; therefore the detailed interface formation and growth of Co/Pt interfaces is in itself of great interest.

In this Letter, we present STM results from Co interlayer diffusion on Pt(111). The results demonstrate, for the first time, how interlayer diffusion on the atomic scale may be studied by STM. As we prepare a surface with two-dimensional vacancy islands and deposit a small amount [0.04 monolayers (ML)] of Co, only a few number of atoms are deposited inside the vacancy islands and diffuse to the steps, whereas a large number of adatoms reach the step from the upper terrace and can, in principle, descend the step.

The STM measurements were performed at room temperature (RT) in a UHV chamber with a base pressure below 5×10^{-11} mbar. All STM images were obtained in constant current mode with the sample negative. The Pt sample was prepared in a separate chamber with a base pressure in the high 10^{-11} mbar range. The sample was cleaned by cycles of 2 keV Ar^+ sputtering followed by annealing at 1150 K. In order to produce the vacancy islands, the clean surface was sputtered with 2 keV Ar^+ with an Ar^+ ion dose of 4×10^{13} cm^{-2} at a sample temperature of approximately 650 K. Co was deposited onto the sample at RT with a rate of 1 ML per minute from an electron beam evaporator. One set of experiments was done under "typical" UHV conditions, where the sample was kept in the STM chamber at room temperature for approximately 1 h prior to evaporation, and evaporation resulted in a pressure rise of approximately 2×10^{-10} mbar. In a separate run, to avoid adsorption of residual gas, the sample was kept at 600 K until shortly before the Co evaporation, and the evaporator was cooled with liquid nitrogen, resulting in a pressure well below 10^{-10} mbar during evaporation. We estimate that this procedure resulted in a reduction of possible CO contamination by more than an order of magnitude. No difference was found in the results from these preparations. The cleanliness of the surface was checked by Auger electron spectroscopy. No contaminants such as C and O could be observed within the detection limits in either case.

In Fig. 2a is shown an atomically resolved STM image of a one layer deep vacancy island produced after sputtering at 650 K. In the present study, we find the same general features of the vacancy islands as in Refs. [23,24], the longer sides being *B* steps.

In Figs. 2b and 2c are shown examples of STM images with chemical contrast of the vacancy islands on the surface after 0.04 ML of Co has been evaporated onto the surface. As in our previous study of Co/Pt(111) [25], Co atoms appear darker than Pt atoms. It may be seen that two different types of Co atoms exist at or close to the steps of the vacancy islands. One type is situated *at* the step edges (type 1) while a second type of Co is situated *behind* the first row of Pt atoms on the upper terrace (type 2), as indicated by the white and black arrows, respectively. Thus it is likely that these two different Co

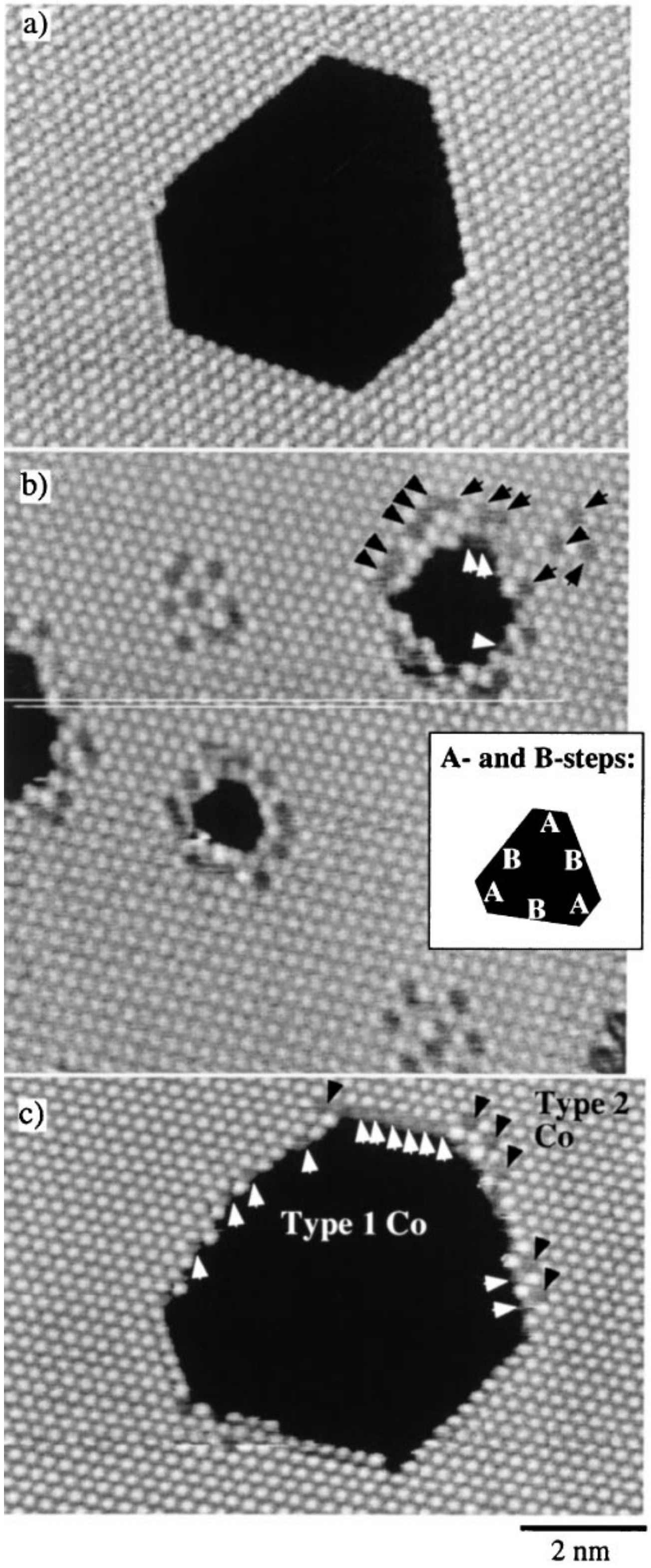

FIG. 2. (a) Atomically resolved STM image of a vacancy island formed by short sputtering at 650 K. (b) STM image with chemical contrast of 0.04 ML of Co deposited at the sputtered Pt(111) surface. Note the completely Co filled small vacancy islands to the upper left and the lower right. (c) Same as in (b), but on a different area of the Pt(111) surface. The white and the black arrows represent type-1 atoms (at edge) and type-2 atoms (behind edge), respectively.

atoms have a different origin, for example, diffusing to or over the step edge.

In order to investigate this further, we counted the number of type-1 and type-2 Co atoms from STM images with chemical contrast of 17 different vacancy islands. As the Co coverage is known to be 0.04 ML corresponding to 4% of the number of Pt atoms in the vacancy island, the number of Co atoms that should be adsorbed within the vacancy island could be calculated. In Fig. 3, the result from plotting the number of counted Co atoms versus the island size is shown. It is evident that the number of type-1 atoms found in the STM images agrees well with the calculated number of Co atoms that should have adsorbed within the vacancy island. Thus we conclude that the type-1 atoms are Co atoms that have adsorbed within the vacancy island and then have diffused to the step of the vacancy island.

In the case of the type-2 Co atoms, only an exchange diffusion process may explain the presence of Co atoms situated behind the first row of Pt atoms. Hence, the type-2 Co atoms originate from Co atoms that have adsorbed on the upper terrace and later diffused to the step edge of the vacancy island where an exchange diffusion process with the Pt atoms at the step edge has occurred.

Two important conclusions may be drawn from Fig. 3. First, if any significant interlayer transport via diffusion *over* the step would occur, the observed amount of type-1 Co atoms would clearly have exceeded that of the ideal number of type-1 Co atoms shown in Fig. 3. The fact that the number of type-1 atoms found in the STM images agrees well with the ideal number of Co atoms that should have adsorbed within the vacancy island is a very strong indication that the Co interlayer transport on Pt(111) occurs only by an exchange diffusion process and not by diffusion over the Pt step.

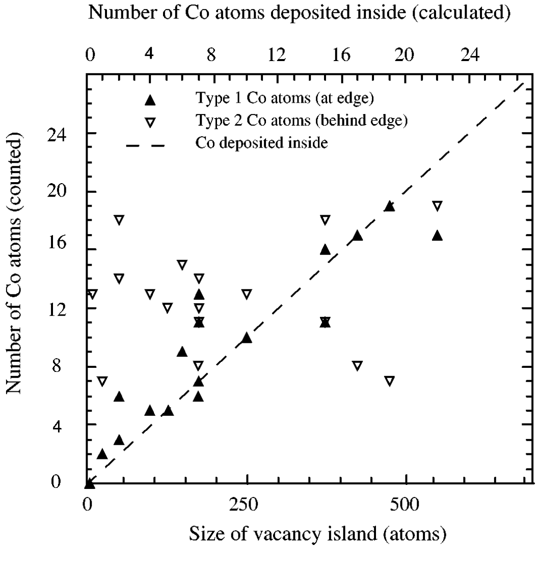

FIG. 3. Plot of the number of counted type-1 and type-2 Co atoms versus the size of the vacancy islands. The dashed line represents the calculated number of Co atoms adsorbed within the vacancy island.

Second, as the amount of the deposited Co is sufficient to fully decorate all step edges, all vacancy island steps would be decorated with at least one row of type-2 Co atoms, provided that the energy for exchange diffusion could be easily overcome at straight *A* or *B* steps. We do not observe this, however, as especially the larger vacancy islands show relatively few type-2 Co atoms (e.g., Fig. 2c). In fact, the number of type-2 Co atoms is independent of the size of the vacancy islands (Fig. 3). Whereas the length of the steps depends on the island size, each vacancy island has six corners, independent of size. The observation that the number of type-2 Co atoms is independent of the vacancy island size (Fig. 3), indicates that the exchange diffusion process at steps in the Co/Pt(111) system does not occur at straight steps but rather at the corners of the islands. This results in the formation of a kink, also providing a kind of "concave corner," which may allow an exchange diffusion process there, shifting the kink position farther along the step (see examples of such processes in Fig. 4). Such a model is supported by the observation that rows of type-2 Co atoms of the vacancy islands usually begin at corners, extend along the steps some distance, and end with a kink (e.g., right upper side of Fig. 2b). Counting the number

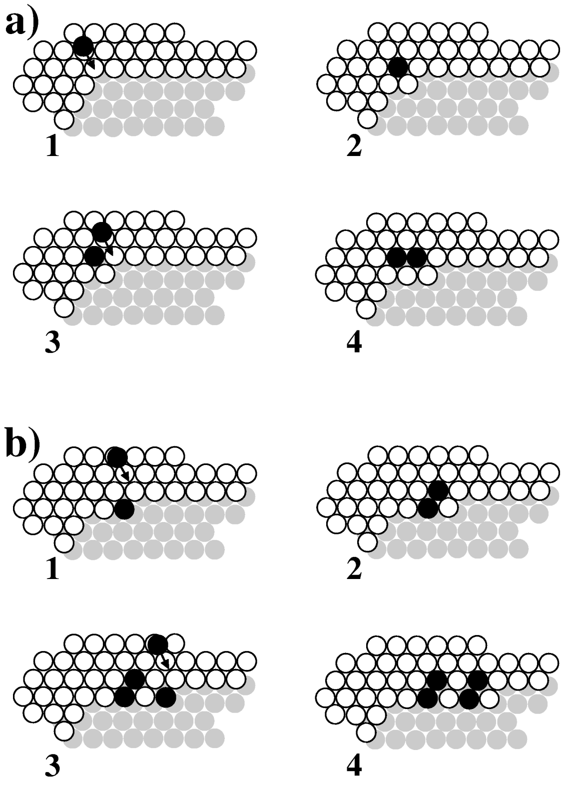

FIG. 4. Schematic top view of models of the exchange process at a corner (kink), as proposed in Ref. [12], and the creation of a kink at the step. (a) A kink is created by the exchange process. (b) A kink is due to a preexisting Pt atom in the corner. This proposed process is related to explain observations in Fig. 2c.

of type-2 Co atoms behind *A* and *B* steps, we do not find a preference for either of them, also indicating that the exchange process does not occur at the straight steps (where one would expect a difference due to the different step geometry), but rather at kinks or corners, where *A* and *B* steps meet. We also note that type-2 Co atoms are never found behind straight steps without kinks. As only those Co atoms finding a corner or kink can be incorporated, the remaining Co will diffuse and attach to an ascending step of the Pt crystal. This explains the low number of type-2 Co atoms with respect to the deposited Co.

Since we have no information on the time scale of the processes involved, we cannot determine diffusion barriers from our experiments. We may conclude, however, that the barriers for exchange at *A* and *B* steps must be higher than the diffusion barrier on flat terraces E_D by at least a few times the thermal energy kT, in contrast to Pt/Pt(111) [3]. Otherwise we would observe single Co atoms having undergone exchange at straight steps. On the other hand, the barrier for the exchange process at corners or kinks must be below or very close to E_D, allowing for easy incorporation of Co at these sites. We consider the results presented in this Letter as the first direct experimental confirmation for the hypotheses that descent from irregular islands (with concave corners and kinks) is facilitated as compared to descent from islands with straight steps. Our findings also support the essence of simulations based on the embedded atom method [12] and effective medium theory [13], predicting low barriers for exchange processes at corners and kinks, respectively. Finally, it should be noted that a facilitated interlayer transport at a corner site is in agreement with the expectation of a facilitated interlayer transport for a descending atom with a highly coordinated transition state, as compared to a descending atom with a lower transition state coordination.

Given the recent result on the influence of CO contamination on growth [10], we have to ask ourselves whether our results could be influenced by CO decorating the steps. Two arguments speak against this: As mentioned previously, we find no difference between the results obtained from very different vacuum conditions. Second, the step density created by sputtering in our experiments is significantly higher than in the deposition experiments as in Ref. [10]. Indeed, an estimate for the experiment performed with the liquid-nitrogen cooled evaporator shows that even at 100% sticking probability the CO adsorbed at the surface would be insufficient to decorate all steps.

In conclusion, by studying low coverages of Co on a Pt surface with a high density of steps with STM, we have shown that the interlayer transport of Co on Pt(111) occurs most easily by an exchange process at kinks or concave corners, and not at straight steps. This exchange diffusion process is observed to occur at highly coordinated Pt step sites, such as corners.

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