Ultrathin Films of Co on Pt(111): an STM View

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The growth, structure and morphology of ultrathin Co layers with a thickness up to 15 layers deposited at room temperature on Pt(111) have been studied by using scanning tunnelling microscopy (STM) with atomic resolution and chemical discrimination between Co and Pt. This chemical contrast has been confirmed by simulations with an FLAPW (Full Potential Linearized Augmented Plane Waves) ab-initio computer code based on density functional theory. By the help of this contrast between Pt and Co atoms in STM constant current images it is shown that in the early stages of submonolayer growth Co is incorporated into the Pt surface, thereby forming dislocation lines. We were also able to demonstrate that Co atoms descend from the upper terrace to the lower one by an exchange diffusion process with the Pt atoms at the step edges. It is shown that this interlayer diffusion does not take place at straight steps, but rather at corners or kinks. The first completed Co monolayer (ML) is almost pseudomorphic (Co in the Pt fcc lattice sites) with a high density of defects due to the lattice mismatch. The second layer exhibits a moiré structure, with the Co in-plane lattice distance close to that of bulk Co. The step edges which are very rough at a coverage of two monolayers become smoother with increasing Co deposition. The growth mode is two-dimensional (layer-by-layer) around two to three monolayers and changes afterward into three-dimensional growth (island growth). We observe that the change of the step edge morphology is also correlated to this change from 2D to 3D growth mode. The reason for the 2D growth at the beginning is attributed to the strained interface between the Co overlayer and the Pt(111) surface which hinders the formation of straight steps. Therefore, many kinks and corners are formed, increasing the probability for interlayer diffusion by the above mentioned exchange process. With increasing number of layers the strain decreases, steps become smoother, interlayer diffusion decreases and therefore island growth develops. Up to the highest coverage (15 ML) studied the growth is characterised by a mainly twinned fcc-like stacking. Only a small amount of hcp stacking has been observed. Further experiments showed that preadsorption of carbon monoxide acts as a surfactant which extends the layer-by-layer growth up to higher Co coverages.

1. Introduction

Co–Pt thin films and multilayer systems are not only interesting from a fundamental basic research point of view, but are also candidates as components in high density magneto-optical (MO) storage media. This is so because of the particular magnetic properties these systems exhibit [1–3]; the perpendicular magnetic anisotropy (PMA) observed for very thin Co layers in Co–Pt multilayers is necessary for MO recording. Much attention has been devoted to understanding the origin of the observed perpendicular anisotropy [4–6]. It has been shown that the magnetic properties depend on the

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thickness of the Co layers [7] as well as on the detailed structural properties of the Co film. The crystalline orientation [8, 9], the amount of alloying between Pt and Co [9] and the exact thickness of the Co layers (possibly related to the fcc-to-hcp transition [10, 11]) have been observed to influence the magnetic properties.

Due to the complexity of a multilayer interface system it is fruitful to study and gain understanding of the magnetic and geometric properties during the initial interface formation for a single Co and Pt interface, such as the Co/Pt(111) interface. A recent surface magneto-optical Kerr effect (SMOKE) study of thin Co films on Pt(111) [12] reports a linear increase of the PMA as the Co coverage is increased from 0.8 to 3.7 ML (1 ML is defined here as the amount of atoms in one Pt(111) layer). At a Co coverage between 4 and 6 ML, in-plane and out-of-plane magnetisation was found to coexist. The out-of-plane magnetisation was observed to decrease to zero at about 6 ML of Co, whereas the in-plane magnetisation continued to increase. Such a behaviour, which is also similar to that of Co–Pt multilayers, merits a detailed structural investigation.

In fact, the structure and morphology of thin Co deposits on Pt(111) has been studied extensively in the past [13–20]. For instance, Grütter and Dürrig [13] have previously used scanning tunnelling microscopy (STM) to study thin Co films deposited on Pt(111) at room temperature (RT). They reported a quasi-layer-by-layer growth mode up to a Co coverage of 3 ML, including a large number of defects in the first layer and a moiré structure in the second layer. Above 3 ML a three-dimensional (3D) growth mode was observed and furthermore indications were found that Co grows with an hcp stacking sequence above 3 ML. At higher Co coverage the Co film appeared granular. Co growing in a predominantly hcp stacking was also found by an extended X-ray absorption fine structure (EXAFS) study for Co films thicker than 4 ML [15]. Low-energy-electron-diffraction studies (LEED) [3, 16–18] have shown that the first ML is nearly epitaxial on the Pt(111) surface. Above approximately 1.5 ML of Co, the Co lattice relaxes to close to that of bulk Co. At higher Co coverage a sixfold fine structure appears around each LEED spot, interpreted as a modulation of the Co overlayer, consistent with the STM observations of the moiré structure [13] due to a large coincidence cell of the modulated surface structure. Surface X-ray diffraction (SXRD) experiments [19] concluded that a multilevel surface consisting of five different levels is formed after Co deposition of 3 ML. The most dominant feature observed up to a Co coverage of six layers was a component in the out-of-plane diffraction due to disorder in the lattice constant in the out-of-plane direction, again consistent with the modulated surface structure of a moiré structure. In this study the stacking of the Co at higher coverage, 8 and 12 ML, was found to be predominantly twinned fcc. For a 10 ML thick Co film deposited at RT, a Co film consisting of planes stacked in fcc, twinned fcc and hcp has also been reported [20].

We have recently presented results from the initial stages of growth of Co on Pt(111) [21], the interlayer diffusion [22] and from the growth of Co deposited on the Pt(111) surface at room temperature up to a coverage of 15 ML Co [23, 24] by using Scanning Tunnelling Microscopy (STM), Low Energy Ion Scattering (LEIS) and Auger Electron Spectroscopy (AES). When depositing 0.1 monolayers (ML; 1 ML is defined here as the amount of atoms in one Pt(111) layer), the formation of a local Co induced Pt reconstruction producing long, double, dislocation lines on the Pt(111) surface is observed [21]. A similar, local reconstruction of the Pt(111) surface has been observed
after depositing Pt at 400 K [25]. In this reconstruction the atoms between the pair of lines were found to be located on hcp sites while the atoms outside the lines are located on fcc sites. The two observed bright lines are due to partial dislocations between the first and the second layers. Such a contraction of the topmost layer due to stress relief is in agreement with theoretical studies [26], and related to the well known \((N \times \sqrt{3})\) “herringbone” surface reconstruction of Au(111) [27]. In [21] we were able to confirm, with chemically resolved STM images, that the Co induced reconstruction is due to the incorporation of Co in the topmost Pt layer.

In [23] STM results from Co films deposited in a range of coverages on Pt(111) at RT have been reported. We have shown that the Co atoms in the first Co layer take preferably the Pt fcc lattice sites and partial dislocations (surface defects) are formed. The second Co layer displays a moiré structure; the Co in-plane lattice parameter is found to take a value close to that of bulk Co. The growth of the Co film is observed to be almost flat or two-dimensional (2D) up to a Co coverage of about 3.5 ML. At coverages of 5 ML and higher, islands exhibiting a three-dimensional (3D) growth are observed. These islands are found to grow in a predominantly twinned fcc-like stacking [23].

2. Experimental

All measurements were performed in a UHV chamber with a base pressure below \(5 \times 10^{-11}\) mbar. The scanning tunnelling microscope (STM) used for the results presented in the following is a customized Omicron micro-STM operated in constant current mode at negative sample bias. The residual noise vertical to the surface is in the range of a few picometers. The Pt sample was prepared in a separate chamber with a base pressure of approximate \(1 \times 10^{-10}\) mbar. The cleanliness of the Pt(111) surface and of the Co covered surfaces was checked by AES, no contaminants such as C and O could be observed within the detection limits. Also low energy electron diffraction (LEED) measurements have been done. The clean Pt(111) surface exhibited a sharp \((1 \times 1)\) LEED pattern. The size of the terraces of the sample was found to be approximately 50 nm as observed with STM. Co was deposited from a water-cooled electron beam evaporator. The typical evaporation rate was 0.5 ML/min as measured by a quartz crystal micro balance. In separate experiments, 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 negligible pressure rise (below \(10^{-10}\) mbar) during evaporation. No difference was found in the results from these preparations. A retarding voltage was applied to the end of the evaporator in order to suppress Co ions from the evaporator, since such ions have previously been found to influence the growth of thin films [28]. The error in Co coverage was estimated from repeated measurements to be less than 10% as determined from the ratio between the Co 773 eV and the Pt 237 eV Auger peak-to-peak signals.

Since we could obtain chemical resolution in STM it is interesting to determine whether this can be explained by the electronic structure of the surface. According to the theory of Tersoff and Hamann [29], where no tip–surface interaction is taken into account and the tip wave functions are assumed to have s-type symmetry, an STM constant current image represents contours of equal local density of states (LDOS) above the surface at the centre of the tip atom, energetically near the Fermi edge. We have
therefore performed calculations of the LDOS of alloy surfaces by using the FLAPW method (Full Potential Linearized Augmented Plane Waves) based on density functional theory [30]. To compare with STM images we integrate the LDOS around the Fermi edge and analyse the corrugation of this value (i.e., difference of electron density between hollow and on top sites) in dependence on the distance from the surface [31].

The goal of these calculations was to find out whether the difference of LDOS above different atoms of a compound is enough to explain the STM images or if other mechanisms as tip–sample interaction or special tip conditions have to be considered.

3. Chemical Discrimination between Co and Pt Demonstrated on Pt_{25}Co_{75}(100)

Previous STM measurements on a Pt_{25}Co_{75}(100) bulk alloy surface showed a very pronounced chemical contrast with long range chemical ordering forming a c(2 × 2) structure along with a shifted row reconstruction [32] (Fig. 1). In many images, the difference of the apparent height between Pt and Co is so large (around 10–50 pm) that only one atom species is visible as protrusion. Although the surface composition is close to 50% Pt and 50% Co, a comparison of STM images with differently prepared surfaces and comparison with quantitative LEED indicates that Pt is the chemical species appearing higher in STM. Ab-initio calculation of the local density of states (LDOS) also confirmed this finding.

The calculated height difference for PtCo was around 5–10 pm (Fig. 2) which is about a factor of 2–3 smaller than the typical chemical contrast in experiment. More important was the possibility to con-

Fig. 1. STM constant current topograph of the (100) surface of a Pt_{25}Co_{75} crystal with a surface composition of roughly Pt_{50}Co_{50} (10 × 10 nm², V = −29 mV, I = 0.46 nA). Note the regular distribution of height (Pt) and dark (Co) atoms in many parts of the image, forming a c(2 × 2) ordered structure, with some small (1 × 1) areas in between. Besides the chemical contrast one can also observe a shifted row reconstruction (rows of brighter atoms from top right to bottom left, see Ref. [32]). Irregular white patches are due to impurities. The arrows mark the position of the linescan. The difference of apparent height between Co and Pt (chemical contrast) is up to approximately 20 pm.
firm by this simulation that Pt is the apparently higher (brighter) species in STM images. This is in contrast to the previously measured Pt alloys where Pt always showed less apparent height than the second alloy constituent (Ni, Rh) [33–36]. It turned out that for PtCo an alloying effect transfers electrons from Pt to Co but these electrons are more localised near the core of the Co and the decay of the electron charge density into the vacuum above Pt atoms is much weaker than above Co. This is why Pt appears higher (brighter) in STM.

It should be noted that even if stable chemical contrast is present because of pronounced electronic structure difference a tip change (possibly an adsorbate that is picked up by the tip) can increase the apparent difference in height. This is seen in Fig. 3. During scanning (this is done from lower left to upper right) the tip changed several times, causing a quantitative

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**Fig. 2.** Calculated LDOS corrugation of PtCo (100) binary alloy surfaces as a function of tip–sample distance calculated within the Tersoff-Hammann approach (grey area marks results obtained with different evaluation procedures). The range of Co corrugations does not overlap with the Pt corrugations, therefore the calculation shows that Pt and Co should be clearly distinguishable by STM, with Pt being the apparently higher (brighter) species. The calculated corrugation difference at typical tip–sample distances (hatched area) is, however, smaller than observed experimentally (cf. Fig. 1).

**Fig. 3.** Atomically resolved STM constant current topograph of Pt$_{25}$Co$_{75}$(100) (10 x 10 nm$^2$, 0.5 mV/1.26 nA). The image shows the same surface as Fig. 1 but was recorded with an unstable tip. The grey scale is adjusted to make all atoms visible although the tip changed its length significantly. The two white lines indicate the positions of the linescans (A) and (B) in the lower panel, exhibiting an apparent height difference between Pt and Co (chemical contrast) of approximately 10–20 and 40–50 pm, respectively. The vertical offset of the two curves is arbitrary.
change in the apparent height of the Co atoms. In the line scan it is obvious that two different contrast values are present, one with a corrugation difference of 10–20 pm and another with about 50 pm. Since the tunnelling parameters are constant only a tip change can be the reason for this magnification in the chemical contrast. Therefore this image supports our model [33] that even if the difference in electronic structure between two species is rather small, there is the possibility of a special tip structure that helps to magnify the difference. On PtCo(111) surfaces also a very stable chemical contrast was achieved in STM constant current images and has been confirmed at least qualitatively by ab-initio calculations of the surface LDOS [33]. We therefore can conclude that on a PtCo alloy surface a stable chemical contrast can always be achieved and in all cases Co atoms appear as the dark species.

4. Submonolayer Deposition of Co on Pt(111) and Visualisation of Interlayer Diffusion

Submonolayer deposition of Co and Pt(111) leads to decoration of the step edges and also formation of dislocation lines on the terraces, a phenomenon which starts already at room temperature but becomes more important at slightly higher temperature [21]. Fig. 4a shows an STM image of such a Co induced reconstruction on Pt(111) after deposition of 0.04 ML Co. The bright lines in the STM images are Co induced Pt double lines running in the [211] direction. In this image, the Pt atoms are well resolved and the STM image shows chemical contrast. The darker atoms in or near the double lines can be identified as Co atoms. Counting the number of Co atoms in Fig. 4a it is found that there is one Co atom in each atomic row in the [012] direction, in agreement with a dislocation system having an overall Burgers vector of (1/2) [012]. It is therefore clear that the double line reconstruction is formed via incorporation of Co atoms in the topmost Pt layer, causing relief of the tensile surface stress in this layer and inducing the dislocation lines separating the hcp stacking (region between the double lines) from the fcc regions. A schematic model of such a partial dislocation is shown in Fig. 4b.

An interesting feature in Fig. 4 is the observation that many of the Co atoms are placed to the left of the double line reconstruction. This indicates a high mobility of the double line reconstruction in the

Fig. 4. a) STM (13 × 13 nm²) image of a Pt(111) surface after deposition of 0.04 ML Co displaying a Co induced double line reconstruction; Co atoms embedded in the Pt surface appear dark. The model b) shows how fcc stacked Co are separated from smaller stripes of hcp Co by partial dislocations. In these dislocations, first-layer atoms occupy bridge sites, explaining the (higher) brighter appearance of the double dislocation lines.
In order to study interlayer diffusion on the atomic scale, we have created vacancy islands in the clean Pt(111) surface by sputtering with 2 keV Ar\(^+\) with an Ar\(^+\) ion dose of \(4 \times 10^{13}\) cm\(^{-2}\) at a sample temperature of approximately 650 K. Fig. 5 shows an STM image of the Pt(111) surface after such a procedure, showing one monolayer deep vacancy islands with atomic resolution, displaying the same features as found previously [39].

In Fig. 6 we show an example of an STM image with chemical contrast of vacancy islands after 0.04 ML of Co has been evaporated onto the surface. As explained previously Co atoms appear darker than Pt. 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, respec-
tively. Thus it is likely that these two different Co atoms have a different origin, for example diffusing to or over the step-edge.

In order to investigate this further, we have counted the number of type 1 and type 2 Co atoms in 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, we can calculate the number of Co atoms that should have adsorbed within the vacancy island and diffused to the step from the lower side. In Fig. 7, 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. The existence of the exchange process is also obvious when looking at the groups of Co atoms in the surface where a hole has obviously filled up completely (e.g. Fig. 6, top left). In these small holes, the number of Co atoms having landed in the holes is negligible, thus all Co atoms must have come from the upper terrace, having undergone interlayer diffusion. As we do not observe a compact group of Co atoms in these places, filling up the hole cannot be the result of diffusion over the step edge, but the Co atoms must have rather pushed Pt atoms into the hole, finally creating the locally mixed arrangement of Pt and Co atoms observed in the surface.

Similar conclusions may be drawn in a more quantitative way from Fig. 7. First, if any significant interlayer transport via diffusion over the step would occur, the observed amount of type 1 Co atoms (filled triangles) would clearly have exceeded that of the calculated number of type 1 Co atoms (broken line). The fact 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 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.

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![Fig. 7. Plot of the number of type 1 and type 2 Co atoms versus the size of the vacancy islands. The dashed line gives the average number of Co atoms deposited within the vacancy island as calculated from the deposition rate.](image-url)
Second, as the amount of the deposited Co is sufficient to fully decorate all step edges, all vacancy island steps would be decorated with a least one row of type 2 Co atoms, provided that the energy for exchange diffusion could be easily overcome at straight steps. In fact, the number of type 2 Co atoms (open triangles) is independent of the size of the vacancy islands (Fig. 7). 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 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. Such a process results in the formation of a kink, also providing a kind of “corner” which may allow an exchange diffusion process there, shifting the kink position further along the step. We also note that single 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.

Our findings also support the essence of simulations based on embedded atom method [37] and effective medium theory [38], predicting low barriers for exchange processes at corners and kinks, respectively [40]. 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.

5. Coverage of 1–5 ML Co on the Pt(111) Surface

Figure 8 shows an STM image of an 1.2 ML thick Co film deposited on Pt(111) at RT. In the image, three different areas may be observed: (a) the Pt(111) surface, (b) the first Co layer directly on top of the Pt(111) surface layer, and (c) the second Co layer on top of the first Co layer. STM images with higher resolution from the corresponding areas as shown in Fig. 8 are presented in Fig. 4 (Pt(111) substrate with Co-induced double line reconstruction) and Fig. 9. Turning to the appearance of the first Co layer, Fig. 9a shows an STM image with chemical contrast of Co on...
Pt(111) from a 1.2 ML thick Co film deposited on Pt(111) at RT. The image shows Co atoms which have diffused and attached to a Pt step edge (lower right part of the image), thus the Pt substrate is directly underneath the Co atoms seen in the image. The bright spot in the image (upper left) is due to second-layer Co atoms adsorbed on the first Co layer. In the first Co layer, double lines of brighter Co atoms are observed which are interpreted as partial dislocations, now induced by the lattice mismatch of $-9.4\%$ between the Co (nearest-neighbour (nn) distance 2.51 Å) and the Pt (nn 2.77 Å) lattice constants (Fig. 4b). It can be shown [23] that Co takes preferably the Pt fcc lattice sites, with a smaller number of Co atoms in disordered (bridge) or in hcp sites due to dislocations in the Co overlayer. In addition, brighter single atoms may also be observed in the Co layer. These atoms are Pt atoms, which may be realised by comparing the similar appearance of these atoms with the Pt atoms at the Pt step edge (lower right in Fig. 9a), indicating a very limited interdiffusion of Pt and Co on the terrace.

The formation of the second Co layer on top of the first layer results in the formation of a moiré structure as shown in Fig. 9b. This structure again results from the different in-plane lattice spacing of the Co overlayer as compared to that of the Pt lattice in the Pt(111) surface, and has been observed previously with STM in this system [13]. From the periodicity of the moiré structure it is possible to deduce the contraction of the in-plane lattice spacing as compared to the in-plane lattice spacing in the Pt(111) surface from the moiré formula [41]. We find that the periodicity of the moiré structure is $(12.7 \pm 1.1)$ Co atoms resulting in a Co in-plane lattice constant contracted by $(7.9 \pm 0.7)\%$ as compared to the Pt(111) in-plane lattice distance. The corresponding number for bulk Co is 9.4\%.

As we increase the Co coverage on the Pt(111) surface, the Co-induced moiré structure persists, as shown by a set of $100 \times 100 \text{ nm}^2$ STM images in Fig. 10. From STM images of these coverages we can also conclude that the dislocations observed in the first Co layer (see Fig. 9a) are lifted as the second Co layer is being formed [23].

Figure 10b shows an STM image of an approximately 3.5 ML thick Co film on the Pt(111) surface. In this case, five levels displaying the moiré structure may be observed.
The steps of the adislands have become more straight (the number of kinks and corners has been reduced). The corrugation of the moiré structure at the surface is decreasing as the coverage is increasing, reflecting the number of levels between the surface and the interface between the Pt(111) substrate and the first Co layer (causing the moiré structure). It should also be noted that we cannot determine whether Co grows in an fcc or an hcp stacking sequence based on the lattice constant as obtained from the moiré structure, since the in-plane lattice distances for Co(111) and Co(0001) are very similar.

6. Coverage of 3.5–15 ML Co on the Pt(111) Surface

Figure 11 shows a set of 300 × 300 nm² STM images with Co coverage ranging from 3.5 to 15 ML deposited on Pt(111) at RT. As the influence of the moiré structure is reduced with higher Co coverage (5 ML and higher), we observe pyramidal islands with triangular shape. The triangular shape is due to the existence of two types of steps on a (111) surface, the so-called A and B steps, with (111) and (100) microfacets, respectively. If one facet has a different growth speed (e.g. because it is preferred energetically but the detailed process is irrelevant in the present context), instead of hexagons (sixfold symmetry) we will observe triangles (threelfold symmetry). Further, if the same microfacet is favoured independent of the Co thickness, and if the step–step distance is large enough to allow any direction of the step, fcc stacking and hcp stacking will lead to triangles stacked facing
the same or the opposite direction, respectively. Examples of these two cases are indicated in Fig. 11b. Thus, we may conclude that in the top layers both fcc and hcp stacking are present at a Co coverage of 5 ML, however, with clear predominance of fcc stacking. Even though these arguments are convincing and have been used in previous STM investigations [13], the fact that Co is observed to grow in an fcc stacking sequence is surprising. An additional proof for this conclusion came from analysing defects observed on some islands which are a clear fingerprint of a stacking fault which may only exist in an fcc stacked film [23]. These stacking faults are observed at least on seven of the islands in Fig. 11d. No dislocations typical for hcp stacking have been found on any of the islands identified as fcc via the shape of the terraces. If the orientation of the triangular terraces is alternating, we have to conclude that they are stacked in an hcp sequence, as indicated in Fig. 11b. Further, as stated above, it is clear that one of the step orientations is favoured. The stacking faults also yield the relevant information namely that the longer sides of the triangles are A steps [23], as opposed to the predominant facet present during growth of Pt on Pt(100) at intermediate temperatures, which was found to be a B step [42]. Further, two opposite directions of the triangles may be identified as indicated in Fig. 11c, demonstrating the existence of fcc stacking.

Fig. 11. STM images (300 × 300 nm² each) of Co films on Pt(111) at different Co coverages. Due to the different growth speeds of the two types of step edges, the islands display threefold and not sixfold rotational symmetry. The shape of successive terraces allows to distinguish between fcc and hcp stacking as well as to detect twinned fcc growth. STM images shown with illumination from top left.
twins, the stacking sequence being ABC ... and CBA ..., due to stacking faults in a lower level. It should be noted that the existence of the twins, if the domains of the twins have an approximately equal area as in the present case, will cause the observed diffraction pattern of the Co film in LEED to have a sixfold symmetry. Finally, Fig. 11d shows an STM image of a 15 ML thick Co film. The appearance of the islands is similar in Fig. 11c, the difference being that the island sizes become larger as the Co coverage is increased. The present study for Co coverage of above 5 ML directly demonstrates that Co grows with a predominantly fcc stacking sequence. This result is in agreement with previous X-ray studies [19, 20], but in disagreement with the observations made in the earlier STM study [13] and EXAFS measurements [15]. Above 5.5 ML, indirect investigations based on the magnetic properties indicated Co films stacked in a fcc sequence [43], but no clear distinction between hcp and fcc could be made.

Concerning the determination of the growth mode in Fig. 12 the fraction of the terrace levels as estimated from the STM images in Figs. 10a and 11a–11d is shown to give a quantitative criterion allowing to distinguish between 2D and 3D growth of the Co films. In the case of pure 2D growth, interlayer diffusion across step edges to a lower terrace must be present, resulting in a small number of levels (ideally two) visible by STM. In the case of pure 3D growth, in which no interlayer diffusion is present, the distribution of the terrace levels is expected to follow a Poisson distribution [44]. Therefore, the expected Poisson distribution of relative areas of the levels for each Co coverage is also plotted in Fig. 12. It may be seen from this figure that the experimental data agree fairly well with the Poisson distribution at higher Co coverage, but at lower coverage two terrace levels make up most of the image area, adding support for a 2D growth mode in this coverage region.

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**Fig. 12.** Relative surface area of the different levels (i.e., different Co thicknesses in monolayers) as estimated by analysis of the STM images shown in Figs. 10 and 11, compared to the corresponding Poisson distributions for pure 3D growth with no interlayer diffusion. Note the improved agreement between the experimental and calculated values as the Co coverage is increased, showing that the growth becomes more and more 3D.
In classical growth theory focused on thermodynamic equilibrium, one would certainly not expect the growth mode observed, because one should expect Co/Pt(111) to grow in either Stranski-Krastanov (layer plus island) or Volmer-Weber (island only) growth mode, depending on the exact surface and interface energies (sufficiently exact values are not available to decide). If, by some non-equilibrium processes, the Co layer has grown thick enough to accommodate the misfit in the layers below, the system should be equivalent to homoepitaxial Co growth, allowing layer-by-layer growth again. As described above, the actual growth mode is the very opposite, underlining the importance of non-equilibrium processes.

We have shown above the importance of kinks and corners for interlayer diffusion, and, hence, for the growth mode of fcc(111) surfaces. Straight steps without kinks and corners are difficult to overcome by the adatoms and therefore lead to three-dimensional growth, whereas more irregular step shapes are necessary for layer-by-layer (2D) growth. We have shown that from beginning on the Co layers are very strongly strained and it is the inhomogeneous strain field of the Pt–Co interface which keeps the step edges irregularly shaped, and therefore 2D growth takes place as long as the strain is present. With increasing layer thickness this strain becomes weaker and weaker, the steps more straight and therefore the growth mode changes from 2D to 3D.

7. Influence of CO on the Growth Mode of Co on Pt(111)

The influence of CO present during deposition can be seen in Fig. 13. As mentioned at a coverage of 8 ML, growth in UHV ($10^{-10}$ mbar) results in clearly three-dimensional growth, with more than ten levels exposed (Fig. 13a). We have repeated the experiment with pre-adsorbed CO ($5 \times 10^{-9}$ mbar for 200 s) and keeping the same CO partial pressure during growth. This leads to saturation of the surface with CO, visible as a ($\sqrt{3} \times \sqrt{3}$)R30° superstructure in small-area scans (not shown). The result (Fig. 13b) is

Fig. 13. STM images (300 x 300 nm² each) of 8 monolayers Co deposited on Pt(111) a) in ultra-high vacuum conditions and b) at $5 \times 10^{-9}$ mbar CO. For b), dosing CO was started 200 s prior to deposition, causing growth to start on an already CO-covered surface. Images shown with illumination from top left.
close to 2D growth, with only a few isolated pyramids protruding up to five layers from the average height.

We believe that these pyramids are due to defects enhancing the nucleation at the topmost terrace. Nevertheless, with adsorbed CO the occupation of the different levels is very different from that in Fig. 13a, with most of the surface consisting of very few terrace levels. We conclude that adsorbed CO allows interlayer mass transport in Co/Pt(111) growth. As Fig. 13b shows, CO leads to increased roughness of the steps, which is associated with a reduced roughness of the film. Again, this points out the importance of rough steps, i.e., kinks and corners, for interlayer diffusion and, hence, for the growth mode.

8. Summary

In summary, we have studied the evolution of the structure, growth, and morphology of thin Co films deposited at RT on Pt(111) using STM. Besides the interest in this system for magnetic layer applications the motivation to analyse this system comes from the chemical contrast we have achieved in STM on CoPt alloy surfaces and which we could explain by ab-initio calculations of the electronic structure of the surface.

We have shown that the interlayer mass transport, which is important for the type of growth mode is an exchange process taking place with highest probability at corners and kinks. This leads to the conclusion that rough step edges with a lot of kinks and corners are crucial for 2D growth of Co on Pt(111) at room temperature.

We have also demonstrated that the first Co layer resides predominantly in the Pt fcc hollow sites. The strain in the Co layer is relieved by the formation of dislocations resulting in smaller areas of Co in hcp sites, the fcc and hcp areas being separated by Co in bridge sites. The second Co layer is found to relieve the dislocations, resulting in the formation of a hexagonal moiré structure, the Co in-plane lattice distance being close to that of bulk Co. The moiré structure persists up to a Co coverage of at least 5 ML. The growth appears to be smooth or 2D up to a Co coverage of about 3.5 ML. This is because of the rough step edges which favour the interlayer diffusion by exchange processes at kinks and corners. The reason for these rough step edges is inhomogeneous strain induced by the moiré structure. Above this coverage the steps become very smooth because of the decreasing strain in the surface and a 3D island growth is observed. The Co layers in these triangular shaped islands are shown to be stacked in a predominantly twinned fcc stacking.

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