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Growth and morphology of Rh deposits on an alumina film under UHV conditions and under the influence of CO

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Abstract

Adsorption of certain gases may alter the structure of small metal particles deposited on a surface. If the particles are prepared by vapour deposition, the morphology may also be changed by the presence of these gases during growth. We have investigated the growth and morphology of Rh under ultrahigh vacuum (UHV) conditions and under the influence of CO using a thin, well-ordered Al_2O_3 film as substrate. First, the growth modes at UHV pressures were characterized with the help of spot profile analysis low energy electron diffraction (SPA-LEED) and scanning tunnelling microscopy at two substrate temperatures: 90 and 300 K. At 300 K, we observe the decoration of domain boundaries between different antiphase domains of the film. The particles are mainly disordered, only a small fraction is crystalline. Keeping the substrate temperature at 90 K, smaller (disordered) aggregates form, which are mostly located inside the domains. If the deposits are exposed to CO, in both cases structural changes are detectable: SPA-LEED results point to a spreading of the particles, resulting in an expansion of their surface area. Exposing the sample to CO during deposition, on the other hand, leads to the formation of a carbonyl-like species in the case of large amounts of Rh. Its decomposition gives rise to a characteristic peak in the thermal desorption spectrum. © 1997 Elsevier Science B.V.

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1. Introduction

The growth of metals on oxide substrates has been the subject of many studies in the past (e.g. see the review article in Ref. [1] and references cited therein). One of the reasons for the interest in these systems results from their utilizability as model systems for supported metal catalysts, since they facilitate a detailed investigation of the interplay between the structure of such composite systems and their interaction with adsorbates.

* Corresponding author. Fax: (+49) 30 8413 4312; e-mail: baeumer@fhi.berlin.de There are several examples showing that it is within the bounds of possibility to establish correlations between particle size and electronic properties on the one hand and adsorption behaviour or catalytic activity on the other hand [2,3].

One important aspect, however, which is often neglected in ultrahigh vacuum (UHV) experiments is the fact that the structure of small metal aggregates may change upon adsorption of certain gases. One prominent example is the interaction of CO with Rh deposits. Studies on technical Rh/Al₂O₃ catalysts have revealed that adsorbed CO exerts a considerable structural influence on the metal particles. They are completely disrupted [4], resulting in the formation of isolated Rh¹(CO)₂ species

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which can readily be observed by infrared spectroscopy [5]. This process, taking place at temperatures as low as 150 K [6], is partially reversible by thermal desorption (TD) of CO, leading to agglomeration of Rh¹ to Rh aggregates [6–8].

On the basis of studies on the decomposition of $Rh_6(CO)_{16}$ on Al_2O_3 , a mechanism for the formation of the dicarbonyl species via Rh oxidation by surface hydroxyl groups has been proposed [9,10]. In addition, Cl present on the surface appears to promote this process [11]. In a study on the chemistry of Rh/TiO₂(110), however, it has been shown that disruption upon CO adsorption can also occur on a hydroxyl-free substrate [12,13]: for this case, a stabilization of the dispersed Rh by oxygen vacancies was suggested.

Although the mechanism may differ from case to case, it is still obvious that the driving force for the structural rearrangement is the stability of Rh carbonyls involving two or more strong CO–Rh bonds. However, morphological changes upon CO adsorption are not always connected with disruption. In fact, by field ion microscopy a CO-induced faceting of Rh field emitter tips taking place at temperatures of 240 K and above was observed [14].

Apart from structural effects that adsorbates sometimes have on metal particles, they may also control the formation itself if they are present during the growth process. Here, thermodynamic as well as kinetic aspects can play a part: either the adsorbate changes interface energies and, therefore, the growth mode, or it alters activation energies for some of the elementary steps taking place. In both cases, it is possible to obtain structures which are not accessible otherwise, i.e. without the "surfactant" [15,16].

The aim of this work is to characterize the growth of Rh on a thin well-ordered Al_2O_3 film including the structural influence of CO. First, we discuss the structure of particles resulting from deposition at different substrate temperatures under UHV conditions. Then, we turn to the changes in morphology found after CO adsorption; finally, the growth in an ambient atmosphere of CO is described. The electronic structure of the particles as well as cluster-size-dependent adsorp-

tion properties will be discussed in separate papers [17,18].

2. Experimental

We performed the experiments in two different UHV systems. The low energy electron diffraction (LEED) investigations were carried out in a chamber equipped with a Levbold spot profile analysis (SPA)-LEED system (specified transfer width: 900 Å; typical primary beam currents: 50 pA-1 nA). The spot profiles shown in the following have been recorded along the [001] direction of the NiAl substrate (deposition experiments at 90 K) or along the reciprocal lattice vector b_2^* (see Section 3.1) of one of the rotational domains of the oxide film (deposition experiments at 300 K). However, the scaling of the plots refers to the NiAl reciprocal lattice vector a_2^* along [110], i.e. the distance between the (00) and the (01)spot (1.54 Å⁻¹), which has been used for k-space calibration of the SPA-LEED instrument.

TD measurements were carried out with a differentially pumped quadrupole mass spectrometer mounted inside a tube with a conical aperture (about 5 mm diameter) eliminating molecules not directly desorbing from the sample surface. During the experiment, the crystal was positioned approximately 0.3 mm in front of the hole. The heating rate amounted to approximately 1.5 K s⁻¹.

In this chamber, the NiAl(110) single crystal was fixed between two thin tantalum wires spot welded to tantalum rods. With liquid nitrogen, the crystal could be cooled to about 90 K. Heating was possible by radiation from a filament or by electron bombardment.

The scanning tunnelling microscopy (STM) images were taken in a second UHV system. Here, the sample was mounted on a small molybdenum plate, which could be transferred between an Omicron STM/AFM system and the main chamber equipped with a hemispherical analyser and an X-ray gun for XPS, as well as with a LEED optics and all instruments necessary for the preparation of the surface. In order to control the crystal temperature, an NiCr/Ni thermocouple sticking to the sample was used. The electrical contacts were

realized by plug-socket connectors between sample holder and sample plate.

The clean NiAl(110) surface was prepared by several cycles of sputtering (Ar^+ ions, 700 eV) and annealing. The ordered Al_2O_3 film was obtained as previously reported in the literature [19]. After dosing 3600 L O₂ at a sample temperature of 550 K, the crystal was annealed to 1120 K. The quality of the oxide could be checked via its LEED profiles and intensities (LEED chamber) [20] or by STM (STM chamber). A simple tool for ensuring that the oxidation of the surface was complete is provided by TD spectroscopy (TDS) of CO, since no CO adsorbs on the clean oxide film at 90 K, whereas CO desorption from nonoxidized NiAl is observed at 300 K [19,21].

In both chambers, Rh metal (Heraeus, >99.9%) was deposited with a commercial evaporator (Focus, EFM 3) based on electron bombardment and allowing evaporation from a rod. It was calibrated by a quartz microbalance. In the following, the nominal film thickness as obtained by the microbalance is used to quantify the amount of Rh deposited. The deposition rates varied between 0.6 and 1.0 Å min⁻¹ (1 Å Rh corresponds to 7.3×10^{14} atoms cm⁻²).

3. Results and discussion

3.1. The defect structure of the alumina film

In this section, we would like to discuss the defect structure of the thin alumina film and its influence on the profile of the specular LEED beam, since this aspect is essential for nucleation and growth of Rh. However, as this was the subject of a former study [20], only the most relevant points will be reported here.

Oxidation of the NiAl(110) surface results in a rather complex LEED pattern, which was first observed by Müller et al. [22]. An analysis of this pattern reveals that the oxide film consists of two rotational domains. The unit mesh is rather large $(17.9 \text{ Å } (\boldsymbol{b_2}) \times 10.6 \text{ Å } (\boldsymbol{b_1}))$, nearly rectangular and commensurate along the [110] direction of the substrate. Along the [001] direction, however, no

commensurate relationship between the two lattices exists. With respect to this direction, the unit mesh vectors b_1 of the two domains are rotated by 22.7°; the angle between [110] and b_2 , on the other hand, amounts to 24.0°.

As shown in a combined SPA-LEED/STM investigation [20], the defect structure of the film is dominated by a network of domain boundaries. One kind of boundary separates the rotational domains. More important than this type, however, is a second type existing between antiphase domains within one rotational domain. In a characteristic manner, the major part of these boundaries runs along the b_1 directions. In this way, the film is cut into stripes by the boundary network: the domains are rather extended in these directions (about 500 ± 300 Å), whereas the average domain width only amounts to approximately 120 Å.

Concerning the oxide LEED pattern, the existence of antiphase domains gives rise to an oscillation of the half-width or a periodic splitting of the spots as a function of the parallel component of the scattering vector [20]. This, however, is not the only indication: as shown in Fig. 1, the (00) beam consists of a sharp central spike and a broad anisotropic shoulder. Note that a maximum broadening is found along b_2^* of both rotational domains, i.e. perpendicular to the long antiphase domain boundaries mentioned above. Therefore, it is justified to connect the anisotropy with the boundary network: without going into details, it can be explained by an inhomogeneous surface structure with different scattering factors at the boundaries and within the domains themselves (e.g. see Ref. [23]).

In which way the network of domain boundaries is of relevance for the nucleation and growth of Rh will become evident in the following section.

3.2. Deposition of Rh: growth at different temperatures under UHV conditions

Apart from the (00) spot profile of the clean oxide film, Fig. 1 also contains profiles after deposition of 8 Å of Rh at a sample temperature of 90 K and 16 Å of Rh at room temperature. In both cases, a diffuse shoulder is visible, which,



Fig. 1. Specular beam LEED profiles (40 eV) for clean $Al_2O_3/NiAl(110)$ and after Rh deposition at 90 K and 300 K respectively. Note the different length scale in the case of the 90 K deposit. Relevant directions in reciprocal space are indicated in the scheme.

however, is isotropically distributed around the sharp peak in the former case. In the latter case, on the other hand, the anisotropy is even more pronounced. This already demonstrates that the growth of Rh is strongly dependent on the substrate temperature during deposition.

First, we start with the situation at 90 K. Fig. 2 contains all relevant SPA-LEED data for this part of the work: on the left-hand side, a series of (00) spot profiles for different Rh coverages can be

found together with a profile of the clean oxide film. A shoulder in the shape of a ring evolves and gains intensity as the nominal film thickness increases. Furthermore, the inset in the middle provides additional information about the damping of the oxide LEED pattern (the (02) spot was used here). On the right-hand side, a series of profiles acquired at different electron energies is displayed, showing that no significant changes are observable as this parameter varies.



Fig. 2. Rh exposure dependence (left) and electron energy dependence (right) of the (00) spot profile for Rh deposition at 90 K. The inset in the middle shows the relative intensity of the most intense oxide LEED spot as a function of the amount of Rh deposited.

From these findings, the following conclusions concerning the growth mode can be drawn.

- The comparatively slow damping of the intensity of the oxide spots cannot be explained by a layer-by-layer growth of the metal. (Here, we assume implicitly that the metal overlayer does not scatter into the direction of the oxide spots, an assumption which is corroborated by the next point.) Rather, it is compatible with a three-dimensional growth of metal particles.
- Moreover, the missing energy dependence of the profiles points to disordered particles: provided that islands with discrete layers (e.g. (111) layers) existed on the surface, the intensity ratio between peak and shoulder and, possibly, the shape of the shoulder should be a function of the electron energy, since the phase difference for scattering at different layers would vary with the de-Broglie wavelength of the electrons resulting in in-phase (minimum diffuse intensity) and out-of-phase (maximum diffuse intensity) scattering conditions. This is not the case.
- The shoulder is isotropic, ruling out an anisotropic correlation of island sizes and distances as expected if the domain boundaries strongly determined the nucleation process.

Disordered or amorphous areas on a surface usually have negligible scattering factors and can,

therefore, be considered as "black holes". In this case, the intensity of the oxide spots can be used to calculate the fraction of the surface not covered with metal islands. With the help of this piece of information it is possible to get quantitative information about island diameters and distances according to a formalism described elsewhere [24]. The results are compiled in Fig. 3 (dark symbols). Obviously, the particle diameters are rather small: the average number of atoms per island ranges from 30 atoms for 1 Å of Rh to 450 atoms for 8 Å of Rh. Note that the island density is rather high even for 1 Å, the smallest coverage investigated here, and decreases for higher coverages. This clearly demonstrates that coalescence plays an important role even at an early stage of the growth process.

The STM pictures presented in Fig. 4 corroborate the SPA-LEED results. They were obtained after deposition of 0.1 Å of Rh and are representative for the distribution of particles growing at 90 K. Although the domain boundaries are decorated to some extent - it is clearly recognizable that they are running mainly along two directions which are identified as the b_1 directions of both rotational domains – a large number of aggregates is also located inside the domains. The island density showing up amounts to 6×10^{12} islands cm⁻². Since this value is below the maximum density at 1 Å of Rh as calculated from the SPA-LEED results (see Fig. 3), it can be concluded that, at a Rh exposure of 0.1 Å, nucleation still dominates the growth process.

It is quite instructive to compare the STM image



Fig. 3. Rh exposure dependence of average Rh island diameter and island density before (dark circles) and after (light circles) CO dosage for the 90 K deposits as determined from the SPA-LEED data.



Fig. 4. STM images (overview and close-up) of Rh deposited at 90 K on the alumina film: (a) 0.1 Å Rh, 3000 Å × 3000 Å (CCT, U = +5.1 V, I = 2 nA); (b) 0.1 Å Rh, 600 Å × 600 Å (CCT, U = +4.1 V, I = 1.2 nA). The stripes clearly visible in the close-up are a characteristic feature of the oxide film (see Ref. [20]).

for preparation at 90 K with the STM results for deposition at room temperature which can be found in Fig. 5. Here, the situation is totally different, as already indicated by the LEED profiles. Considering the left part of Fig. 5, which represents an overview with a large scan range (Rh exposure: 1.4 Å), it turns out that at 300 K the domain boundaries are efficiently decorated. Only in the case of large domains some additional particles do exist inside them (the island density due to homogeneous nucleation within the domains is lower than 10^{12} islands cm⁻²). This finding immediately explains the anisotropy of the (00) beam mentioned above: since the difference between the scattering factors at the boundaries and within the domains still increases by the nucleation of Rh, it is not surprising that the anisotropy also becomes more pronounced. The right part of Fig. 5 shows a close-up (Rh exposure: 5 Å) contributing an interesting detail: some of the aggregates visible there seem to be crystalline; they have triangular or hexagonal shapes and a flat top. The majority, however, have a domed surface.

Analogous to Fig. 2, Fig. 6 contains a series of profiles of the (00) LEED reflex for deposition at room temperature elucidating the development for different coverages. Furthermore, the intensity of the oxide LEED pattern at different Rh exposures is supplied again:

• It is especially noteworthy that, in contrast to deposition at 90 K, the intensity of the oxide reflex chosen here increases after metal deposition in the regime of small coverages (≤ 2 Å). This can only be explained by an influence of



Fig. 5. STM images (overview and close-up) of Rh deposited at 300 K on the alumina film: (a) 1.4 Å Rh, $3000 \text{ Å} \times 3000 \text{ Å}$ (CCT, U=2.2 V, I=1.2 nA); (b) 5.0 Å Rh, $1000 \text{ Å} \times 1000 \text{ Å}$ (CCT, U=0.9 V, I=1.2 nA). The particles marked with circles in the close-up are two examples of the aggregates which seem to be crystalline: they have a regular shape and a flat top.

the substrate on the structure of the growing metal film, leading to a situation where the scattering factor of the metal-covered areas cannot be neglected. For larger amounts of deposited metal, however, damping is observed again, corroborating the three-dimensional growth mode found with STM.

• Similar to the situation at 90 K, the profiles are not electron-energy dependent. This finding is compatible with disordered aggregates being in the majority, as already deduced from the STM results.

Again, a quantitative evaluation of the SPA-LEED data would be desirable. However, there are two aspects leading to a breakdown of the procedure described in Ref. [24], one being the anisotropy of the spots. The other difficulty results from the fact that, at least for small amounts of deposited Rh, the covered areas can no longer be considered as "black holes". Therefore, statistical data corresponding to Fig. 3 are lacking here. Nevertheless, the STM measurements reveal that the particles are somewhat larger than at 90 K.

3.3. Adsorption of CO on the Rh deposits

In order to study the influence of CO on the structure of the Rh particles, the sample was exposed to 10 L CO after deposition under UHV conditions and then investigated via SPA-LEED. Fig. 7 allows to judge the changes in the profiles of the specular beam and the intensities of the oxide spots upon adsorption for both preparation



Fig. 6. Rh exposure dependence of the (00) beam profile for Rh deposition at 300 K. Here, the scan is oriented along the reciprocal lattice vector b_2^* of one of the oxide rotational domains. The signals at $\pm 23\%$ a_2^* are first-order oxide spots. The inset shows the relative intensity of the most intense oxide LEED spot as a function of the amount of Rh deposited.

conditions. Note that deposition and adsorption experiments were carried out at the same temperatures (90 K and 300 K respectively).

Obviously, the effects observable are dependent on the initial situation: whereas at 90 K the shape of the profiles shows only minor changes, drastic changes are detectable at 300 K. The shoulder maxima along the b_2^* directions become less discernible due to a drastically increased half-width. On the other hand, the additional damping of the oxide LEED pattern occurring upon adsorption is much stronger in the case of the low temperature experiments.

For both situations, the observations suggest that the aggregates are subject to structural rearrangements when exposed to CO.

- The modification of the spot profile at 300 K points directly to changes within the lateral arrangement of the particles, whereas the reduction of the oxide spot intensity suggests an increase of the surface fraction covered with Rh. Both points can be explained by a spreading of Rh over the surface resulting in larger island diameters and, hence, in an expansion of the island surfaces.
- In contrast to that, the small changes in the diffuse shoulder at 90 K demonstrate that only



Fig. 7. The (00) spot profile before and after CO dosage for preparation at 90 K (left) and 300 K (right). The insets show the corresponding dependence of the oxide LEED pattern intensity on Rh exposure and CO dosage.

minor changes within the island arrangement occur upon adsorption. The drastic weakening of the oxide spots, on the other hand, could again be understood in terms of a flattening of the Rh particles. Quantitative results from the evaluation of the spot profiles according to the procedure mentioned above are plotted in Fig. 3 (light circles).

It is worth noting that the structural modification is reversible in the case of the larger particles prepared at 300 K. After heating the sample to 500 K, the former profile of the (00) beam can be restored. In contrast to this, the smaller particles prepared at 90 K seem to undergo irreversible changes (the intensity of the oxide spots recovers only negligibly upon heating). It has to be taken into consideration, however, that this may also be a consequence of the thermal treatment itself.

3.4. Deposition of Rh in an ambient atmosphere of CO

The presence of an adsorbate *during* metal deposition may considerably modify the growth process. In order to study such phenomena, Rh was evaporated onto the oxide film at 90 K, *while* an ambient pressure of CO amounting to 2×10^{-6} mbar was maintained in the chamber. Immediately after the metal deposition was finished, the CO dosage was terminated. The results of a LEED spot profile analysis and a TD spectrum can be found in Figs. 8 and 9.

There are several interesting differences to observe when comparing the profiles of the specular beam and the intensities of the oxide spots for growth under UHV conditions on the one hand and for growth in a CO atmosphere on the other hand. First of all, the drop of the oxide spot intensities (inset of Fig. 8) as a function of the amount of metal deposited is very steep in the latter case. Beyond 1 Å it is even steeper than for growth in UHV at 90 K and subsequent CO dosage. This already indicates that the surface is covered very efficiently by the overlayer formed.

Moreover, the profiles obtained for the higher coverages (>1 Å) are indicative of a lateral arrangement of the islands which is also modified.



Fig. 8. The (00) spot profile for Rh deposition at 90 K in UHV and in an ambient atmosphere of 2×10^{-6} mbar CO (two Rh exposures). The inset shows the damping of the oxide LEED pattern for the UHV deposits before (dark circles) and after (light circles) CO dosage and for Rh growth in a CO atmosphere (triangles).

This is most obvious for 4 Å of Rh, as can be seen in the upper part of Fig. 8. Here, the constant high background and the low intensity of the specular beam are due to a complete lack of long-range order of the deposit covering the substrate. For 1 Å of Rh, on the other hand, the profiles are rather similar (lower part of Fig. 8), suggesting a comparable surface morphology. In all cases, no specific energy dependence could be established, so that growth of ordered particles was safely excluded.

Another clue to the structure results from TDS. While the spectra for small amounts of Rh deposited with and without CO background pressure closely resemble each other, a characteristic feature shows up in the former case for larger amounts (see Fig. 9): a sharp peak situated at 345 K dominates the spectrum followed by a smaller shoulder at 450 K.

The processes occurring upon heating can also be followed with the help of LEED. The inset of



Fig. 9. TD spectrum for 16 Å of Rh deposited in a CO atmosphere (heating rate: 1.5 K s^{-1}). The inset shows the annealing temperature dependence of the oxide LEED pattern intensity for 2 Å of Rh deposited in a CO atmosphere. Intensity measurements were performed at 90 K after heating the sample to the indicated temperatures.

Fig. 9 shows the intensity of the oxide spots at 90 K after annealing the deposit to the indicated temperatures. As plotted in the inset of Fig. 9, the main desorption peak is connected with a certain degree of recovery of the oxide LEED pattern: the intensity increases in this temperature regime. Between 600 and 800 K, however, the intensity decreases once again, but it is possible to return to the situation before deposition (clean oxide film) by heating to 1100 K.

In this context, it is noteworthy that, apart from the desorption temperatures of course, the TD spectrum and the LEED intensity curve are nearly identical to the corresponding traces recorded after deposition of 20 Å of Pd onto the alumina film under the same conditions, as described by Sandell et al. [16]. In this study it has been shown that a carbonyl-like species grows on the surface instead of metallic aggregates. Therefore, it is possible to interpret the present pieces of information in the following way:

- Deposition of large amounts of Rh in an ambient CO atmosphere also leads to the growth of a carbonyl overlayer, which decomposes at 345 K. In conjunction with this process, the Rh remaining on the surface coalesces: the shoulder at 450 K can be assigned to desorption of CO from metallic aggregates in agreement with the TD spectra obtained for the Rh deposits prepared under UHV conditions on this film and on other alumina substrates [25-27]. Since the compact aggregates cover a smaller area of the substrate, the oxide spots gain intensity when the overlayer decomposes. Analogous to the behaviour of Pd, the loss of intensity upon further heating points to diffusion of Rh through the oxide film into the metal substrate, connected with a partial destruction of its longrange order. If, however, the temperature is raised to values which are otherwise needed for the preparation of the film [19], the structure can apparently be fully restored.
- For small amounts of Rh the findings coincide with the corresponding observations for growth at low pressure and subsequent CO adsorption, indicating that CO has no significantly different impact on the final product.

4. Conclusions

4.1. Growth

The experimental results described show that nucleation and growth of Rh on the thin alumina film used as a substrate in this study are dependent strongly on the sample temperature during deposition. At 90 K, small disordered aggregates with diameters between 8 and 25 Å (nominal film thickness: 1-8 Å) are formed. In this case homogeneous and heterogeneous nucleation play a role. If, however, the sample is kept at room temperature, deposition results in larger particles which decorate the network of domain boundaries running through the oxide film. As revealed by SPA-LEED, the major part is also disordered, but STM images suggest that at least some aggregates are crystalline.

Thus far, a number of studies concerning the growth of Pt, Pd and Ag on $Al_2O_3/NiAl(110)$ has been published [24,28–31], and it is worthwhile comparing the behaviour of Rh to these cases. Pt forms very tiny islands consisting of only a few atoms [28,29]; Ag, on the other hand, forms very large crystallites [30]. For both metals, growth at 90 and 300 K exhibits only small differences. Pd is an intermediate case, and it shows a rather similar behaviour to Rh [24], although the Rh aggregates formed under the same conditions tend to be slightly smaller. The growth of Pd is temperature dependent, too.

Accordingly, the following order can be established with respect to the cluster sizes:

 $Pt < Rh \le Pd < Ag.$

In order to explain this trend, we note the correlation with the enthalpies of formation of the respective oxides: PtO_2 : $-172.0 \text{ kJ mol}^{-1}$; RhO: -90.1 kJ mol⁻¹; PdO: $-85.4 \text{ kJ mol}^{-1}$; AgO: $-12.1 \text{ kJ mol}^{-1}$ [32]. Assuming that the enthalpies reflect the strength of interaction between the metal and the oxide, the above correlation demonstrates that the interaction between metal and oxide is decisive for the growth here. Such a relationship has also been found for several transition metals on TiO₂ [33,34] and on oxidized W single crystals [35]. However, taking the temperature dependence for Rh and Pd into account, it is immediately clear that kinetic factors are by far not negligible for a theoretical description of the growth behaviour. This, however, is beyond the scope of this paper.

4.2. Structural influence of CO

SPA-LEED experiments have been carried out in order to clarify the influence of CO on the structure of the Rh deposits at 90 and 300 K. In both cases, the results point to increasing island diameters, i.e. a spreading of the particles.

Considering the remarks in Section 1 about morphology changes of deposited Rh particles observed upon CO adsorption, it becomes evident that a general trend is showing up here. Apparently, there is a strong tendency of Rh particles to increase their adsorption capability either by disruption to carbonyl species [4–6,13] or by an expansion of the surface area [14], as in the present case.

So far it has not been possible to observe such changes by STM. These measurements, however, are considerably complicated by the electronic structure of the substrate [20] and by the comparatively large corrugation of the metal-particle-covered surface.

4.3. Formation of a carbonyl overlayer

Exposing the sample to CO during Rh deposition leads to the formation of a carbonyl-like species in the case of large amounts of Rh. Its decomposition gives rise to a characteristic sharp peak in the TD spectrum at 345 K. This process is connected with the coalescence of Rh to metallic aggregates.

As stable Rh carbonyls can be prepared (e.g. see Refs. [36,37]), it is possible to compare their thermal behaviour to the corresponding behaviour of the overlayer discussed in this study. Solid $Rh_4(CO)_{12}$, for example, decomposes at about 400 K, giving $Rh_6(CO)_{16}$, which in turn decomposes at 470 K [37]. These decomposition temperatures are higher than the decomposition temperature of the carbonyl species under investigation, i.e. the solid carbonyls exhibit a higher thermal stability. This may be taken as an indication that the overlayer does not consist of isolated well-defined carbonyl molecules.

As already mentioned in Section 3.4, the SPA-LEED and TDS results resemble those of a Pd carbonyl species prepared on the alumina film in the same way [15,16]. In this case, it has been proven by electron spectroscopic measurements that a branched structure with a certain number of metal-metal bonds grows on the surface. Anyhow, on the basis of the present results, it is impossible to tell definitely whether isolated Rh carbonyl species or complex, highly ramified structures form on the surface.

In spite of the similarities, there is also a major difference between Pd and Rh: the Pd carbonyl species forms even for very tiny amounts of deposited material. A mechanism has been proposed where the rearrangement to compact aggregates is kinetically inhibited during growth. As the SPA-LEED findings for small amounts of Rh, on the other hand, look very much like those obtained for particles which were prepared under UHV conditions and exposed to CO afterwards, it seems that, in contrast to Pd, the thermodynamically most stable situation is reached for small aggregates independent of the preparation conditions. Apparently, kinetic inhibition plays a minor role here.

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