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Metal deposition in adsorbate atmosphere: growth and decomposition of a palladium carbonyl-like species

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Abstract

Vapour deposition of Pd with CO background pressure onto an ordered alumina film kept at 90 K results in the formation of a palladium carbonyl-like compound. The growth and decomposition of this $Pd_x(CO)_y$ species is investigated using SPA-LEED (spotprofile analysis), thermal desorption spectroscopy (TDS) and photoemission of both core and valence levels. It is found that the nucleation and growth process is drastically modified in the presence of CO. The TD spectrum for the carbonyl-like species exhibits a sharp and dominant CO desorption peak at 190 K, which is not observed for Pd deposits grown under UHV conditions. This feature appears for coverages ranging from fractions of a monolayer to multilayers and is associated with decomposition of the compound. The binding energy shifts observed for increasing amounts of $Pd_x(CO)_y$ indicate that metal-metal bonds are formed during the growth. Upon heating, two different processes occur. (I) The compound decomposes under formation of compact, metallic Pd clusters which are present up to 500 K. (II) Heating to higher temperatures results in diffusion of the Pd atoms into the oxide film. It is demonstrated how these processes can be directly monitored by recording the intensity of the oxide LEED pattern as a function of temperature. Finally, we briefly discuss the data in terms of possible growth mechanisms of the $Pd_x(CO)_y$ species.

Keywords: Aluminum oxide; Carbon monoxide; Carbonyls; Chemisorption; Clusters; Compound formation; Growth; Low energy electron diffraction (LEED); Palladium; Thermal desorption spectroscopy; Visible and ultraviolet photoelectron spectroscopy; X-ray photoelectron spectroscopy

1. Introduction

Growth and adsorption properties of metals on oxide surfaces have attracted considerable attention due to their fundamental importance in heterogenous catalysis [1-13]. The geometric and electronic structure of the metal deposits developing during the process of nucleation and growth is determined by various factors, e.g. by the properties of the metal and oxide surface, their interaction, as well as deposition conditions, such as temperature and deposition rate [14–16]. Due to the weak interaction of metal clusters with oxide substrates, usually a three-dimensional growth mode is observed (Vollmer–Weber growth). However, in many cases growth is controlled by the kinetics of certain elementary processes rather than by thermodynamic properties [6,17].

Investigations of these effects on an atomic level on technical support materials are seriously complicated by the polycrystalline or amorphous structure of those samples, exhibiting a variety of inequivalent adsorption sites which are difficult to characterize [18]. Moreover, their accessibility by structure sensitive experimental methods is

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restricted. This problem can be circumvented by applying model systems based on oxide single crystals [3] or well ordered oxide films on metal substrates. Ordered alumina films may be grown either on an inert substrate [19] or by direct oxidation of an aluminium-containing single crystal, such as the alumina film on NiAl(110) used in this study [20]. This oxide film has been extensively characterized with respect to the geometric and electronic structure, defects and adsorption properties [20–23], and has already been employed as a model substrate for metal deposition [24–27].

It has been recognized that the presence of strongly interacting adsorbates might significantly influence the growth and structure of heteroepitaxial systems. In the case of metal growth on oxides, adsorption after metal deposition might lead to restructuring of metallic islands or even to their disrupture and redispersion [6,28–33]. If, on the other hand, the adsorbate is already present during the process of nucleation and growth, the energetics of the elementary steps involved might be drastically modified. This is illustrated by the function of surfactants, which, pre-adsorbed on the substrate, can be utilized to alter the growth mode of epitaxial systems, e.g. Refs. [34–36].

An alternative way of modifying growth processes is given by metal deposition in the presence of an adsorbate in the gas phase. For metals grown on oxides various adsorbates only weakly interact with the substrate, but strongly chemisorb on the metal itself. Consequently, even though not adsorbing on the substrate, chemisorption on the metal aggregates during growth may strongly influence the clustering process. It might on the one hand provide a tool to modify dispersion, size distribution and structure of metal aggregates; on the other hand, new structures might be formed, which may otherwise not be accessible. For example, in a recent study it was shown for Pt films on $TiO_2(110)$ that growth in CO atmosphere results in an increased wetting [37]. This behaviour was interpreted mainly in terms of thermodynamical arguments.

In a recent, brief report, we presented the first results on Pd deposition in a gas atmosphere at low temperature (90 K) [38]. CO was chosen as an adsorbate, since it is known to form strong chemisorption bonds on metallic Pd, e.g. Ref. [39]. According to the so-called Blyholder model, which is the most commonly used picture, these bonds involve hybridization between the metal d-states and the CO $2\pi^*$ orbital. The presence of CO during the evaporation was found to strongly effect the Pd cluster growth; instead of metallic particles, a carbonyl-like compound was formed of which several layers could be grown. This result was somewhat surprising, since the only binary Pd carbonyls reported in the literature so far were prepared in zeolithes [40-42] or by matrix isolation [43,44]. Indeed the latter technique, which is based on co-condensation of metal vapour and an inert gas containing the desired ligand at low temperature, is related to our experimental procedure. The decomposition of this new species, which we denote $Pd_x(CO)_v$, was manifested in the thermal desorption (TD) spectra as a sharp peak at 190 K. By comparing the areas of the C 1s and Pd 3d peaks measured with X-ray photoelectron spectroscopy (XPS), a CO/Pd ratio of about 1.7 could be estimated.

In this paper we present a detailed study on the growth and decomposition of this novel adsorbate system, using LEED profile analysis, TDS (thermal desorption spectroscopy) and PES (photoelectron electron spectroscopy) of both core and valence levels. In contrast to the results for $Pt/TiO_2(110)$ [37], the modifications of the Pd growth induced by the adsorbate atmosphere might be attributed to kinetic rather than thermodynamical effects as discussed in the final section of this paper.

2. Experimental

The LEED profile measurements were performed using a SPA-LEED system (Leybold) [45] with a specified transfer width of more than 800 Å. For the NiAl(110) single crystal, however, the minimal half-width of the spots was determined by the mosaic spread of the crystal (about 0.2°). This effect limits the effective transfer width for the range of electron energies used in this study to a value of 200–300 Å. All profiles shown were recorded along the [001]-direction of the NiAl substrate. The width of the profiles is given relative to the NiAl reciprocal lattice vector 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.

Thermal desorption measurements were carried out with a differentially pumped mass spectrometer, which was equipped 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 from the aperture and heated from behind by radiation from a filament. The heating rate was about 1.5 K s^{-1} .

The UV photoelectron (UP) spectra were recorded at BESSY at the TGM3 beamline using a hemispherical electron energy analyzer rotatable in two orthogonal planes for angular resolved measurements. The spectra presented here were recorded at a photon energy of 42 eV and at grazing emission (70° off normal). The total resolution was 0.3 eV.

The X-ray photoelectron (XP) spectra were measured using a Leybold spectrometer equipped with a hemispherical analyzer and a multi-channel detection system. Two photon sources were available, monochromatized Al K α and a twin anode with the possibility for using either unmonochromatized Mg K α or Al K α radiation. The Pd 3d spectra were recorded with monochromatized Al K α with a total resolution of about 1.2 eV whereas the C 1s-spectra were recorded with unmonochromatized Al K α at a resolution of about 1.5 eV. All XP spectra were measured at normal emission. The binding energies for all the photoemission spectra are relative to the Fermi level of the NiAl(110) substrate.

The NiAl(110) single crystal was mounted between two thin tantalum wires spot welded to tantalum rods. Cooling to approximately 90 K was possible using liquid nitrogen. The sample was heated by radiation from a filament or by electron bombardment. The clean NiAl(110) surface was prepared by several cycles of sputtering (Ar⁺ ions, 500 eV) and annealing. Cleanliness and composition of the surface was checked by AES. The ordered Al₂O₃ film was prepared as previously reported in Ref. [20]. After dosing 1200 L O₂ at a sample temperature of 550 K the crystal was annealed to 1200 K. After preparation the quality of the oxide was checked via its LEED profiles and intensities [22]. A simple way of checking whether oxidation of the surface is complete is provided by CO-TDS, since no CO adsorbs on the clean oxide film at 90 K, whereas CO desorption from non-oxidized NiAl is observed at 300 K [20,25].

Pd metal (Heraeus, >99.95%) was deposited employing two different types of evaporators: a home built Knudsen cell with an alumina crucible and one, which is based on electron bombardment and allows evaporation from a Pd rod (Omicron). Both were calibrated by a quartz microbalance. Deposition rates between 1.2 and 2.4 Å min⁻¹ were used (1 Å Pd corresponds to 6.8×10^{14} atoms cm⁻², 1 monolayer of close packed Pd (derived from the bulk atomic radius) corresponds to 1.53×10^{15} atoms cm⁻² or 2.25 Å Pd). For deposition in CO atmosphere, a partial pressure of approximately 2×10^{-6} mbar CO was adjusted via a leak valve, which was opened immediately before and closed immediately after deposition.

3. Results and discussion

3.1. Growth of the $Pd_x(CO)_y$ species

3.1.1. LEED

Exploring the changes which are caused by the presence of CO during the growth process we would like to give a short overview on the growth of palladium deposited onto $Al_2O_3/NiAl(110)$ under UHV conditions and then compare to the growth in adsorbate atmosphere.

A detailed picture on how the metal behaves on the alumina film under various conditions is provided by the LEED spot-profiles and the intensity of the LEED pattern of the oxide substrate (a detailed description of the oxide superstructure has been reported previously [20,22]). With increasing metal coverage its characteristic pattern vanishes and, for deposition at 300 K, eventually new LEED spots appear. The inset in Fig. 1 shows the relative intensity of the most intense oxide spots as a function of metal exposure (in those cases where



Fig. 1. LEED spot-profiles of the (00)-reflex along the NiAl [001]-direction for Pd deposition under various conditions. The inset shows the corresponding gradual decrease of the relative intensity of the most intense oxide superstructure spots with respect to the clean oxide.

the spot could be subdivided into a *C* use part and a central spike, only the latter was taken into consideration). Deposition at 300 K results in a slow decay of the oxide intensity. Even after deposition of several monolayers of metal the substrate LEED pattern is clearly visible. At high coverages a diffuse hexagonal pattern (real space lattice constant: 2.8 Å) appears. In contrast to this, deposition at a substrate temperature of 90 K leads to a more rapid attenuation and no additional spots due to the metal are observed. However, if Pd is deposited at CO background pressure (substrate temperature: 90 K), the LEED pattern completely vanishes already at exposures exceeding 2 Å Pd.

Furthermore, metal deposition leads to characteristic changes in the LEED spot-profiles. In Fig. 1 profiles of the (00)-reflex along the [001]-direction of the NiAl substrate are shown. They refer to

situations with roughly the same attenuation of the oxide LEED pattern. For comparison, a profile for the clean oxide is given at the bottom. In all cases metal deposition gives rise to the development of an additional diffuse shoulder. For the room temperature deposit a narrow shoulder with a pronounced energy dependence of both width and relative intensity is observed. Low temperature deposition results in a much broader, ring-shaped shoulder without clear energy dependence. Upon deposition in CO atmosphere, a diffuse shoulder is observed, which is clearly different from both other situations: Its width is intermediate between these cases and independent of the electron energy. For different metal coverages, spot-profiles of the (00)-reflex are shown in Fig. 2. With increasing metal exposure the shape of the diffuse part



Fig. 2. LEED spot-profiles of the (00)-reflex along the [001] direction of the NiAl substrate for different amounts of $Pd_x(CO)_y$, i.e. for Pd deposited at 90 K in CO atmosphere. The inset shows the corresponding estimated average island sizes for growth in CO atmosphere as a function of Pd exposure. For comparison, island sizes for growth in UHV at 90 and 300 K are shown.

changes from a more Lorentzian to a ring-shaped type of shoulder.

The slow attenuation of the oxide LEED spots for deposition at 300 K is consistent with the formation of 3D islands (Vollmer–Weber growth mode), leaving a considerable amount of oxide uncovered, even at high metal exposures. As clearly shown by the appearance of the additional hexagonal LEED pattern, which, due to its lattice constant, can be identified as that of Pd(111), wellshaped crystallites with the (111) orientation and azimuthal alignment to the oxide are formed.

More detailed information on the growth of these crystallites is provided by the LEED spotprofiles [46,47]. In all cases metal deposition results in the appearance of a diffuse part in addition to the central spike. The profile, relative intensity and energy dependence of the diffuse part contain information on size and distance distributions of islands as well as their geometric structure and defects [48-52]. Spatial correlations are directly reflected in the shape of the diffuse part. Broad island distance distributions result in shoulder-shaped diffuse profiles, whereas more regularly spaced islands give rise to a ring-shaped profile centered around the Bragg position.

Upon deposition at 300 K, we observe a narrow shoulder in agreement with formation of larger islands. The well ordered structure of the Pd islands gives rise to the pronounced energy dependence of the shoulder due to constructive and destructive interference between the oxide substrate and different metal layers. In such a case the diffuse part of the spot-profile is not governed by the island distribution only, but also by defects, e.g. steps, on the islands themselves. However, if we are interested in island sizes, we can minimize the latter contribution by measuring spot-profiles at in-phase energies of Pd(111), where different metal layers do not contribute to the diffuse part of the profile due to constructive interference.

Consequently, the observed profiles can be analyzed in terms of a simple model containing only two types of scatterers [53]. Thus, we obtain an estimation for the average island size as a function of metal exposure. For example, deposition of 2-16 Å Pd at 300 K results in the formation of crystallites with average sizes ranging from approx-

imately 30 Å to 50 Å (see Fig. 2). Details concerning the data analysis procedure are given elsewhere [54].

For deposition at 90 K, a broad ring appears instead of the narrow shoulder observed at 300 K. Such rings have been observed for various epitaxial systems [46,50,52]. Moreover, for $Pt/Al_2O_3/NiAl(110)$ very similar profiles have been found [26]. The diffraction ring is the consequence of a peaked island distance distribution forming during the process of nucleation and island growth. The missing energy dependence points towards poorly ordered metal aggregates. As the scattering amplitude of such disordered aggregates can safely be neglected, the diffuse profile directly reflects the island size and distance distribution. Hence, the average island sizes (see Fig. 2) can be estimated to range from approximately 10 (exposure = 2 ÅPd) to 25 Å (exposure = 8 Å Pd) [54].

It has to be emphasized that the derived island sizes are rather crude estimations, since the applied models involve several drastic simplifications. However, the results obtained by the LEED spotprofile analysis have been confirmed by preliminary STM measurements at 300 K as well as at 90 K [54,55]. The STM results furthermore show that at all temperatures nucleation preferentially starts at defects on the oxide, e.g. domain boundaries and steps.

We will now proceed by discussing Pd deposition in CO atmosphere and a substrate temperature of 90 K. The strong damping of the LEED pattern indicates that the oxide substrate is more efficiently covered and the absence of any LEED pattern at higher coverages proves that there is no long-range order within the adsorbate islands. This is also reflected in the lack of energy dependence of the diffuse profile, since the amorphous structure of the deposit results in a negligible scattering factor [50]. Consequently, no energy dependent interference effects between oxide substrate and adsorbate islands can be expected.

As can be seen in Fig. 1, the width of the diffuse profile is in between those of the 90 and 300 K deposit without CO. As mentioned before, a coverage dependent change in the profiles from a broad shoulder to a ring-shaped profile can be attributed to an alteration of the island correlation developing during the process of nucleation and growth. Starting from almost randomly distributed islands at low Pd coverages, they become more regularly spaced as we proceed to a situation, where major parts of the substrate are covered.

Average island sizes and distances can be estimated by applying the same model as for the islands grown under UHV conditions. The corresponding numbers are given in the inset in Fig. 2. The island density is significantly lower as compared to deposition without CO atmosphere, although, as already mentioned, absolute values might contain systematic deviations due to imperfections of the applied models. However, it is obvious that nucleation and island growth is drastically modified by the presence of the adsorbate during the deposition process. The adsorbate can affect these processes in various manners, e.g. the mobile species on the surface might be carbonyls as proposed for other adsorbate induced structural rearrangements [30]. In this case, the strength of interaction with the oxide substrate and within the compound can be expected to be different as compared to adsorbate-free metal atoms and aggregates, which will finally influence the nucleation and growth kinetics.

3.1.2. TDS

Thermal desorption spectra for CO have been recorded for all deposition conditions discussed so far. Again, we will start with a short summary of the adsorption behaviour for the metal islands grown under UHV conditions. Corresponding desorption spectra are published elsewhere [38,54]. Afterwards, we will turn to the changes induced by the presence of CO during growth.

As discussed in the previous section, deposition of Pd at 300 K results in the formation of larger 3D crystallites, exposing preferentially the (111) faces. Consequently, the thermal desorption spectrum obtained for 20 Å Pd (deposited at 300 K) [38] agrees well with desorption spectra reported for CO/Pd(111) [56]. The spectrum is dominated by a prominent feature between 400 and 500 K with a low temperature shoulder between 300 and 400 K.

For lower metal coverages and, in particular, lower deposition temperatures, we obtain smaller

islands. They exhibit less well-ordered crystal surfaces and, therefore, an increased density of defect atoms. From such islands we observe strongly increased desorption in the low-temperature region between 100 and 350 K. This effect is discussed in more detail elsewhere [54]. In principle, there are two effects which could contribute to this behaviour. (1) With decreasing cluster size, the number of defect sites (e.g. steps, kinks) increases, allowing for coordination of additional CO, which desorb at a lower temperature. (2) Small clusters might exhibit different adsorption properties due to a modified electronic structure. Further changes could be caused by the interaction with the oxide substrate, as suggested for CO adsorption on $Pt/Al_2O_3/NiAl(110)$, where an additional low temperature desorption also appears [25].

Completely different desorption spectra are obtained for the $Pd_x(CO)_y$ species. Fig. 3 shows TD spectra for different Pd coverages, ranging from fractions of a monolayer to several monolayers. A sharp feature at 190 K strongly dominates the desorption spectra, and additional features are observed at 280, 360 and 450 K. Qualitatively, the same features are present at all coverages, although their relative intensities change. The inset in Fig. 3 shows a plot of the total intensity of desorbing CO as a function of Pd exposure. The amount of CO increases almost linearily up to multilayer coverages of Pd.

The large amount of CO adsorbed, almost proportional to the amount of metal deposited, points to the formation of a carbonyl-like species with rather well-defined stoichiometry [38]. Accordingly, the narrow desorption feature at 190 K can be assigned to the decomposition of this species, resulting in the evolution of CO and the formation of metallic Pd particles. Consequently, the coverage-independence of the decomposition feature indicates a well-defined thermal stability of the species. As will be shown in a following section, the desorption features at higher temperature can be assigned to a step-wise transformation, finally resulting in the formation of compact metallic islands.

TD spectra for various molecular transition metal carbonyls adsorbed on metallic, semiconducting and isolating substrates have been reported



Fig. 3. TD spectra for increasing amounts of $Pd_x(CO)_y$. The total amount of desorbing CO as a function of Pd exposure is plotted in the inset.

[57-61]. Similar to the spectra shown here, they frequently exhibit several CO desorption features, assigned to molecular desorption, decomposition of fragments and desorption from metallic clusters. The sublimation peak can usually be identified by detecting the Me⁺ signal or other metal containing fragments [57,58,61]. As for the Pd carbonyl species no Pd⁺ could be detected, we rather assign the feature at 190 K to a first step of decomposition. Molecular desorption, on the other hand, can only be expected for sufficiently small and isolated molecules. Therefore, this observation points to aggregates containing a substantial number of metalmetal bonds rather than small isolated carbonyl molecules.

Finally, it has to be pointed out that the decomposition of the carbonyl-species is an irreversible process. After decomposition it cannot be restored by CO exposure. Also small metal aggregates grown at 90 K under UHV conditions cannot be converted into the carbonyl-species, even by very large CO exposures (> 10^4 L). This might be taken as an indication that the kinetics plays a major role in the formation of the carbonyl-species. We will come back to this point in the final section of this paper.

3.1.3. PES

In Fig. 4, UP spectra for three different situations are shown; the bottom spectrum is recorded after deposition of 2 Å of Pd at 90 K with CO background pressure, whereas the next two represent the situations where 2 Å Pd has been deposited under UHV conditions at 90 and 300 K, respectively, followed by a dose of 20 L CO. The clean oxide spectrum is shown at the top for comparison. It is readily observed that the CO/2 Å Pd (300 K) situation differs drastically from the other two situations; in the binding energy (BE) region 0-5 eV, the Pd 4d band appears with a DOS



Fig. 4. UP spectra showing the valence region for Pd deposited on $Al_2O_3/NiAl(110)$ under different conditions. The spectrum for the clean oxide is shown at the top for comparison.

(density of states) strongly reminding of CO on metallic Pd [38]. Based on the previous results for CO adsorbed on different Pd single crystal surfaces, the CO-induced states, 4σ and the almost degenerate $5\sigma/1\pi$, are expected at around 11 and 8 eV, respectively [62,63]. These are in this case extremely weak. Turning next to the CO/2 Å Pd (90 K) situation, the major parts of the Pd 4d states appear at higher binding energies, leading to a significant decrease of intensity near $E_{\rm F}$. The most apparent change is that the 4σ and $5\sigma/1\pi$ peaks are now much more intense, i.e. the relative amount of CO has increased. These peaks also have slightly higher binding energies. Finally, when Pd has been deposited in CO-atmosphere, further changes appear; the Pd 4d states form a doublet with just a very weak tail extending to the Fermi level, the relative amount of CO has increased and the CO-induced peaks have shifted to even higher binding energies.

The observed differences between CO adsorbed on 2 Å of Pd deposited at 90 and 300 K, respectively, can be understood when considering that the Pd clusters grown at low 90 K are much smaller than those formed at 300 K, which allows for a higher degree of Pd-CO coordination in the low temperature case. This is reflected by the increased relative intensities of the 4σ and $5\sigma/1\pi$ peaks, and, due to the hybridization with the CO $2\pi^*$ orbital, gives rise to intensity variations in the Pd 4d states. The changes appearing when depositing Pd in CO atmosphere are thus consistent with a further increase of the CO/Pd ratio. The spectra shown in Fig. 4 therefore clearly demonstrate that changes in the growth mode of Pd on the alumina film yield characteristic changes in the valence photoemission spectra, and next we will concentrate upon the properties of the species formed when the evaporation takes place in CO-atmosphere.

Fig. 5 shows the UP spectra for increasing amounts of Pd evaporated with CO background pressure, where the emission from the clean oxide has been subtracted for exposures up to 2 Å. The overall shape of the spectrum seems to be constant, with peaks appearing at binding energies of about 12, 9 and 2-5 eV, respectively, but the valence levels shift towards lower binding energies as the Fig. 5. UP spectra for increasing amounts of $Pd_x(CO)_y$. Features related to the substrate have been subtracted for exposures up to 2 Å Pd.

exposure increases. As previously pointed out, the intensity close to the Fermi level is negligible even after deposition of large amounts of Pd, which excludes successive formation of large metallic particles and instead indicates that a carbonyl-like species is formed [38]. The peaks at 12 and 9 eV, i.e. 4σ and $5\sigma/1\pi$, respectively, are found at slightly higher binding energies than in the case of CO/20 Å Pd.

The corresponding Pd 3d XP spectra are presented in Fig. 6. It is found that also the Pd core levels exhibit a shift towards lower binding energies as the deposited amount of $Pd_x(CO)_v$ increases. In Fig. 7, the C1s spectra for Pd exposures 2 and 20 Å are compared. The C 1s binding energy for the 20 Å situation is lower, which is consistent with the previous observations, and the peak is in both cases found to be asymmetric towards the high binding energy side. However, the most notable feature in these spectra is the presence of a strong satellite. The satellite, which is especially apparent



Pd,(CO),/AI,O3/NiAI(110)

PES

hv = 42 eV

Difference

spectra



Fig. 6. Pd 3d XP spectra for increasing amounts of $Pd_x(CO)_{\nu}$.



Fig. 7. C 1s XP spectra for 2 and 20 Å $Pd_x(CO)_y$.

in the 20 Å spectrum, is situated at a binding energy 5.8 eV above the main peak.

The intensity of this feature relative to the main peak is much larger than for CO adsorbed on metallic Pd [64], it is more comparable to what has been observed for carbonyls [65]. The satellite for the compound appears to be somewhat broader than in the carbonyl spectra, which can be due to several reasons; the spectrum might consist of several components since we observe a coverage dependent BE shift, and a broadening may also occur if the number of metal-metal bondings increases.

The spectral features appearing in the core and valence regions for different carbonyls are difficult to interprete in terms of a specific geometrical structure [65]. Effects due to different CO bonding coordinations have been observed to induce shifts of the order of 1 eV in the O 1s spectra, whereas the other levels were largely unaffected. Unfortunately, in the case of the $Pd_{r}(CO)_{v}$ species, the overlap with the Pd $3p_{3/2}$ level makes shifts in the O Is level very difficult to observe, and the O is line from the oxide film will of course also contribute to the spectrum. Furthermore, a splitting of the metal d-states into two peaks separated by approximately 1 eV (see Fig. 5) has previously been observed for some carbonyls [65]. This effect is due to the crystal field splitting upon formation of the Me d-CO $2\pi^*$ bonds and thus related to the structure of the compound, but it does not give any conclusive evidence, since, at the present resolution, different geometrical structures may lead to similar peaks in the valence photoemission spectrum.

However, in spite of the above-mentioned complications, we will try to draw some conclusions regarding the properties of the $Pd_x(CO)_y$ compound based on the observed BE shifts appearing for increasing amounts, which have been summarized in Fig. 8. The aim is to conclude whether the overlayers consist of separate, small carbonyl molecules or if chemical bonds are formed upon adsorption.

In the case of separate carbonyl molecules condensing on a surface, results on $Cr(CO)_6$ show that the binding energy decreases 0.6 eV when a gas phase molecule is condensed in a thick film [65].



Fig. 8. Plots of the binding energies for the $Pd_x(CO)_y$ related peaks as a function of Pd exposure.

This lowering is caused by the image potential screening upon ionization and the shift is found to be the same for all the electronic levels. This behaviour is not comparable to the present case, since the decrease is found to be as much as 0.9-1.5 eV when increasing the exposure from 0.2 to 20 Å. Another discrepancy is that the core levels shift slightly more than the valence levels. Moreover, the 0.2 Å situation is not comparable to gas phase since the substrate provides image screening. Hence the lowering of the BE when comparing small amounts of carbonyl molecules on the surface to the thick film is expected to be even smaller than 0.6 eV, assuming that the behaviour of $Cr(CO)_6$ is representative. In fact, the normal case for physisorbates is an increase of the BE for increased film thickness [66], which also rules out the possibility for a first layer consisting of separate molecules chemically bonded to the oxide with a second layer that is physisorbed.

Binding energy shifts could also be caused by gradual geometrical changes of the molecules, e.g. in CO-coordination. Due to the complications mentioned above, this is very difficult to tell from the PE spectra. However, the TD spectra indicates no major variations in the structure since the same sharp decomposition peak is observed for all coverages. Successive shifts towards lower binding energies for increasing coverages is typical for supported metal clusters on inert substrates. The binding energies decrease rapidly at very low coverages and thereafter level out, reaching the value of the bulk metal [67]. This can be attributed to changes in both the initial and the ionized final state. The initial state effects can be caused both by charge redistributions due to interactions between the atoms within the cluster and by interactions between the cluster and the substrate. The final state effects are the possibility for a positive charge left on the cluster due to inefficient charge transfer from the substrate and changes in the ability for the cluster to provide local screening.

This type of BE decrease for increasing cluster size has specifically been observed for Pd on an Al₂O₃ single crystal [68] and on a thin aluminium oxide film formed on polycrystalline Al [69]. The coverage dependent BE shifts for the $Pd_x(CO)_y$ species observed in Fig. 8 show a striking similarity to the previous results for Pd/Al_2O_3 [68,69]. This indicates that there is some kind of interaction between the $Pd_x(CO)_y$ units adsorbing on the surface, i.e. chemical bonds between the metal atoms are formed during the growth. Since the Pd-levels for the compound shift in a manner similar to the growth of Pd-clusters, the most tentative explanation would be that $Pd_x(CO)_{v}$ structures of increasing size are formed, which maintain non-metallic properties as well as a welldefined stoichiometry and local structure even at the highest exposures of Pd.

3.2. Decomposition of the $Pd_x(CO)_y$ species

3.2.1. TDS

In Fig. 9, it is shown how the TD spectra of the compound change upon successive heating. The spectra were obtained as follows: The carbonyl was prepared as usual by metal deposition (2 Å Pd) in CO atmosphere at 90 K. Then a TD spectrum was recorded, but interrupted at certain temperatures ranging from 220 to 820 K (marked a-g in Fig. 9). The sample was cooled to 90 K and exposed to 20 L CO. Afterwards, a TD spectrum covering the whole range of desorption temperatures was recorded.



Fig. 9. TD spectra for successive heating of $2 \text{ Å } Pd_x(CO)_y$ (see text).

The most striking observation is that the sharp desorption feature at 190 K irreversibly disappears upon heating to 220 K (Fig. 9a). Likewise, the peaks at 280 and 360 K vanish upon annealing to 320 and 400 K (Figs. 9b and c). The only feature left is a peak at 450 K with a broad low temperature shoulder (Fig. 9c). Heating to even higher temperatures results in a disappearance of this peak, too. The remaining, weak features shift with increasing annealing temperature towards lower desorption temperatures (Figs. 9d–9f). The total amount of CO drastically decreases with increasing temperature, and after heating to 820 K a complete loss of CO adsorption capability is observed (Fig. 9g).

The irreversible disappearance of the several low temperature desorption features indicates that these should be interpreted in terms of a step-wise decomposition of the carbonyl compound. After annealing to about 400 K a desorption spectrum is obtained, which is rather similar to CO desorption from metallic Pd islands prepared by deposition of 2 Å of Pd at a substrate temperature of 300 K [54]. This suggests that during the heating process the desorption of CO allows the Pd to coalesce into compact aggregates with properties approaching those of metallic Pd.

It remains the question how the various features observed can be assigned to certain structural transformations. The narrow desorption feature at 190 K represents the primary decomposition of the initially rather well-defined structure, whereas the widths of the remaining features are comparable to the desorption peaks characteristic for metallic Pd aggregates. However, as the experimental methods applied so far do not provide information on the local geometry, a further discussion clearly requires supplementary experimental data.

In the temperature region between 400 and 800 K the disappearance of the desorption features of metallic Pd at 450 K can be interpreted in terms of diffusion through the oxide film into the NiAl substrate. CO desorption features between 100 and 200 K have been observed for transition metal oxides and small Pt aggregates on $Al_2O_3/NiAl$ and therefore might be an indication for small Pd aggregates in close contact with the oxide [25].

3.2.2. PES

Figs. 10a and 10b show the UP spectra for a temperature series before and after subsequent exposure of additional CO, respectively. Since the TD spectra show a CO desorption peak at 190 K. but with small amounts of CO left up to temperatures of about 450 K, two measurements were made for the temperatures 340-800 K; one immediately after heating and one where the heated surface was dosed with 20 L CO at 90 K. The first observation is that the relative intensities of the CO-related peaks 4σ and $5\sigma/1\pi$ decrease rapidly and a clear shift towards lower binding energies occurs when the temperature is increased from 90 to 340 K. At higher temperatures, these features appear to shift back towards higher binding energies (this is best seen for 4σ , see Fig. 10b), but the positions are difficult to determine at temperatures above 600 K. Changes appear also in the binding energy region 0-5 eV. In the temperature region 230–500 K, the intensity close to the Fermi level increases, but vanishes again at higher temperatures, where instead the Pd 4d states seem to shift towards



Fig. 10. (a) UP spectra for successive heating of 2 Å $Pd_x(CO)_y$. The positions of the Pd 4d states are marked with lines. (b) The same situations after an additional dose of 20 L CO at 90 K.

higher binding energies (Fig. 10a). This is accompanied by a steady decrease in the relative intensity of these features.

The corresponding Pd 3d spectra are presented in Fig. 11. Starting with the spectra where the heating was followed by CO adsorption, the binding energies decrease up to 340 K, but increase again for temperatures above 500 K. The spectra with no additional CO show the same general behaviour, but these spectra are found to gradually merge into the others, indicating smaller CO-induced changes for higher temperatures in accordance with the UPS results. It can also be noted that the peaks in the 340 K spectrum, both with and without additional CO, appears to be broader compared to the other spectra.

Starting the discussion with the changes occurring at temperatures up to 500 K, the lowered BEs for both the core and valence levels and the increased intensity close to the Fermi level indicate that compact, metallic Pd clusters are formed, in agreement with the TDS results. This is also consis-



Fig. 11. Pd 3d XP spectra for heating of 2 Å $Pd_x(CO)_y$ with and without additional CO.

tent with the decrease in the amounts of CO adsorbed after heating, since more compact clusters results in a lower CO/Pd-ratio. Furthermore, the binding energies of the 4σ and $5\sigma/1\pi$ peaks in the 340 K spectrum, 11.4 and 8.2 eV, respectively, are close to the values of about 11 and 8 eV observed for single crystal surfaces [62,63]. That the Pd 3d spectra recorded after heating to 340 and 500 K both show clear effects upon adsorption of additional CO is not surprising, since it has been shown that the surface components of the substrate core levels may display significant shifts upon CO adsorption [70,71].

Additional support for the Pd agglomeration process can be found in Fig. 12. Here, the UP spectrum for heating 2 Å $Pd_x(CO)_y$ to 340 K is compared to the situation where first 2 Å Pd is deposited at 300 K and thereafter dosed with 20 L of CO. As previously mentioned, the Pd growth at 300 K is characterized by the formation of 3D clusters which are larger than those formed at 90 K. It can be seen in Fig. 12 that the spectrum for the heated $Pd_x(CO)_y$ compound is nearly identical to the CO/2 Å Pd (300 K) situation, and, by



Fig. 12. A comparison between the UP spectra for CO/2 Å Pd deposited at 300 K (top) and 2 Å $Pd_x(CO)_y$ heated to 340 K and thereafter dosed with 20 L CO (bottom).

comparing with Fig. 4, is quite different from the CO/2 Å Pd (90 K) spectrum. Thus, the clusters formed after heating the compound to 340 K seem to have an average size comparable to the islands formed when Pd is deposited at 300 K.

It was also observed that the Pd 3d peaks in the 340 K spectrum "without CO" were broader than in the other cases. At this temperature, there is still some CO left on the surface and the formation of compact clusters might also lead to the presence of bulk atoms. Both these effects lead to increased intensity on the high BE side [71]. The broadening of the peak can thus be explained by the presence of different Pd atoms.

The observations in the temperature region 500-800 K indicate that a new process takes place. The dramatic decrease of the intensity close to the Fermi level in combination with higher Pd 3d and Pd 4d binding energies demonstrate that the Pd clusters lose their metallic character. The Pd 3d_{5/2} binding energy measured after heating to 800 K is found to be 337.0 eV, which is comparable to what we obtain for a very low coverage (0.2 Å) of Pd on the oxide [72]. That is, the binding energy agrees with a situation with relatively disperse Pd-atoms in contact with the oxide. The spectra furthermore exhibit a vanishing tendency for CO adsorption and a decreased Pd 4d intensity relative to the oxide features. A comparison of UP spectra recorded at normal versus grazing emission and at different photon energies indicate that the Pd 4d intensity after heating to 800 K more follows the intensity of the NiAl(110) features than those of the oxide surface.

All these observations are consistent with the occurrence of diffusion of the metal atoms into the oxide film, as suggested in the TDS discussion. Diffusion of Pd-atoms has also been observed when deposited on Al_2O_3 films formed on polycrystalline Al provided that the film is thin enough [69]. What is not clear in the present case is whether the Pd atoms dissolve into the NiAl substrate, oxidize or form an interface layer underneath the oxide. Previous data show that the BE for Pd atoms in contact with metallic Al are higher than for Pd metal [73]. Moreover, based on the BE of the Pd 3d peaks in the 800 K spectrum the possibility for PdO formation cannot be

excluded either [74]. It is therefore not possible to unambigously determine the nature of the Pd atoms only from the BE shifts.

3.2.3. LEED

The influence of the annealing process on the LEED spot-profiles is shown in Fig. 13. The profiles of the (00)-reflex were obtained in a procedure similar to the one for the TD and PE spectra: 2 Å of Pd were deposited at CO background pressure at 90 K and afterwards heated to the respective temperatures. The LEED profiles (along the [001] direction of the NiAl(110) substrate) were then recorded at 90 K after dosing with 20 L CO. The diffuse profiles do not significantly change upon annealing up to about 340 K. Clear changes are only observed after heating to 500 K or higher, where the diffuse shoulder becomes more narrow.



Fig. 13. LEED spot-profiles of the (00)-reflex along the [001] direction of the NiAl substrate after successive heating of 2 Å $Pd_x(CO)_y$. The inset shows a plot of the corresponding estimated average island sizes, calculated on the basis of the LEED profiles and the relative intensity of the oxide LEED pattern (see Fig. 14).

A more pronounced temperature dependence is found, if instead of the LEED profiles the intensity of the oxide LEED pattern is recorded during the heating process. Experimentally, this was realized as follows. After preparation of the carbonyl (2 Å Pd deposited in CO atmosphere) at 90 K, the sample was heated to 800 K using the same heating rate as in the TD experiments (1.5 K s^{-1}) . The intensity of the oxide LEED pattern as a function of temperature was sampled by measuring the peak intensity of one of the most intense oxide spots, indicated in the schematic LEED pattern in the inset of Fig. 14a. The prominent contribution to the temperature dependence of the intensity is the exponential decay due to the Debye-Waller factor [75]. This effect was removed by dividing by the intensity spectrum of the clean oxide film (after background subtraction). Within the kinematic approximation, the square root of the central spike intensity of the oxide spots should be proportional to the oxide coverage [49]. Following the LEED intensities, all processes occuring upon thermal



Fig. 14. (a) Relative intensity of the oxide LEED spot, indicated in the schematical LEED pattern in the inset, for thermal decomposition of $2 \text{ Å } Pd_x(CO)_y$ (see text). (b) Schematical representation of the processes taking place in the temperature regions given in (a).

treatment can be directly monitored as a function of temperature, thus providing information complementary to the TD spectra. The spectra are plotted in Fig. 14a, and four different regimes can clearly be distinguished: Up to approximately 170 K, the intensity of the oxide spots do not change (with respect to the clean oxide, Fig. 14a, regime I). Between 170 and approximately 400 K a pronounced increase is observed (regime II), followed by a temperature region, where the relative intensity decreases again (regime III). Finally, at temperatures higher than 700 K the oxide LEED pattern recovers partially (regime IV).

The four regimes observed in Fig. 14a can be interpreted in terms of the different processes discussed before in connection with the TD and PE spectra. They are schematically illustrated in Fig. 14b. Up to approximately 170 K (regime I), the carbonyl species is stable and efficiently covers the oxide film. In regime II decomposition of the carbonyl is accompanied by CO desorption and step-wise transformation into compact, three dimensional islands. These metallic aggregates cover a much smaller fraction of the surface, a process which leads to a pronounced increase of the oxide LEED intensity. Additionally, the relative intensity might increase due to desorption of CO itself, which in the case of small clusters also contributes to the attenuation of the oxide LEED spots. Within temperature regime III (400-700 K), diffusion into the oxide is the predominating process. This is accompanied by a destruction of the long-range order of the oxide film, which is reflected in the LEED pattern by a clear drop in the relative intensity of the oxide spots. As soon as the metal has vanished from the surface, the oxide film recovers upon further annealing (regime IV). Recently, a behaviour comparable to regimes III and IV has been observed for Pt/Al₂O₃/NiAl(110) [26].

In order to obtain additional evidence for the interpretation given so far, we have repeated the LEED intensity experiment with 2 Å Pd deposited at 90 K in UHV. For the small 3D islands formed under these conditions, no major changes and, consequently, no increase in the relative oxide intensity are expected in the low temperature region. Indeed, the experiment only shows three

regimes (see Fig. 15a): constant relative intensity, i.e. a constant fraction of covered oxide, up to about 400 K, a pronounced intensity decrease up to 700 K due to diffusion through the oxide, and finally, above 700 K a slight recovering of the oxide superstructure.

Further analysis of the LEED profiles reveals some additional information concerning the process of thermal treatment. Island sizes have been estimated applying the same evaluation procedure as for deposition at 90 K without CO atmosphere [54]. The results are shown in the inset of Fig. 13. The overall behaviour of the calculated island sizes follows the oxide intensity curve shown in Fig. 14a. Starting from rather large islands of the carbonyl species (diameter ~ 90 Å), they transform into much smaller aggregates of compact shape upon decomposition in the temperature region between 170 and 400 K. After heating to 340 K an average island size of 30 Å is found, a value which is close to the island size found for 2 Å Pd deposited at 300 K under UHV conditions [54]. As mentioned before, the shape of the diffuse shoulder does not change up to 340 K. Since the shape of the diffuse part of the LEED spot directly reflects the spatial



Fig. 15. (a) Relative intensity of the oxide LEED spot, indicated in the inset of Fig. 14a, for the thermal treatment of 2 Å Pd deposited at 90 K under UHV conditions. (b) Schematical representation of the processes taking place in the temperature regimes given in (a).

distribution of the islands, we can furthermore conclude that, upon decomposition, the carbonyl islands do not coalesce but each carbonyl aggregate transforms into one compact metallic island.

Substantial changes in the diffuse profiles are observed in the temperature region between 500 and 800 K, where diffusion into the oxide is the dominating process. Up to 700 K, the island size increases to approximately 60 Å. Within this temperature regime the expression "island", however, should be interpreted in terms of disordered aluminium oxide patches with some Pd left on the surface rather than pure Pd aggregates. These oxide patches, which have lost their long-range order, may coalesce, resulting in an increase of their average distance and finally shrink and vanish upon annealing to temperatures higher than 700 K (Fig. 13). Defects such as steps or domain boundaries might be of fundamental importance for the process of diffusion into the oxide film: for Pd deposition under UHV conditions resulting in the formation of metal islands which are preferentially located at defect sites [54,55], inward diffusion is found in the same temperature region (Fig. 15a) as for the carbonyl species. More detailed information on these processes might be obtained by future microscopic measurements.

3.3. Growth and structure of the $Pd_x(CO)_y$ species

We have shown that a Pd species with rather unusual carbonyl-like properties can be grown under certain conditions on an alumina substrate. The question remains what the structure of this species could be, and why it is formed under these particular conditions. Obviously, the experimental data do not allow a straightforward structure determination. However, there are several requirements that a possible structure and growth model has to satisfy. (1) The compound has a homogenous composition (the CO/Pd ratio has been estimated to be about 1.7 ± 0.6 , [38]) and a thermal stability independent of coverage, which points to a homogenous local structure (TDS). This is also indicated by the coverage independent shape of the Pd 4d induced doublet in the valence PE spectra. (2) The species shows no indication of long-range order (LEED). (3) It grows in form of islands, which cover the oxide substrate very efficiently (LEED). (4) With increasing coverage, Pd cores of increasing size are formed, containing an increasing number of metal-metal bonds. Nevertheless, in the high coverage limit it does not approach the situation of CO covered metallic Pd islands (XPS, UPS). (5) The species is formed at sufficiently low temperature and irreversibly decomposes into metallic Pd islands at higher temperature. Under such conditions, it is not unlikely that the kinetics of certain elementary steps control the growth process.

In a previous letter, we have given a brief discussion of possible structures [38]. If a species consisting of separate molecules is taken into account, the instability of Pd(CO)₄ and stoichiometry estimation from XPS requires metal cores consisting of several Pd atoms. However, the PES results favour a situation, where aggregates of increasing size are formed rather than small separate carbonyl molecules. Therefore, we have proposed the formation of a purely one-dimensional or branched cable-like structure, which might be anchored on the oxide surface. Such pseudo onedimensional growth paths have been reported for other carbonyl species [76]. In particular, it has to be pointed out that such a structure would be compatible with all experimental data, as an increasing number of metal bonds can be formed, while a well-defined local structure and stoichiometry is preserved.

What kind of growth process might lead to such non-compact, ramified or low-dimensional islands? At sufficiently low temperature, some of the elementary processes necessary for the formation of compact islands may be kinetically inhibited. For example, further diffusion processes might be inhibited as soon as an atom, after a random walk on the substrate surface, is attached to an existing island. This results in the so-called diffusion limited aggregation (DLA) process, which leads to the formation of islands of low, fractal dimension [77,78]. However, for metal vapour deposition, a "random rain"-model, where the trajectories of atoms impinging from the gas phase, are straight lines rather than Brownian paths has been put forth, and it has been shown that such a model also leads to highly ramified clusters [79].

Let us apply these ideas to our system (a schematical representation of the growth processes is given in Fig. 16). Considering an isolated atom, it may be attached to an existing island either by direct adsorption from the gas phase or by adsorption on the oxide and diffusion. If kinetically possible the atom might diffuse on the island until it reaches the energetically most favourible adsorption site, which is the one that maximizes its coordination (step and kink sites). Thus, compact islands of regular shape are formed.

Provided that on the CO saturated islands grown in adsorbate atmosphere, the Pd may be attached to an existing island, but diffusion along the island surface is kinetically inhibited, the atom is unable to maximize its coordination number. This assumption is not unlikely, since, in contrast to the adsorbate-free island, such diffusion processes would involve breaking or at least weakening of metal-CO bonds. Thus, further deposition of Pd might result in the formation of a noncompact, highly ramified island, as illustrated in Fig. 16. At sufficiently high temperatures, the diffusion barrier can be overcome. The Pd atoms move to sites which offer a higher Pd coordination



Fig. 16. A schematic representation of a possible growth mechanism for the $Pd_x(CO)_y$ species (see text).

leading to desorption of CO: the species decomposes into CO and metallic Pd islands.

Finally, we would like to stress that this scenario is consistent with all experimental data available sofar. However, a conclusive proof of this model clearly requires a more detailed understanding of the molecular structure and morphology of the system. Such additional information, which would allow a further verification, might possibly be obtained by future EXAFS and STM studies.

4. Conclusions

Evaporation of Pd onto an alumina film kept at 90 K and with a background pressure of CO results in the formation of a carbonyl-like compound. As shown by SPA-LEED, the carbonyl grows in islands which rapidly cover the oxide substrate. The average island sizes are significantly larger than upon deposition under UHV conditions at the same temperature. In contrast to CO desorption from Pd deposits grown without adsorbate background pressure, the carbonyl species exhibits a sharp and dominant decomposition feature at 190 K in the thermal desorption spectrum of CO. This feature is observed for coverages ranging from fractions of a monolayer to multilayers. The photoemission spectra of this species exhibit characteristic peaks in the valence region which do not change in shape with increasing coverages. The PES results furthermore show that the $Pd_r(CO)_v$ -related peaks shift towards lower binding energies for increasing amounts in a manner indicating that, although the local structure and stoichiometry is preserved, large complexes with increasing number of metal-metal bonds are formed.

The thermal decomposition of the carbonyl species occurs via several steps in the temperature range from 170 to approximately 350 K. During this decomposition process, carbonyl islands transform into compact, metallic Pd particles. Upon further heating, metal diffuses through the oxide film into the NiAl substrate. This process eventually leads to a complete loss of CO adsorption capability. We have furthermore demonstrated how the processes occuring upon thermal treatment can be directly monitored by recording the intensity of

the oxide LEED pattern as a function of temperature.

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