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# Evidence for $Pd_x(CO)_y$ compound formation on an alumina substrate

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## Abstract

Although stable binary Pd carbonyls are unknown in the gas phase, we found strong evidence for a stable carbonyl-like Pd compound on an oxide surface: by in situ vapour deposition of Pd at a rate of $2 \times 10^{13}$ atoms $s^{-1}$ $cm^{-2}$ onto an alumina substrate (90 K) at a pressure of $2 \times 10^{-6}$ mbar CO, a binary compound of Pd and CO is formed which is stable up to 190 K. As substrate serves a well-ordered aluminium oxide film grown on a NiAl(110) single crystal surface. The system was characterized under UHV (ultrahigh vacuum) conditions by means of TDS, LEED, UPS and XPS in a coverage range between $1.4 \times 10^{14}$ Pd atoms $cm^{-2}$ and $1.4 \times 10^{16}$ Pd atoms $cm^{-2}$. The decomposition at 190 K results in the formation of metallic Pd particles and is accompanied by a sharp and dominant feature in the thermal desorption spectra.

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## 1. Introduction

When exploring the diffusion and nucleation processes that govern the growth of metal clusters on surfaces, the conditions most commonly varied are the deposition temperature and the deposition rate [1]. However, it is obvious that the presence of a strongly interacting adsorbate might dramatically change the energetics of any elementary step involved in the growth process, e.g. as illustrated by the role of so-called surfactants, which, preadsorbed on the substrate, alter the growth modes of various epitaxial systems, see e.g. Refs. [2,3].

In the case of metals grown on oxide substrates, adsorbates often weakly interact with the oxide but strongly chemisorb on the metal itself. Thus, although not adsorbing on the pure substrate, their presence in the gas phase during the growth can be expected to have a strong influence on all clustering processes carried out under non-UHV (ultrahigh vacuum) conditions. Therefore, growth processes modified by an ambient pressure of an adsorbate may provide cluster–adsorbate structures which are otherwise not accessible.

In this Letter we present the result of the growth of palladium on a well-ordered and atomically flat aluminia film grown on NiAl(110) [4] in a CO atmosphere. We observed that under suitable conditions this results in the formation of a palladium carbonyl compound stable up to approximately 190 K.

The thermal stability of the compound is rather extraordinary: binary Pd carbonyls prepared by matrix isolation show a decomposition temperature of 80 K [5,6]. In the gas phase, stable binary Pd carbonyls have never been observed. Merely in zeolites, where the cage and channel structures prevent them from further coalescence, Pd carbonyls of different

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size have been observed at room temperature, e.g. $Pd_6(CO)_x$ and $Pd_{13}(CO)_x$ [7–9].

## 2. Experimental

The TD (thermal desorption) spectra were recorded in an UHV system which is additionally equipped with a SPA-LEED (spot-profile analysis LEED) system (Leybold). This instrument allows quantitative measurements of reflex intensities and profiles.

Photoemission experiments were carried out in two different UHV systems equipped with hemispherical electron energy analysers, one rotatable in two orthogonal planes for angular resolved UPS (UV photoelectron spectroscopy), one fixed for XPS (X-ray photoelectron spectroscopy). The valence photoemission spectra were recorded at BESSY Synchrotron Radiation Center (Berlin) at the TGM3 beamline. The total resolution was 0.3 eV.

The NiAl(110) single crystals could be cooled to approximately 90 K with liquid nitrogen and heated by radiation from a filament or by electron bombardment. The clean NiAl(110) surface and the ordered $Al_2O_3$ film were prepared as previously described in the literature [4].

The Pd metal (Heraeus, > 99.95% Pd) was deposited using two different types of evaporators, a home built Knudsen cell and one based on electron bombardment (Omicron). Both were calibrated by a quartz microbalance. Deposition rates between 1.4 and $2.8 \times 10^{13}$ atoms $cm^{-2}$ $s^{-1}$ (1.2 to 2.4 Å $min^{-1}$) were employed (1 Å Pd corresponds to $6.8 \times 10^{14}$ atoms $cm^{-2}$).

## 3. Results and discussion

The well-ordered and atomically flat alumina film used as the substrate in this study has been subject to detailed investigations exploring its geometric and electronic structure as well as its adsorption properties [4,10–14]. Concerning the latter, it should be emphasized that no CO adsorbs on the clean oxide film at 90 K, i.e. the deposition temperature used in this study.

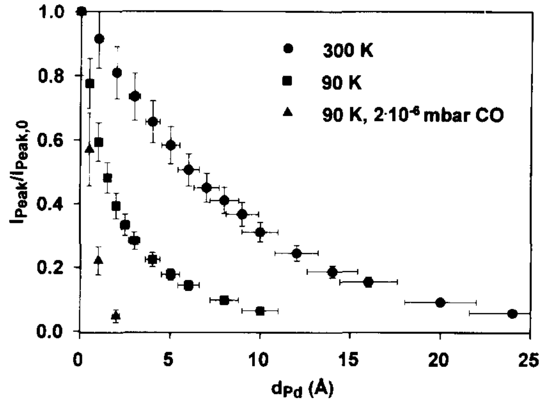

Fig. 1. Relative intensity of the most intense LEED reflexes of the $Al_2O_3$/NiAl(110) substrate as a function of the Pd exposure for three different deposition conditions: deposition at 300 K, deposition at 90 K and deposition at 90 K at a CO background pressure of $2 \times 10^{-6}$ mbar CO.

The oxide forms a characteristic superstructure giving rise to a complex LEED pattern, which gradually vanishes upon deposition of metal. Fig. 1 shows a plot of the relative intensity of the most intense oxide spots with respect to the clean oxide as a function of metal coverage. The slow decay for deposition at 300 K indicates a Vollmer–Weber (3D) growth mode leaving a significant amount of the substrate uncovered even at high metal coverages. For deposition at 90 K the decay is more rapid due to a higher nucleation density leading to the formation of smaller clusters. The Pd growth under various conditions will be dealt with in more detail elsewhere [15]. Here, we concentrate on the deposition at CO background pressure ($p_{CO} = 2 \times 10^{-6}$ mbar). The corresponding plot shows that in this case the LEED pattern completely vanishes for deposition of more than 2 Å Pd, corresponding to roughly one monolayer of metallic palladium. This indicates that the growth changes to a more two-dimensional mode.

In Fig. 2 CO thermal desorption spectra (heating rate 1.5 K $s^{-1}$) for increasing amounts of Pd deposited at CO background pressure are shown. For comparison, the TD spectrum of 20 Å Pd deposited at 300 K (adsorption temperature 90 K, CO exposure 20 L, 1 L = $10^{-6}$ Torr s) is also displayed. The broad desorption feature between 400 and 500 K and the low temperature shoulder are comparable to desorption spectra from Pd(111) single crystal surfaces

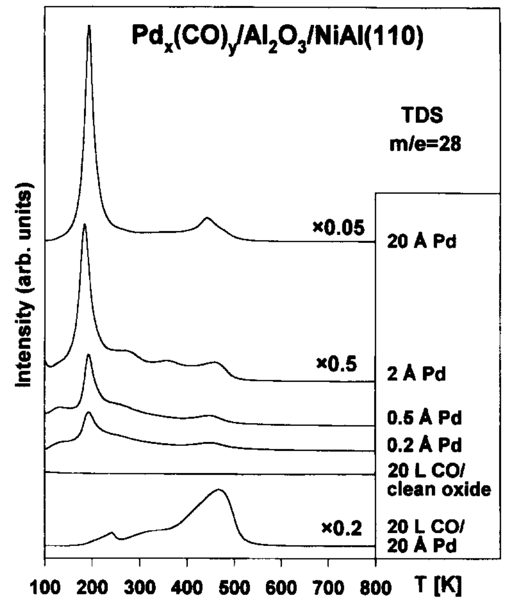

Fig. 2. Thermal desorption spectra for different coverages of Pd deposited on $Al_2O_3$/NiAl(110) at CO background pressure in comparison to the TD spectrum of 20 Å Pd saturated with CO after deposition at 300 K (heating rate: 1.5 K $s^{-1}$).

[16]. Similar features are found, if the metal is deposited at a substrate temperature of 90 K [15]. The additional peak at 240 K is due to a small amount of coadsorbed hydrogen. Comparable coadsorption peaks have been reported for CO, $H_2$/Ni(100) [17].

The desorption spectrum changes dramatically if the metal is deposited at CO background pressure (substrate temperature 90 K): The desorption spectra are now dominated by a sharp feature between 180 and 200 K, which is followed by various broader features appearing at temperatures up to 450 K. Compared to the deposition at 300 K (resulting in the formation of 3D islands), the total amount of adsorbed CO drastically increases. Furthermore, the total amount of desorbing CO is roughly proportional to the amount of metal deposited. As this is valid for the whole coverage range from 0.2 to 20 Å, this observation cannot be interpreted in terms of metal island growth, but rather in terms of the formation of a compound with a fairly well defined stoichiometry. This interpretation is supported by the fact that the total amount of desorbing CO for the 20 Å situation by far exceeds the amount of CO that could be adsorbed on metallic islands, even at highest Pd coverages.

Comparable desorption spectra have been observed for transition metal carbonyls deposited on various substrates, see e.g. Ref. [18] and references therein. In case of these relatively stable carbonyls, molecular desorption can be identified by detecting the $Me^+$ signal. However, no $Pd^+$ peak could be found during the desorption process, even at highest metal coverages. Consequently, we assign the dominant peak in the CO desorption spectra to the decomposition of the compound, resulting in the evolution of CO and formation of metallic Pd particles. The narrow width and constant temperature of the decomposition peak points to a well-defined and coverage-independent thermal stability of the carbonyl species.

The following broader desorption features can be attributed to stepwise structural rearrangements during the heating process involving the formation of bigger Pd islands. Finally, CO desorption from these metallic Pd islands gives rise to the last desorption feature at 450 K [15].

In order to obtain a first clue to what the stoichiometry of the system might be, we have recorded XP spectra of the Pd 3d and C 1s regions for an exposure of 20 Å Pd. By comparing the peak areas (using empirically derived sensitivity factors taken from Ref. [19]), a relation of 1.7 ± 0.6 CO molecules per Pd atom was obtained. However, this number has to be considered as an rather crude estimation since possible variations in the shake-up intensities are disregarded.

We now proceed by discussing the electronic structure of the compound. Fig. 3 shows valence photoemission spectra for increasing amounts of Pd deposited at $p_{CO} = 2 \times 10^{-6}$ mbar. All binding energies are relative to the Fermi level of the NiAl(110) substrate. For comparison, the situation where first 20 Å Pd are deposited at 300 K and thereafter dosed with CO (20 L) is shown at the top of the figure, the spectrum of the clean oxide substrate is shown at the bottom.

With increasing exposure, new features appear that become totally dominating for deposits exceeding 2 Å Pd: two peaks at binding energies of about 12 and 9 eV, respectively, and a doublet feature at

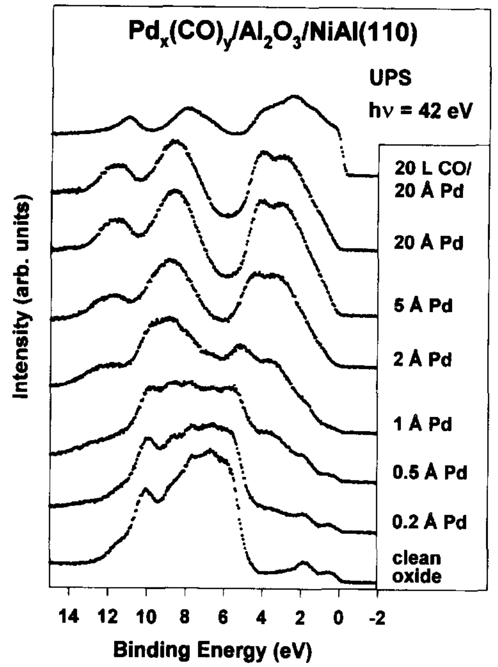

Fig. 3. Valence photoemission spectra for different amounts of Pd deposited at CO background pressure. The spectra were recorded at grazing electron emission (70°C off normal) and normal incidence. For comparison the PE spectrum for 20 Å Pd deposited at 300 K and afterwards saturated with CO is shown at the top of the figure.

2–5 eV. In order to further establish the positions of the Pd$_x$(CO)$_y$-induced features at coverages below 5 Å, difference spectra were obtained by subtraction of the clean oxide spectrum. The result is shown in Fig. 4. The overall shape of the spectrum appears to be the same for increasing amounts, but the binding energies of the peaks gradually decrease; from initial values of 13.1, 9.8, 4.9 and 4.0 eV at 0.2 Å Pd, they reach values of 11.9, 8.8, 4.1 and 3.1 eV for exposures above 5.0 Å.

A doublet feature in the region 2–5 eV has been observed in some cases of Pd deposition, e.g. for Pd on Nb(110) and Cu(111) [20,21], but in these cases the doublet gradually merges into a broad band with a considerable intensity close to $E_F$, which is characteristic for metallic Pd. Moreover, deposition of increasing amounts of Pd on Al$_2$O$_3$/NiAl(110) at 90 K without CO background pressure shows a behaviour similar to what has previously been observed for Pd/graphite, i.e. no pronounced doublet structure, but a broad feature that develops into the typical bandstructure for Pd metal [15,22]. However, it is readily observed in Figs. 3 and 4 that this is not the present case; the shape of the doublet is independent of the coverage, and even more prominent is that no Fermi level is developed even for very large amounts of Pd. The spectra clearly differ from the CO/20 Å Pd situation shown at the top of Fig. 3, where the Fermi level may be clearly located. Thus, we can safely exclude successive formation of large metallic particles.

The peaks observed in the photoemission spectra can be identified by comparison with previous results for CO on Pd single crystals and different transition metal carbonyls. In the PE spectra for CO on Pd(111) and (100) surfaces, CO-induced states have been observed at binding energies of about 11 and 8 eV, which have been assigned to the 4$\sigma$ and the almost degenerate 5$\sigma$/1$\pi$ levels, respectively, e.g. Refs. [23,24]. Almost identical features have been observed for several carbonyls in the same

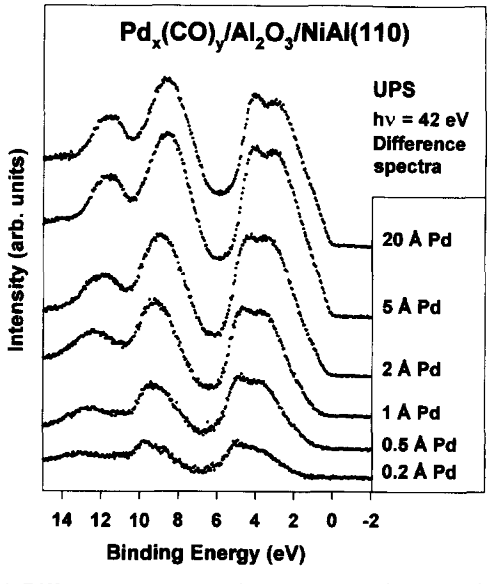

Fig. 4. Difference spectra at various coverages of Pd deposited at CO background pressure corresponding to the PE spectra shown in Fig. 3. The emission from the oxide substrate has been subtracted.

binding energy region, both in condensed films and in gas phase, when adjusting for the substrate work function [25]. We therefore find it most reasonable to assign the two peaks appearing at binding energies of 11.9 and 8.8 eV (at an exposure of 20 Å) as due to the $4\sigma$ and $5\sigma/1\pi$ levels, respectively.

In this context, it is well known that by monitoring the relative intensities of these two peaks in angular resolved measurements, the orientation of adsorbed CO molecules can be determined [26,27]. We therefore performed angular resolved measurements for the $Pd_x(CO)_y$ compound, but no preferential CO orientation could be observed.

Another feature in the PE spectra to be discussed, is the doublet which in the 20 Å situation exhibits features at 4.1 and 3.1 eV. It is quite obvious that these are Pd 4d-derived states, but the point in question is the nature of the splitting. There are basically two effects which might contribute to this effect, namely the spin–orbit interaction and crystal field effects. However, the spin–orbit splitting plays certainly a minor role: for small Pd clusters deposited on Ag ($Pd_1$, $Pd_2$, $Pd_3$) a value of about 0.35 eV was found [28], which is in excellent agreement with the gas phase value [29]. Therefore, a splitting due to interaction with the CO levels and, depending on the structure of the compound, metal–metal interactions as well seems to be more reasonable. In the case of carbonyls, crystal field splitting of the metal d states into two peaks separated by about 1 eV has for example been observed in the photoemission spectra of $Ni(CO)_4$ and $Ru_3(CO)_{12}$ [25,30] ($Pd(CO)_4$ is not stable!). For $Pd(PF_3)_4$ a splitting of 2.3 eV has been found [31], which, however, should be larger than for a carbonyl complex since $PF_3$ exerts a stronger ligand field than CO. The values show that the doublet feature observed for the $Pd_x(CO)_y$ compound is most probably dominated by crystal field splitting.

Although the present data are not sufficient for a definite structure determination, we would nevertheless like to discuss some possible structures. The high and, as concluded from the TD spectra, rather constant CO/Pd ratio up to several monolayers of Pd in combination with the absence of a Fermi level indicates a compound formation over a wide coverage range. Furthermore, the sharp TD features could be interpreted in terms of a rather well-defined structure. However, all binary Pd carbonyls reported in the literature so far are rather unstable, e.g. $Pd(CO)_4$ has been observed after matrix isolation, but decomposes already at 80 K [5,6]. Nonetheless, it cannot be excluded that higher nuclearity carbonyl clusters are stable up to significantly higher temperatures. Moreover, the Pd/CO ratio of about 1.7 points to a metal core consisting of several atoms. Thus one possible model for the species formed under the conditions reported in this paper could be the formation of clusters with one or only few different metal cores consisting of comparable numbers of Pd atoms.

As mentioned in Section 1, stable Pd carbonyls of different size have been observed in zeolites at room temperature [7–9]. It is not unlikely that these systems are stabilized by interaction with the zeolite environment. In addition to that, Pd carbonyl species of high stability are known which are formed by replacing only a few CO molecules by other ligands [32].

Taking this into account, a carbonyl species could be suggested which is stabilized by a chemical interaction with the oxide film. However, it is not clear how such a species, anchored on the substrate, could grow up to the equivalent of several monolayers of Pd. One possible explanation for such a behaviour might be a pseudo one-dimensional growth path, which has been reported in the literature for various transition metal carbonyls, see e.g. Ref. [33]. For example $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ clusters have been structurally characterized [34,35]. It has to be pointed out that there is no principal limit for the growth of such cable-like structures anchored on a surface, either purely one-dimensional or additionally branched. Still, in comparison to the molecular clusters mentioned above the Pd species in this study might be structurally less well defined.

In conclusion, we have shown that by evaporation in a CO atmosphere a new Pd species can be grown on an alumina surface. A carbonyl-like compound with rather well defined stoichiometry (CO/Pd ratio of 1.7 ± 0.6 as estimated from XPS) is formed over a large coverage range. From fractions of a monolayer up to multilayers of Pd valence band photoemission shows the same characteristic features. Even for the highest coverages no metallic Fermi level is observed. As shown by TDS, decomposition of the compound occurs at approximately 190 K.

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