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Metal−Organic Chemical Vapor Deposition of Palladium: Spectroscopic Study of Cyclopentadienyl-allyl-palladium Deposition on a Palladium Substrate

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The deposition and subsequent decomposition of a cyclopentadienyl-allyl-palladium precursor on a Pd(111) single crystal was investigated by a combination of X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Because the precursor decomposes readily on metal surfaces, a deposition system with its inner surfaces completely covered by chemically inert materials such as glass or Teflon was used to keep the precursor molecules intact prior to the deposition process. Upon adsorption on the palladium substrate surface, the precursor molecules are chemically modified even at temperatures as low as 170 K. At higher temperatures, the precursor decomposes, the oxidation state of the palladium changes from +2 to 0, and the ligands remain adsorbed at the palladium surface. Attempts to remove the hydrocarbon ligands by etching with molecular hydrogen were not successful.

Introduction

Metal−organic chemical vapor deposition (MOCVD) of metals on different types of substrates offers a number of potential advantages over physical vapor deposition methods such as metal evaporation or sputtering. Among the advantages of MOCVD are low substrate temperatures during deposition, fast growth rates, the ability to cover complex topologies conformally, and the potential for selective area deposition.[1] Despite the large potential of the method, there is generally very little known about the exact precursor decomposition mechanism involved in the deposition of the metal thin films. The knowledge of such details, however, is a prerequisite to optimize the MOCVD precursors, the decomposition process, and, most importantly, the purity of the metal deposits.

In this work, we focus on the decomposition of cyclopentadienyl-allyl palladium, Pd(η^5-Cp)(η^3-allyl), or short Cp-(allyl)Pd (see Figure 1), on a palladium substrate. Previous work has shown that this palladium complex is a suitable precursor for low-temperature palladium deposition.[2−5] When the deposition is carried out using an inert carrier gas such as He, deposition temperatures as low as 260 °C have been reported. When a small amount of hydrogen, that is, 1 vol %, in the carrier gas, is added to the carrier gas, a significant lowering of the deposition temperatures is observed and the deposition of metallic films at temperatures as low as 30 °C has been reported.[6] Bright metallic palladium films were observed up to deposition temperatures of 60 °C, while above this temperature Pd powder was obtained suggesting that under these conditions decomposition occurred already in the gas phase.[6]

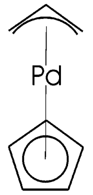

Figure 1. Structure formula of the (Cp)Pd(allyl) precursor.

In a typical MOCVD deposition process, one wants to avoid conditions where the precursor molecules already react in the gas phase. The general goal is that the decomposition reaction takes place at the surface of the substrate, which can be a metal, an oxide, or even an organic surface. In the first stage of the deposition, palladium nuclei will form on these substrate materials. Here, the decomposition of the precursor will depend strongly on the properties of the substrate material as well as on the environmental conditions. After this initial nucleation process, the deposition of the palladium will continue via a growth of the palladium nuclei and then yield small palladium clusters or ultrathin palladium films. At this second stage, decomposition of the precursor on the already existing palladium deposit will become dominant and will subsequently control the growth of the palladium film. This second stage will occur in every MOCVD deposition process. Therefore, this work is first focused on the decomposition of the precursor on a palladium

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substrate. In future studies, we plan to extend our mechanistic studies to the processes occurring on different substrate materials typically used in applications of palladium MOCVD, for example, SiO_2, Al_2O_3, and MgO. We believe that this sequence is useful to separate the contributions specific for each substrate and the contribution from the deposition of the palladium precursor on palladium.

On the basis of their experimental results, Hierso et al. suggested that the decomposition of the palladium precursor in the presence of hydrogen occurs on the palladium surface and involves adsorbed species easily hydrogenated.[4,6] The aim of this work is to investigate the initial steps of the adsorption and decomposition of the Pd precursor on a well-defined Pd(111) single-crystal surface. The decomposition of the precursor is monitored by XPS and NEXAFS spectroscopy.

Experimental Section

All NEXAFS and most of the XPS experiments were carried out in a UHV-system operated at the HESGM beamline of the synchrotron facility BESSY II in Berlin. TDS (thermal desorption spectroscopy) and the remaining XPS experiments were carried out using a separate UHV-system located at the Ruhr-University in Bochum. Both UHV-systems consist of a loadlock, a preparation chamber, and an analysis chamber. The analysis chamber of the UHV-system at BESSY (base pressure better than 1×10^{-10} mbar) was equipped with a LEED-optics (Vacuum Generators), a quadrupole mass spectrometer (Balzer), an ion sputter gun, a Al/Mg twin anode X-ray source (VG), an energy analyzer (Clam2, VG), and a homemade electron detector based on a double channel plate (Galileo). The UHV-system in Bochum is equipped with a XPS-spectrometer consisting of Al/Mg twin anode X-ray source (Leybold), a LH 10 energy analyzer (Leybold), a sputter gun, and a quadrupole mass spectrometer (Balzer). The Pd(111) single crystal was mounted on a transferable sample holder equipped with an electron impact heater and a type K thermocouple. Using liquid nitrogen, the sample could be cooled to temperatures below 160 K.

The Cp(allyl)Pd-precursor, Pd(η^5-Cp)(η^3-allyl), was prepared and cleaned according to the prescription provided in refs 7−9 and subsequently stored in an inert gas at temperatures below −18 °C until it was used for the MOCVD experiments. For the deposition of the palladium precursor, different dosing systems have been used. All dosing systems have in common that between the experiments the precursor was stored in an evacuated and cooled glass-vessel to avoid contamination and decomposition of the precursor prior to the experiments. The system first used for the experiments consisted of a glass vessel connected to the UHV system by stainless steel tubes. Dosing of the precursor was carried out by backfilling the analysis chamber through a leak valve. Using this commonly applied dosing system, the precursor comes into contact with the inner parts of the stainless steal metal tubes of the dosing system leading to a partial decomposition of the precursor at the inner surfaces of the tubes; as a result, ill-defined and nonstoichiometric multilayer films were observed to form on the cooled substrate (see below).

To avoid any contact of the precursor with metallic surfaces prior to deposition, an improved dosing system was constructed. All inner walls of the evaporating systems are covered with inert materials. The outer part of the evaporator is separated from the analysis chamber by a gate valve. On the inner part behind the gate valve, the evaporator consists of two concentric tubes with the inner one made of glass. It has been designed in a way that the sample can be brought close to its end to deposit most of the material on the sample and avoid contamination of the analysis chamber with the Pd precursor. The tube is also equipped with a shutter and a hydrogen line with an integrated hot filament at its end to produce atomic hydrogen. A thermostat with a coolant liquid was used to store the precursor at temperatures below −18 °C between the deposition experiments. Raising the temperature of the thermostate allowed outgassing of the precursor and adjustment of the desired vapor pressure of the precursor during the experiments. Further details of the evaporator will be described elsewhere.[10]

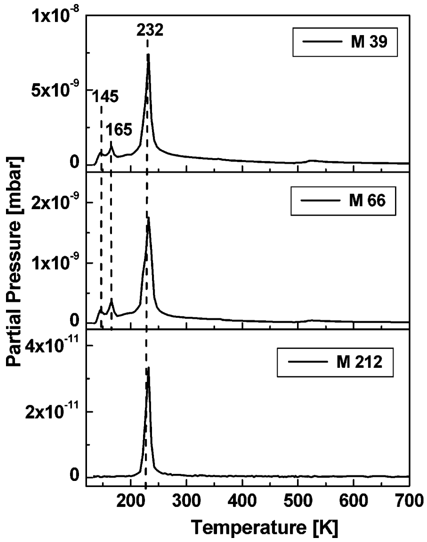

Figure 2. Thermal desorption spectra for different masses obtained on a multilayer deposited onto SiO_2 by backfilling the chamber.

The Pd(111) crystal used for the experiments was cleaned by repeated cycles of ion sputtering (1 keV ion energy) and flashing the crystal for less than 1 min to about 900 K. The absence of carbon or any other contaminations prior to deposition was evidenced by XPS.

Results and Discussion

TPD Experiments. In a first experiment, the multilayer desorption temperature of the Pd precursor was determined using temperature programmed desorption (TPD). A multilayer of the precursor was deposited onto an oxidized silicon wafer acting as an inert substrate. Deposition of the multilayer was carried out by cooling the substrate to 140 K and then backfilling the chamber through a leak valve to a pressure of 1×10^{-7} mbar. The dosing time was 15 min. The desorption of the precursor was monitored with a mass spectrometer at a constant heating rate of 3 K/s using a Feulner cup.[11] For this heating rate and exposure, the maximum of the TPD curve was located at 232 K (see Figure 2). For TPD spectra recorded at mass 212 (Cp(allyl)Pd), only the multilayer desorption peak is observed. When spectra are recorded at mass 66 (C_5H_6) and 39 (C_3H_3), additional peaks at 145 and 165 K are observed. Of course, these peaks

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cannot correspond to a desorption of the intact molecule; they correspond to the desorption of contaminations within the multilayer. One source for these fragments is the decomposition of the precursor during heating in the TPD experiment even on the relatively inert SiO_2 surface (note that a small Pd residue was found after the experiment). Another possible and more plausible explanation is a partial decomposition of the precursor on the path from the doser to the sample and condensation of precursor fragments on the sample prior to the TPD experiment. It is obvious that the precursor is very sensitive to decomposition and great care must be exercised to avoid experimental artifacts caused by unwanted decomposition prior or during the deposition experiments.

Multilayer Deposits. To study the decomposition mechanism of the precursor on a palladium substrate, the precursor was deposited onto a Pd(111) single crystal held at a substrate temperature of 170 K. In a first set of experiments, deposition was carried out as in the TPD experiments for the silicon oxide substrate by backfilling the chamber through a leak valve. Yet the XPS analysis of the deposited metal organic film revealed that the deposits were nonstoichiometric, indicating at least a partial decomposition of the precursor on its path to the sample (see below). For the second set of experiments, we have therefore used the improved dosing system described above. The vapor pressure of the precursor inside the evaporator was adjusted by setting the thermostat to 273 K. The Pd-crystal was cooled to a temperature of 160 K, and a multilayer was deposited by exposing to the precursor for 15 s by opening the gate valve of the evaporator. No Pd $3d_{5/2}$ and Pd $3d_{7/2}$ substrate signals at 335.1 and 340.4 eV were detectable in XPS measurements, indicating that the thickness of the deposit was more than about 20 nm. The Pd 3d and C 1s core level spectra of the deposit taken with Al Kα radiation are shown in Figure 3. In the precursor, the palladium is in a charged state (Pd^{2+}) yielding XPS binding energies of 337.7 and 343.0 eV for the Pd $3d_{5/2}$ and $3d_{3/2}$ doublet, respectively.

In the C 1s region, one observes a single line at 284.5 eV binding energy and a “shake-up” satellite at around 289 eV (see top of Figure 3). The ratio of C 1s peak area to the Pd 3d peak area amounts to 0.475. Using the tabulated sensitivity factors for C 1s (1.00) and Pd 3d (16.04) at 1486.6 eV[12] and a factor of 1.03 to correct for the different electron escape depth and the energy dependence of the analyzer transmission for photoelectrons with a kinetic energy of 1150 eV (Pd 3d) and 1200 eV (C 1s), respectively, a C/Pd ratio of 7.8 is calculated. This is in excellent agreement with the stoichiometric value of 8 expected for an intact precursor.

The palladium 3d lines of the precursor are shifted by 2.6 eV toward higher binding energies as compared to the Pd 3d lines of the palladium metal substrate appearing at 335.1 and 340.4 eV for the clean palladium substrate. Binding energies of the Pd $3d_{5/2}$ line around 338 eV are typical for many Pd(II) compounds.[13] Thus, a Pd $3d_{5/2}$ binding energy of 337.7 eV can be taken as an indication that the palladium is in a formally +2 oxidation state in the precursor complex. Lin et al. reported a somewhat higher binding energy of 339.1 eV for the $Pd(hfac)_2$ precursor.[14] The higher binding energy is consistent with a larger chemical shift caused by the more electropositive ligands in the latter complex.

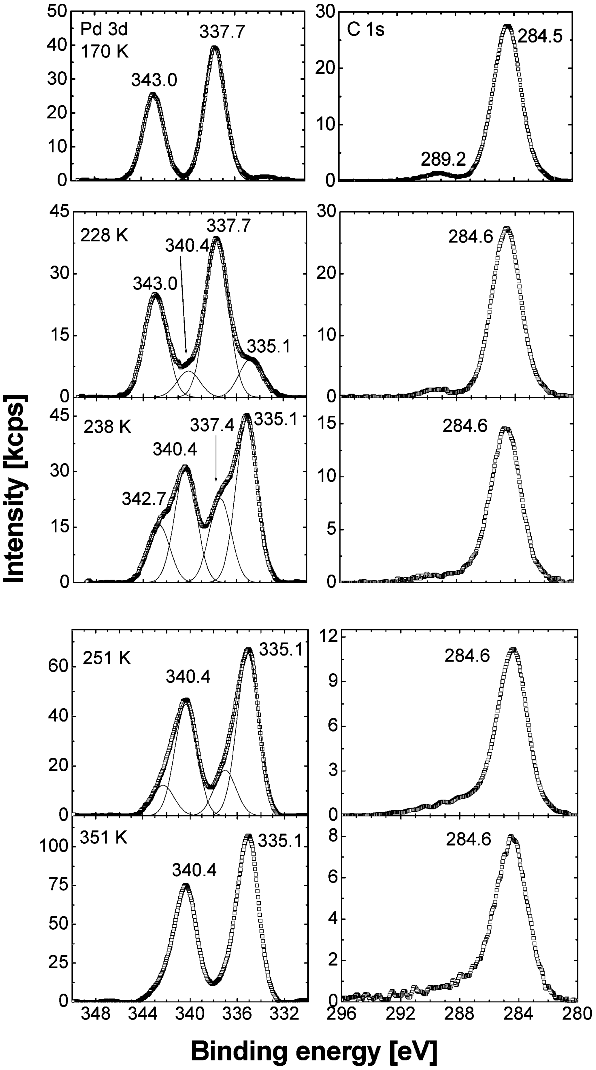

Figure 3. XP spectra at the Pd 3d and C 1s region for a stoichiometric (Cp)Pd(allyl)-precursor multilayer deposit on Pd(111) after deposition at 170 K (top) and for different annealing temperatures.

In the C 1s region, we observe a single C 1s line. The fact that the position of the single C1s line observed in the C1s regime, 285.0 eV, is shifted by a few tenths of an eV with regard to that commonly observed for unsubstituted hydrocarbons is attributed to the chemical shift of the Pd^{2+}.

The shake-up peak at around 289 eV is typical for $\pi-\pi^*$-transitions in conjugated π-electron systems.[15,16] This feature is assigned to the benzene-like π-electron system of the cyclopentadienyl ligand in its anionic state.

Annealing of the deposited multilayer to 217 K does not lead to any significant changes in the XP spectra. After

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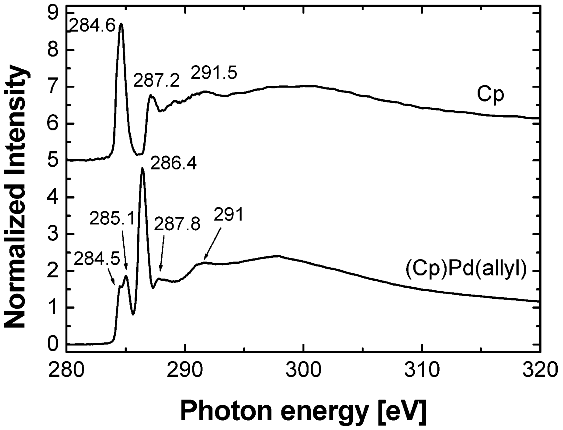

Figure 4. NEXAFS spectra at the C 1s edge for a stoichiometric (Cp)-Pd(allyl)-precursor multilayer deposit on Pd(111) after deposition at 163 K (bottom) and for a cyclopentadiene multilayer.

annealing to 228 K for 5 min, a signal from the palladium substrate is observed in the Pd 3d core level spectrum (see Figure 3, second row), indicating the onset of multilayer desorption. Assuming that the deposited film is still homogeneous, we yield a thickness of the multilayer from the attenuation of the substrate signal amounting to 7.4 nm. This value corresponds to about 12 monolayers of the precursor. Up to this temperature, no change is detected in the line shape of the C 1s signal.

Annealing the sample for 5 min to 238 K leads to significant changes in the C 1s signal (see Figure 3, third row). The main C 1s line develops a slight asymmetry with increased intensity at higher binding energy, and the shake-up satellite signal is not well resolved anymore. This effect increases when further increasing the substrate temperature (see Figure 3, fourth row). At the same time, the Pd 3d core level spectrum shows a reduction of the Pd(II) signal and an increased intensity of the substrate Pd(0) metal signal. Finally, at 351 K (significantly above the multilayer desorption temperature), the calculated thickness of the deposit reaches about 8 Å, and it is not possible to detect a Pd(II) signal anymore (see Figure 3, bottom). The decrease of the Pd(II) signal together with the line shape changes in the C 1s region clearly indicate the decomposition of the (Cp)Pd-(allyl) precursor on the Pd(111) surface. The C1s XPS data reveal that the transition of Pd(II) to Pd(0) is not accompanied by a complete removal of the ligands from the palladium surface.

NEXAFS Spectra. In Figure 4, we show NEXAFS spectra recorded at the C1s line for a thick multilayer of the (Cp)-Pd(allyl) precursor (bottom) and a multilayer of cyclopentadiene (top) both deposited on the Pd surface at a substrate temperature of 150 K. The Pd precursor spectrum exhibits strong resonances at 284.5, 285.1, and 286.4 eV. These resonances correspond to excitations of C 1s electrons into empty π^* orbitals. Based on quantum chemical calculations and a comparison with the cylopentadiene reference, the first two resonances are assigned to the cyclopentadienyl ligand, whereas the resonance at 286.4 eV is assigned to the allyl ligand. The resonance at 287.8 eV is assigned to excitations into Rydberg states, and the remaining broad resonances at 291 and at 297 eV are assigned to excitations into σ^*-orbitals (see Table 1). The π^* resonances can thus be used as fingerprints to distinguish the two ligands.

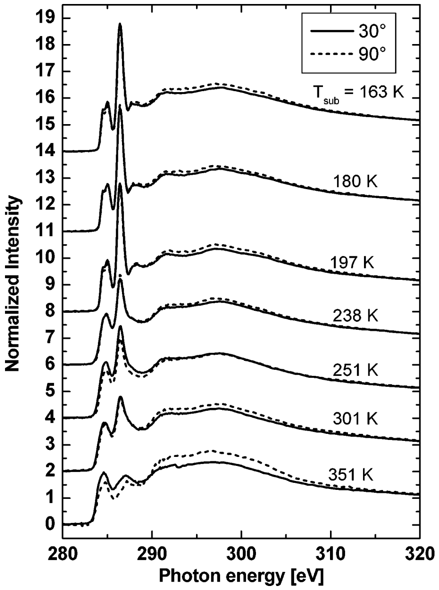

Figure 5. NEXAFS spectra at the C 1s edge for a stoichiometric (Cp)-Pd(allyl)-precursor multilayer deposit on Pd(111) after deposition at 163 K (top) and for different annealing temperatures. At each temperature, the spectra are plotted for two different angles of light incidence.

Table 1. Assignment of the NEXAFS Resonances of the (Cp)Pd(allyl) Precursor

no.	energy position (eV)	assignment
1	284.5	C 1s → π^* (Cp)
2	285.1	C 1s → π^* (Cp)
3	286.4	C 1s → π^* (allyl)
4	287.8	C 1s → Rydberg
5	291	C 1s → σ^* (Cp, allyl)
6	297	C 1s → σ^* (Cp, allyl)

Figure 5 shows NEXAFS spectra which were recorded after annealing the multilayer to different temperatures. The solid lines correspond to spectra recorded at an incidence angle (angle between the $\vec{E}$ vector of the polarized synchrotron light and the surface normal) of 30°, whereas the dashed lines represent spectra taken at normal incidence of the synchrotron light (angle between the $\vec{E}$ vector of the synchrotron light and the surface normal of 90°). The intensities of the resonances depend on the relative orientation of the corresponding transition dipole moment relative to the polarization direction of the light. For hydrocarbon molecules with π-electron systems, the π^* resonance should vanish at normal incidence if the molecular backbone is oriented parallel to the surface, and it should show maximum intensity if the molecular backbone is oriented perpendicular to the surface. Changing the angle of incidence from normal to grazing should then lead to a strong increase of the π^* intensity for flat lying molecules or should lead to a decrease for upright standing molecules, respectively. At the same time, the σ^*-resonances should show the opposite trend. This is expected because their transition dipole moments are oriented orthogonal to those of the π^* resonances. The particular variation of intensities with angle of incidence of the synchrotron light (dichroism) can thus be used to determine the average orientation of the molecules on the surface. For the Cp(allyl)Pd multilayer, no dichroism is observed, thus indicating a random orientation of the precursor molecules.

As in the case of the XPS measurements, a temperature increase to 228 K does not lead to any significant changes in the line shape of the NEXAFS spectra. This indicates that the majority of molecules that remain adsorbed on the surface at this temperature are still intact. Corresponding to the changes detected in the C 1s core level spectrum, also the NEXAFS data show significant changes upon annealing to 238 K (see Figure 5). At this temperature, which is significantly above a multilayer desorption temperature, a large fraction of precursor molecules has desorbed. For the remaining monolayer, the splitting of the first two resonances is no longer resolved and the intensity of the resonance at 286.4 eV is decreased and the resonance at 287.8 eV has completely disappeared. At 286.4 eV, a small shoulder or an asymmetric broadening toward higher photon energies of the third resonance is seen. The first σ^* resonance is shifted by 0.5 eV toward lower photon energies. The linear dichroism is still very weak, indicating a random orientation of the molecules.

Upon heating to 251 K, no new features are seen in the NEXAFS spectra, but after heating to 301 K, a decrease in intensity of the allyl resonance at 286.4 eV is observed (Figure 5). This decrease in intensity is even more pronounced after annealing to 351 K. The resonances attributed to the cyclopentadienyl units remain unchanged. From the corresponding XP spectrum, a carbon layer thickness of 0.5 nm is calculated. At this point, no Pd(II) is detected anymore in the Pd 3d XPS data.

Taking all data discussed above together, the following picture emerges from the analysis of the XPS and NEXAFS multilayer data. For the multilayer, both XPS and NEXAFS indicate the presence of intact precursor molecules. At 228 K, the thickness of the multilayer is found to be reduced and the substrate Pd(0) peaks become visible. The NEXAFS data indicate that the remaining Pd precursor molecules are still intact at this temperature. Heating to 238 K leads to a further reduction in thickness, and both C1s core level and the NEXAFS data reveal significant changes indicating the onset of decomposition of the precursor molecules. At 238 K, the Pd(II) and C 1s signal is reduced to about 50%, and a strong Pd(0) signal is visible (Figure 3). The layer thickness is reduced to about 2 nm corresponding to about three nominal monolayers of the precursor.

The slightly shifted (0.3 eV) XPS signals at 337.4 and 342.7 eV indicate that there is still a significant amount of Pd(II) atoms present in the layer that has not been transferred to Pd(0) and incorporated into the Pd bulk. From the fact that the NEXAFS resonances are significantly broadened and that the second resonance at 286.4 eV has decreased significantly, we conclude that the precursor molecules are not intact but have formed chemical bonds to the palladium substrate. In the NEXAFS spectrum, the allyl resonance shows a larger reduction as compared to the resonances assigned to the cyclopentadienyl units, but the calculated C/Pd(II) stoichiometry of this layer is 7.6 and therefore still close to the stoichiometric value of 8. We therefore conclude that this first step of the decomposition reaction does not change the oxidation state of the palladium and that only a small amount of allyl and cyclopentadienyl fragments is desorbed. On the other hand, the asymmetric broadening of the C 1s core level spectrum on the higher binding energy side is indicative of a carbon species in a different chemical environment. On the basis of the NEXAFS data, this new carbon species is tentatively assigned to hydrocarbon fragments originating from a decomposition of the allyl ligands.

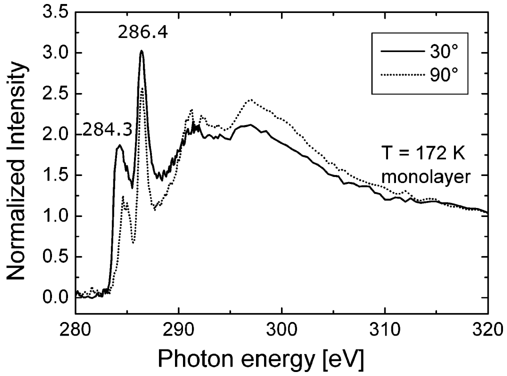

Figure 6. NEXAFS spectra at the C 1s edge for (Cp)Pd(allyl)-monolayer deposit on Pd(111) after deposition at 172 K. The spectra are plotted for two different angles of light incidence.

Monolayer Deposits. In Figure 6, we show a NEXAFS spectrum which was recorded after deposition of about one monolayer of the Pd precursor (as judged from the thickness calculated from the XPS data) at 172 K. The NEXAFS data are very similar to those recorded after annealing the multilayer to 238 K (see Figure 5). A minor difference with regard to the data recorded for the monolayer prepared by desorption of the multilayer is that the NEXAFS data for the monolayer reveal a small dichroism, which was not present for the annealed multilayer. The small dichroism indicates that the symmetry plane of the hydrocarbon ligands is preferentially oriented parallel to the Pd substrate surface. The XP data recorded for this monolayer reveal the absence of a Pd(II) peak. This observation indicates that the Pd atoms are incorporated in the Pd substrate and have accordingly changed their oxidation states from Pd(II) to Pd(0). This transition must have a low activation energy because it was observed immediately after deposition on the cold (172 K) palladium substrate. This observation supports the view that the Pd(II) species observed in the multilayer spectra above the nominal multilayer desorption temperature is not in direct contact with the palladium substrate. To prevent its desorption or movement toward the substrate, the Pd(II) species must be immobilized, that is, by a reaction of the intact precursor molecule on top of the monolayer with precursor fragments created at the palladium surface.

Nonstoichiometric Deposition. In this section, results are shown that demonstrate how the decomposition process changes if a contact of the precursor to metal surfaces prior to deposition has not been excluded. This is perhaps closer to a typical real world situation where palladium deposition is carried out in a CVD reactor, and therefore these data are included here to demonstrate the specific differences.

Nominally again a multilayer of the Pd-complex was deposited on a Pd(111)-surface at 161 K. This time, the deposit was obtained by backfilling the chamber through a

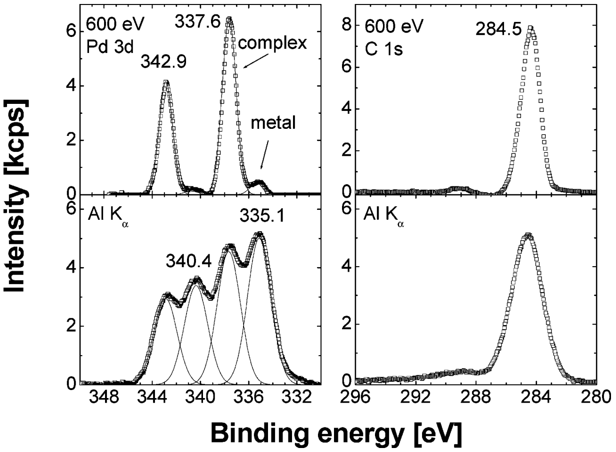

Figure 7. XP spectra at the Pd 3d and C 1s region for a nonstoichiometric multilayer deposit on Pd(111) after deposition at 161 K. The spectra were measured with a synchrotron source at 600 eV excitation energy (top) or with a Al Kα lab source (bottom).

leak valve for 600 s at 1 × 10^{-7} mbar. The Pd 3d (left) and C1s (right) spectra are shown in Figure 7. The spectra on the top were obtained by using synchrotron radiation with a photon energy of 600 eV. The spectra on the bottom were obtained using an Al anode X-ray source. The latter clearly reveals the characteristic Pd 3d core level shift of more then 2.5 eV as compared to the Pd substrate with binding energies of 335.1 eV for the Pd $3d_{5/2}$ line and 340.4 eV for Pd $3d_{3/2}$ line. By using electron escape depths of 25 and 26 Å for photoelectrons with kinetic energies of 1151 eV (Pd $3d_{5/2}$) and 1201 eV (C 1s), a thickness of the multilayer film of 6.4 nm is obtained. Because no experimental electron escape depth values are available, the electron escape depth of the precursor was calculated on the basis of the elemental composition and a density of 2.5 g/cm^3 using the Gries formula in the NIST database.[17] The stoichiometric ratio obtained from the C 1s peak and the Pd 3d peak areas is 11 instead of 8 expected for the intact precursor; that is, the deposited film contains excess carbon. Because of the better energy resolution and the higher surface sensitivity, we will consider in the following only the XP spectra recorded using synchrotron radiation for excitation.

As in the case of the stoichiometric deposit, there is a change of the line shape in the C 1s core level spectrum after heating to 230 K (Figure 8). The C 1s line shows again a shoulder toward higher binding energy. The corresponding spectrum of the Pd region reveals that the signal for the Pd(II) complex is absent and that the palladium atoms are in the metallic state. After further heating to 450 K, the amount of carbon remaining on the palladium surface corresponds to a layer thickness of about 2.5 nm. This value is much larger than that measured for the stoichiometric deposit, where after heating to 351 K only a residue with a thickness of 0.8 nm was obtained. It seems that ligands removed from the central Pd(II) atom prior to deposition (and which are then deposited onto the cold substrate) are more difficult to remove subsequently than those which were still bonded to the Pd(II) atom at the deposition. One reason could be that the free ligands are chemically very reactive and form larger carbon aggregates when they come into contact with the intact precursor molecules or other ligands on the palladium surface. The newly formed carbon species is then more difficult to remove thermally.

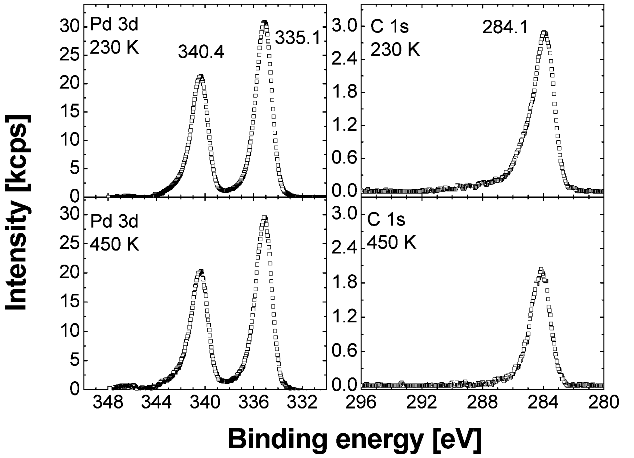

Figure 8. XP spectra at the Pd 3d and C 1s region for a nonstoichiometric multilayer deposit on Pd(111) after annealing to 230 K (top) and 450 K (bottom).

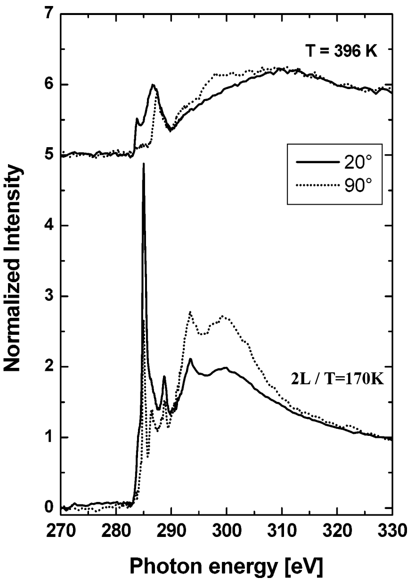

Figure 9. NEXAFS spectra at the C 1s edge for a nonstoichiometric monolayer deposit on Pd(111) after deposition at 170 K (bottom) and after annealing to 396 K in 10^{-5} mbar molecular hydrogen. The spectra are plotted for two different angles of light incidence.

Figure 9 (bottom) shows the NEXAFS spectrum of a monolayer prepared by backfilling the UHV-chamber through a leak valve. Clearly, this spectrum is different from the spectrum obtained with the improved dosing system (see Figure 4). Here, the resonance for the Cp is relatively weak as compared to the very pronounced allyl resonance at 286.4 eV. In the corresponding XP spectra (not shown), only metallic Pd is observed and the C 1s region shows only a single symmetric line. This is an indication that this layer consists of already decomposed precursor molecules. In this case, the allyl ligand appears to be the most prominent species.

This layer was then heated in molecular hydrogen ($p = 1 \times 10^{-5}$ mbar) in four steps up to 500 K. The NEXAFS spectrum of the nominal monolayer after heating to 400 K

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[17] NIST ELECTRON INELASTIC-MEAN-FREE-PATH DATABASE Version 1.1; National Institute of Standards and Technology: Gaithersburg, MD, 2000.

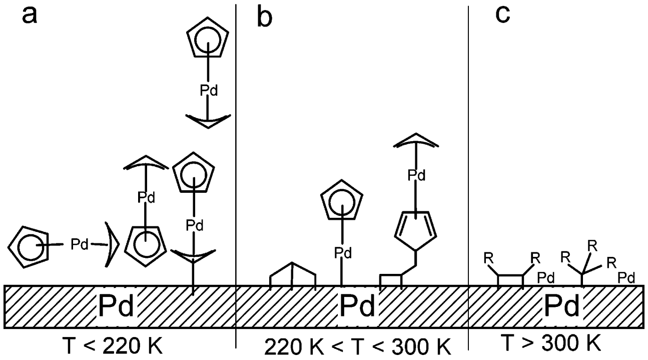

Figure 10. Reaction scheme for a multilayer deposit on Pd(111): (a) adsorption of intact molecules on a perhaps reacted monolayer, (b) reaction of fragments created at the Pd/precursor interface with intact precursor molecules, and (c) complete transformation of Pd(II) to Pd(0) and further reactions of fragments to different carbon species.

is shown also in Figure 9. The amount of carbon is found to be reduced by a factor of 2, but still a large carbon residue remained on the substrate surface. A similar heating experiment done without a hydrogen atmosphere yielded similar results only with a thicker carbon residue. The carbon residue consisted of not well-defined carbon species in each case. These results reveal that the treatment with molecular hydrogen was not sufficient to remove the carbon completely. We are presently unable to explain the apparent contrast between the results reported above and those reported in earlier studies by Hierso et al. where it was found that the addition of hydrogen significantly improves the quality of the deposited palladium films.[4]

Discussion

Previous results indicate that the pure Cp(allyl)Pd precursor complex is thermally rather stable and requires high decomposition temperatures.[4] It was found previously, however, that the decomposition temperature is lowered significantly in the presence of metallic palladium.[4] Our results clearly confirm this picture. Precursor molecules adsorbed on a palladium surface show chemical changes already at substrate temperatures as low as 172 K. A spectroscopic analysis of this first step toward decomposition reveals that the central Pd(II) atom remains largely unchanged. The significant loss of the allyl resonance at 286.4 eV in the NEXAFS spectra recorded for the monolayer indicates that first the allyl ligand is removed from the metal organic compound and is transferred to the substrate. Spectral changes in the Cp regime are only observed when the temperature is raised to room temperature. At this temperature, the XPS data reveal a change from Pd(II) to Pd(0), indicating that the palladium atom gets into direct contact with the substrate palladium. At this temperature, the ligands are still present at the surface on the basis of the present data; however, it cannot be decided whether they are still bound to the original palladium atom or they have been transferred to the palladium surface. This reaction scenario is schematically illustrated in Figure 10. It is not consistent with other observations on the relative stability of the Pd(II) precursor ligands.[18] There it has been proposed that the allyl ligand is more strongly bonded to the central Pd(II) atom than the Cp-ligand. It has to be noted, however, that these results were obtained under rather different experimental conditions (in solution with organic molecules as a reaction partner). In our case, the first step is the interaction with palladium metal accompanied by a subsequent transition from Pd(II) to Pd(0). The interaction with the palladium substrate seems to have a more destabilizing effect on the bond to the allyl ligand rather than on the bond to the Cp ligand.

The NEXAFS data reveal that upon decomposition of the adsorbed precursor molecule the ligands are not simply transferred to the palladium substrate. If this were the case, we would expect to observe a well-defined orientation of the adsorbed ligands, which should result in a pronounced dichroism in the NEXAFS data. The absence of such a dichroism together with the chemical changes as concluded from the changes in shape of the NEXAFS resonances instead reveal that the ligands undergo chemical reactions on the palladium surface with other precursor molecules leading to a not well-defined and not well-oriented layer of different hydrocarbon species. We note that small unsaturated hydrocarbons such as ethene are found to decompose on palladium substrates at higher temperatures; ethylene is found to be converted to ethylidyne on a Pd(111) surface.[19] Steric hindrance as in the case of propene favors thermal desorption (which has been observed to occur around 320 K) over decomposition.[20] On the other hand, palladium is known to catalyze carbon−carbon bond formation. A very prominent example is the palladium-catalyst tricyclization of an acetylene to benzene.[21,22] Therefore, the formation of different carbon species as proposed in our mechanism is consistent with previous observations of the catalytic activity of palladium.

Conclusions

Using a deposition system with chemically inert walls, it is possible to deposit multilayers of the intact precursor onto solid substrates. The deposits showing the correct stoichiometry were characterized by XPS and NEXAFS. Within the multilayer deposited at 161 K, the molecules exhibit a random orientation. Above the multilayer desorption temperature, a remaining thin layer of chemically modified precursor molecules is observed. In separate experiments, it was found that already at a temperature as low as 170 K the Cp(allyl)Pd precursor is chemically modified when in contact with a clean palladium metal surface. Our NEXAFS data reveal that the first step of the decomposition reaction is characterized by a strong interaction between the allyl ligand and the palladium substrate. The next step is the removal of the Pd−Cp and the transition from Pd(II) to Pd(0). Starting from a multilayer palladium precursor, molecules remain adsorbed on the surface even above the nominal multilayer

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desorption temperature. At this stage, they are not yet in contact with the palladium substrate as evidenced by the presence of Pd(II) lines in the corresponding XP data. It is believed that these molecules are immobilized by a reaction with free fragments of already decomposed molecules. Upon further heating to temperatures of 235 K, the palladium in the precursor changes its oxidation state and is reduced to Pd(0), indicative of direct contact between the palladium atoms in the palladium precursor and the palladium substrate. At this temperature, changes in the NEXAFS data also indicate modifications of the structure of the Cp-ligand. The absence of a strong dichroism in the NEXAFS data reveals that the ligands are not simply transferred to the palladium substrate but are chemically modified and react with other ligands and precursor molecules upon further heating. Under our conditions, we were not able to obtain a carbon-free palladium deposit on the palladium surface using the precursor. Filling the UHV-chamber with molecular hydrogen at a pressure of 10^{-5} mbar was not sufficient to remove the residual ligands and the carbon-containing adlayer of a substrate even upon heating the surface up to 500 K.

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