Hexaphenyl thin films on clean and carbon covered Au(111) studied with TDS and LEED

S. Müllegger, A. Winkler *

Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria

Received 12 December 2005; accepted for publication 10 January 2006

Abstract

The adsorption and growth of ordered para-hexaphenyl (6P) films have been investigated both on clean and partially carbon pre-covered Au(111) single crystal surfaces by thermal desorption spectroscopy (TDS) and low energy electron diffraction (LEED) under ultra-high vacuum conditions. The existence of a distinct first and second monomolecular 6P layer that clearly separate from the multilayer regime, which comprise lying molecules with respect to the substrate surface, could be inferred from TDS. For both the 6P monolayer and multilayer grown on pure Au(111) the desorption energies have been determined based on experimental TDS data. In particular, for the monolayer regime a coverage dependence of the desorption energy has been found, which is attributed to repulsive interactions between neighbouring 6P molecules adsorbed on the gold surface. The existence of well-ordered film structures could be inferred from LEED for half monolayer and full monolayer thick 6P films. Based on the LEED and TDS data, structural models are presented for these highly ordered organic films. Multi-step dehydrogenation of 6P molecules adsorbed on clean Au(111) surfaces is reported for temperatures above 650 K together with experimental evidence for the existence of a regular overlayer composed of partially dehydrogenated polycyclic aromatic hydrocarbon (PAH) intermediates. A quite different adsorption/desorption kinetics and film growth has been observed for 6P films grown on carbon pre-covered Au(111) surfaces.

Keywords: Thermal desorption; Organic molecules; Hexaphenyl; Adsorption; Gold; Dehydrogenation; Monolayer structure

1. Introduction

The interest in ultra-thin films of organic semiconducting molecules deposited on regular solid surfaces is due to their high potential as active components in novel device applications [1]. Also the structure and energetics of the organic/inorganic interface as well as the thin film formation are of great importance, since they influence to a great extent the device performance [2,3]. The possibility of organic-on-inorganic hetero-epitaxial growth [4] has opened a large field for tailoring the organic films with the help of pre-defined substrate surface properties (substrate temperature, structure or chemistry) during film deposition. In particular, for the archetype molecule p-hexaphenyl (C_{36}H_{26}, 6P) a considerable amount of research has already been conducted either on the structure and morphology of bulk films [5–8], the adsorption on regular and/or nanostructured solid surfaces [9] as well as on applications in (opto)electronics [10–14].

The results presented in this work complement previous studies on 6P with novel aspects concerning the adsorption/desorption kinetics, monolayer formation and dehydrogenation of 6P on clean and carbon pre-covered Au(111) surfaces. The results are compared to those from a previous study on 6P films grown on Au(111) published by France and Parkinson [15].

2. Experimental

The experiments have been performed under ultra-high vacuum conditions at a base pressure of about 10^{-10} mbar.
A high-purity Au(111) single crystal served as the substrate. The cleanliness of the substrate surface prior to the deposition of the organic films was maintained by room temperature Ar+-ion sputter cleaning \(5 \cdot 10^{-5}\) mbar, 1 keV) and consecutive annealing of the crystal at 1023 K. The structure of the Au(111) surface was checked by low energy electron diffraction (LEED) yielding the well known \(2 \times \sqrt{3}\) surface reconstruction [16]. The sample mounting as well as the details on the organic film preparation and the thermal desorption spectroscopy (TDS) experiments are described elsewhere [17,18]. In the TDS experiments, the original 6P signal (at the mass of \(m = 458\)) has been recorded together with the mass \(m = 61\) of the strongest signal cracking fragment of 6P as observed in our QMS instrument. It has been carefully checked, that the \(m = 61\) signal proceeds simultaneous to the \(m = 458\) signal, but beneficially gives a much better signal-to-noise ratio. The quartz microbalance has been calibrated with the help of an independent thickness measurement for a sufficiently thick organic film by a Tolansky interferometer [19]. This allows a quantitative determination of the pre-exponential factor as discussed below.

Micro-channelplate enhanced LEED experiments (MCP-LEED) were performed at substrate temperatures of 93 K in order to minimize thermal distortions of the images. The organic films, however, were grown at and above room temperature and were consecutively cooled down to 93 K for the MCP-LEED experiments. Details on the analysis of the LEED images are described in Ref. [20].

3. Results and discussion

3.1. Desorption kinetics of 6P on Au(111)

Fig. 1a–c present a compilation of TDS data for 6P grown on an atomically clean Au(111) surface at 300 K for three different coverage regimes. In the low coverage regime shown in Fig. 1a three distinct desorption peaks, labelled \(\beta_1-\beta_3\), can be distinguished: Starting with the lowest coverage curve of 0.16 nm, the desorption proceeds at a considerably high temperature between 625 and 700 K and the corresponding desorption peak is labelled \(\beta_1\). With increasing coverage the maximum of \(\beta_1\) shifts to lower temperatures until saturation is reached at a nominal coverage of roughly 0.26 nm. A second peak, labelled \(\beta_2\), emerges upon a further increase of the film thickness after \(\beta_1\) has almost saturated. Also for the maximum of \(\beta_2\) a negative temperature shift can be observed with increasing coverage and it also exhibits saturation behaviour. Both peaks \(\beta_1\) and \(\beta_2\) can be attributed to a first-order molecular desorption of adsorbed molecules from the Au(111) surface, similar to previous investigations of the four-ring oligophenylene molecule para-quaterphenyl (4P) on Au(111) [20,21]. We denote the saturation \(\beta_1 + \beta_2\) of around 0.35–0.4 nm as 1 monolayer (ML). The negative peak maximum shift observed for both \(\beta_1\) and \(\beta_2\) is an indication for repulsive interactions between neighbouring adsorbed 6P molecules in the (sub)monolayer coverage regime. We argue that the repulsive interaction may be caused by induced localized surface dipoles, resulting in a long range electrostatic repulsion between neighbouring 6P molecules [21]. Even before the \(\beta_2\) peak has saturated, at coverages around 0.5–1 ML a third peak, labelled \(\beta_3\), appears at about 455 K.
Its peak shape is considerably narrower compared to the rather broad $\beta_1$ and $\beta_2$ peaks.

The TD spectra of coverages 0.45–1.1 nm presented in Fig. 1b clearly show that the $\beta_3$ peak can also be saturated similar to the first monolayer ($\beta_1 + \beta_2$). The $\beta_3$ saturation at an overall mean film thickness of about 0.7–0.8 nm strongly suggests that it corresponds to a distinct second layer of 6P molecules. Different from the peaks of the first monolayer shown in Fig. 1b, the second layer peak $\beta_3$ shown in Fig. 1b exhibits a positive peak maximum shift. This may indicate a first-order desorption with attractive intermolecular forces. However, the significantly narrower peak shape of $\beta_3$ compared to $\beta_1$ and $\beta_2$ as well as its almost exponential leading edge rather suggest a zero-order like desorption for $\beta_3$. A possible desorption mechanism explaining the zero-order desorption could be a coexistence of dense packed 6P islands of the second layer being in equilibrium with a dilute phase (6P surface lattice gas), where desorption is equally possible from both phases. This interpretation is further supported by the fact that the second 6P layer produces only a single TD peak, instead of two peaks found for the first monolayer. For 6P coverages $\geq$ 2 ML a fourth peak, labelled $\alpha$, is observed on the low temperature side, which exhibits no saturation as illustrated in Fig. 1c. Its exponential leading edge together with the absence of a saturation behaviour are typical indications for a zero-order molecular desorption. Hence, the peak $\alpha$ is attributed to the 6P monolayer desorption.

From the TD spectrum of the 7 nm thick 6P film presented in Fig. 1c the activation energy of thermal desorption, $E_{\text{des}}$, was calculated for the 6P multilayer according to the well-known leading edge method, yielding a value of $E_{\text{des}} = 2.4 \pm 0.1$ eV/molecules ($230 \pm 10$ kJ/mol). This value is significantly larger than the value of about 136 kJ/mol reported by France and Parkinson. A comparison of our experimental TD spectra with those presented in Ref. [15] reveals further discrepancies in the onset temperatures of desorption as well as in the shape of the monolayer TD spectra. A thorough analysis of Ref. [15], however, reveals major shortcomings in the reported data analysis and interpretation. The multilayer desorption energy was misleadingly evaluated with the help of the peak maximum of the zero-order multilayer desorption peak.

Since the desorption rate has been determined quantitatively (absolute number of molecules per time and unit area), the pre-exponential factor for the 6P multilayer desorption, $v_0$, could be easily determined with the help of an Arrhenius analysis of the Polanyi–Wigner equation [24]. $R_{\text{des}} = v_0 \cdot \Theta_0 \cdot \exp(-E_{\text{des}}/kT)$, yielding a value of $v_0 = 5.6 \times 10^{25}$ s$^{-1}$.

For this analysis a constant value of $\Theta_0 = 5.4 \times 10^{13}$ molecules/cm$^2$ has been used, which corresponds to a saturated monomolecular layer of the 6P multilayer phase. This value has been obtained with the help of the calculated mean surface density of 6P molecules within a particular crystal plane of the 6P bulk structure, i.e., the 6P(21–3) plane, that lies parallel to the substrate surface as determined in separate X-ray diffraction measurements on 30 nm thick 6P films on Au[111] as described elsewhere. Compared to desorption of small molecules like H$_2$ or CO from metal surfaces, yielding typical values of $v_0$ around $10^{13}$ s$^{-1}$, the obtained pre-exponential factor for the 6P multilayer desorption is several orders of magnitude larger. This is in good agreement to previous theoretical and experimental results obtained for large organic molecules adsorbed on surfaces. A possible explanation may be given by transition state theory in terms of an increased number of vibrational and/or rotational degrees of freedom in the transition state of the desorbing 6P molecules compared to the adsorbed species.

Due to the strong overlap of the 6P first monolayer desorption peaks and the pronounced dependence of the 6P monolayer desorption on intermolecular interactions (peak maximum shifts) a determination of the activation energy for desorption, $E_{\text{des}}$, from the 6P monolayer is not straightforward. Hence, an approximative approach for the determination of the 6P monolayer desorption energy has been followed: According to Redhead, for a first-order desorption $E_{\text{des}}$ can be approximately determined from the corresponding peak maximum temperature, $T_p$, by the well-known numerical equation

$$E_{\text{des}} [\text{cal/mol}] = \left( \ln \left( \frac{v_1 T_p}{\beta} \right) - 3.64 \right) \cdot R \cdot T_p [\text{K}],$$

where $v_1$ is the (coverage dependent) pre-exponential factor for first-order desorption, $\beta$ the heating rate (1 K/s) and $R$ the molar gas constant (2 cal/mol). In a first step, the coverage dependence of $v_1$ was neglected and $v_1$ has been approximated by the pre-exponential factor $v_0$ of the 6P multilayer desorption that has been determined independently as described above. In a next step, the peak maximum temperature $T_p$ has been determined graphically from the experimental TDS data for the limiting case of very small coverages ($\Theta \rightarrow 0$) by a linear extrapolation of the peak maximum positions for different coverage TD spectra. This is exemplary illustrated in Fig. 2a for the high temperature peak $\beta_1$, as well as for the $\beta_2$ peak. The extrapolation of $T_p$ for the case of very small coverages helps to minimize the compensation effect in the determination of $E_{\text{des}}$.

The graphic extrapolation yields for $T_p(\beta_1) = 214$ 670 K and for $T_p(\beta_2) = 600$ K, respectively. Inserting these data into the above numerical equation yields the values of the 6P desorption energies corresponding to the first ($\beta_1$) and second ($\beta_2$) half monolayer for very small relative coverages:

$$E_{\text{des}}(\beta_1)|_{\Theta \rightarrow 0} = 3.6 \text{ eV/molecules}$$

and

$$E_{\text{des}}(\beta_2)|_{\Theta \rightarrow 0} = 3.2 \text{ eV/molecules},$$

respectively. Considering the total number of aromatic rings per molecule, the value for the $\beta_1$ peak yields an
energy of approximately 600 meV per ring. This is very similar to the reported 603 meV for benzene monolayers adsorbed on Au(111) [30] and it suggests a nearly linear dependency of $E_{\text{des}}$ for the oligo-phenylenes on the number of aromatic rings. The $\beta_1$ peak could be attributed to the desorption of flat lying 6P molecules with their aromatic planes oriented parallel to the substrate surface, whereas the $\beta_2$ peak corresponds to lying 6P molecules exhibiting a side-tilt of their aromatic planes relative to the Au(111) plane (see below). Hence, the roughly 0.4 eV/molecule lower desorption energy of $\beta_2$ compared to $\beta_1$ reflects the influence of the changed adsorption geometry on the bonding strength to the gold surface.

Reverting back to the discussion of Fig. 1a, the negative peak maximum shift of the monolayer desorption peaks $\beta_1$ and $\beta_2$ has been attributed to repulsive interactions between neighbouring adsorbed 6P molecules within the monolayer. This interaction can be described by introducing a coverage dependent interaction energy, $\omega$, according to

$$ E_{\text{des}} = E_0 + \omega \cdot \Theta, $$

where $\Theta$ is the relative coverage [23,29]. Since it is possible at least for the peak $\beta_1$ to derive from the experimental TD data the $T_p$ values for coverages $>0$ quite accurately, one can determine the coverage dependent monolayer desorption energies of $\beta_1$. Plotting those values against the corresponding coverage reveals an almost linear dependency, as illustrated in Fig. 2b. A linear fit applied to the data yields the interaction energy of $\omega = -0.26 \pm 0.01$ eV between two neighbouring 6P molecules adsorbed in the flat-on configuration on the Au(111) surface (half monolayer). The negative sign indicates the repulsive nature of the interaction. In the case of the $\beta_2$ peak, the strong overlap with the $\beta_1$ spectra has prevented an accurate analysis.

### 3.2. Structure of the half and saturated 6P monolayer on Au(111)

A series of MCP-LEED experiments performed on a half and saturated 6P monolayer film grown on Au(111) has revealed regular, but different, LEED patterns for both films, as shown in Fig. 3. The obtained regular LEED images indicate the existence of a regular structure for both the 6P half monolayer (Fig. 3a) and saturated monolayer (Fig. 3b) on Au(111), respectively. Similar to the recently investigated system 4P/Au(111) [20], regular LEED patterns could only be observed at growth above a certain threshold temperature of roughly 270 K. In order to improve the degree of ordering of the monolayer films, however, the samples used for the following LEED analysis have been grown at a higher temperature of 380 K. It has been thoroughly checked that the LEED patterns (spot positions) did not change within this temperature regime. The LEED analysis itself was done at 93 K to reduce the background signal, but the same pattern was observed at room temperature. The data from a series of several LEED images recorded for different beam voltages between approximately 15 V and 40 V have been collected and transformed to a unique representation at 20 V. The latter is shown as black dots in Fig. 4a for the half monolayer and in Fig. 4b for the full monolayer, respectively. These patterns have been used for the quantitative pattern analysis yielding the parameters of the regular surface unit cells that are summarized in Table 1.

A simulation of the LEED patterns based on these parameters yields the LEED patterns presented as grey dots in Fig. 4a for the half monolayer and Fig. 4b for the full monolayer, showing a good agreement between experiment and simulation. In some cases single reflections appearing in the simulations could not be reproduced by the experiment. This is attributed to the existence of intensity variations and/or extinction of certain LEED reflections that is caused by the structure factor of the surface.
unit cell of the regular organic overlayer. Although the presented LEED data provide no information on the arrangement of the molecules within the surface unit cell, one can utilize additional information from X-ray diffraction measurements. Those have been performed on 30 nm thick 6P films and are described elsewhere [25]. One important XRD result, however, is also relevant for the monolayer analysis: The 6P molecules in the bulk phase exhibit a strong anisotropy in their azimuthal orientation with respect to the substrate surface. In particular, they are aligned parallel to the Au$_{11\overline{2}}$ or Au$_{11\overline{1}}$ direction, respectively. Such a pronounced propagation of a surface specific property into the bulk structure of the 6P film implies that also the molecules within the first half and saturated monolayer have a similar azimuthal orientation. Additionally, the 6P crystallites adopt a particular bulk crystal orientation, i.e., the 6P(21–3) plane parallel to the Au surface. Based on these findings, structural models are proposed for both the 6P half monolayer and the saturated monolayer on Au(111), respectively, as illustrated in Fig. 5a and b. According to the results from quantitative TDS and LEED measurements, the unit cell contains a single 6P molecule for the half monolayer and two 6P molecules for the monolayer. The characteristic edge-face packing structure of the 6P monolayer is in good agreement to the observation of two distinct monolayer desorption peaks in the TD experiments described above, i.e., the $\beta_1$ peak corresponding to molecules with the aromatic plane almost parallel to the Au(111) surface (“face-on”) and the $\beta_2$ peak corresponding to side tilted molecules (“edge-on”). A similar packing motif exists within the 6P(21–3) plane of the 6P bulk crystal structure [31]. The terms “face-on” and “edge-on”, as well as the schematic illustrations in Fig. 5 refer to the average molecular plane for simplicity and disregard a possible non-planarity, i.e., interring twisting of the adsorbed 6P molecules. The presumed polar side-tilt angle of the edge-on oriented 6P molecules could not be investigated with the used experimental equipment. Therefore, additional near edge X-ray absorption fine structure (NEXAFS) experiments have been conducted for 6P half monolayer, monolayer and bulk films grown on Au(111) at 300 K. The proposed edge-face packing structure of the 6P monolayer has been corroborated by the NEXAFS results and will be described in full detail in a forthcoming paper [32]. An average side-tilt angle of the edge-on 6P molecules of roughly 10–20° was obtained and also a small interring twisting in the molecules of the first half monolayer, similar to recent findings in the literature [33,34].

3.3. 6P dehydrogenation surface reaction

A thorough analysis of the TD spectra of 6P on pure Au(111) shown in Fig. 1 reveals a significant divergence between the total amount of 6P molecules that has been initially adsorbed on the Au surface and the amount that has been thermally desorbed intact from the Au surface during the TD experiments. The former could be quantified with...
the help of a calibrated quartz microbalance, whereas the latter was determined from the integral peak areas of the experimental TD curves. A constant sticking coefficient of unity for 6P at room temperature has been assumed on both the gold sample and the microbalance, as described previously [17]. It appears that for 6P coverages >0.5 ML a total amount of roughly 0.2 nm (equivalent of 1/2 ML 6P or $3.4 \times 10^{13}$ 6P molecules/cm$^2$) is constantly missing in each TD spectrum, as illustrated in Fig. 6 by the circles. Recently, it has been demonstrated that the missing amount of 6P molecules, which does not contribute to the TD signal, is dehydrogenated, where molecular hydrogen (H$_2$) is desorbed and graphitic like carbon remains on the surface [18,19]. The 6P dehydrogenation reaction occurs on the Au surface at temperatures >650 K during the TD experiments. Different from that, almost no 6P dehydrogenation, i.e., no missing amount of 6P molecules in the TD experiments, could be found, if the organic film was grown on a Au(111) surface covered by about two monolayers of graphitic like carbon. This is indicated in Fig. 6 by the triangles. In this case, the linear fit of the data points passes approximately through the origin.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>$a$ (nm)</th>
<th>$b$ (nm)</th>
<th>$\gamma$ (deg)</th>
<th>$\Phi$ (deg)</th>
<th>Matrix notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 ML</td>
<td>1.4</td>
<td>3.2</td>
<td>74</td>
<td>48</td>
<td>(5.3, 4.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(-0.4, 10.9)</td>
</tr>
<tr>
<td>1 ML</td>
<td>1.2</td>
<td>3.3</td>
<td>73</td>
<td>40.9</td>
<td>(4.5, 3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1, 12)</td>
</tr>
</tbody>
</table>

$a$, $b$ denotes the side length of the cell vectors, $\gamma$ the cell angle and $\Phi$ the azimuthal rotation angle with respect to the Au surface (cf. Fig. 4).
3.4. Desorption kinetics and growth of 6P on C-precovered Au(111)

The branching into a dehydrogenation surface reaction instead of thermal desorption of the 6P molecules at elevated temperatures is strongest on the atomically clean Au surface. Performing repeated cycles of 6P adsorption/desorption without sputter cleaning the sample surface between the cycles leads to a step-by-step increase of the surface carbon coverage until saturation is reached after several cycles at a C coverage of about 1.5–1.8 ML (equivalent of 2.1–2.5 $\times 10^{15}$ C atoms/cm$^2$). The C coverage was independently determined with the help of quantitative Auger analysis, as described previously [18]. The steady increase of the surface carbon leads to a changed desorption kinetics of the 6P molecules in the (sub)monolayer regime, as shown in Fig. 7a. Five TD spectra of 0.2 nm 6P films each (equivalent of 1/2 ML) are compared. The films have been grown and consecutively desorbed on/from an initially clean Au(111) surface without intermediate sputter cleaning of the surface. Hence, the integral peak area of the first curve is smallest because most of the adsorbed 6P is dehydrogenated. With increasing carbon pre-coverage the amount of 6P that can desorb intact from the surface increases, but also the shape of the 6P desorption spectrum changes. Whereas for the clean surface only the $\beta_1$ peak is visible, with increasing carbon coverage the $\beta_1$ peak broadens and decreases in favour of an increased $\beta_2$ peak. From our previous work we can attribute the $\beta_1$ peak to lying molecules where the aromatic plane is oriented almost parallel to the substrate surface, whereas the $\beta_2$ peak stems from side tilted molecules on the gold surface. Hence, it can be concluded that on the pure gold surface the flat oriented 6P molecules are preferentially dehydrogenated due to a stronger bonding to the surface. The qualitative change of the shape of the 6P (sub)monolayer TD spectrum also indicates a change of the molecular packing structure from an edge-face to an all-edge packing of only side-tilted molecules. A similar effect has been recently observed for the system $p$-quaterphenyl on Au(111) [18].

Simultaneous to the changed 6P (sub)monolayer TD spectrum we have directly measured the signal of the molecular hydrogen released from the surface as the only reaction product of the 6P dehydrogenation surface reaction, as shown in Fig. 7b. In a previous publication we have demonstrated the dehydrogenation of 6P on various clean...
gold surfaces upon thermal treatment \cite{19} and it has been shown that desorption of molecular hydrogen (H\textsubscript{2}) from the surface (reaction product) can be directly observed during the sample heating. Three distinct hydrogen peaks are observed labelled A–C.

In particular, the dehydrogenation of 6P has been utilized to prepare a 2 ML C/Au(111) surface, which has been used as an alternative substrate for the growth of 6P films. In Fig. 8 the TD data of 6P grown on 2 ML C/Au(111) at 300 K for the (a) monolayer and (b) multilayer coverage regime is shown. Comparing the monolayer TD data with those of 6P grown on the clean Au(111) surface presented in Fig. 1a reveals significant differences. Instead of two separate peaks \( \beta_1 \) and \( \beta_2 \), only one monolayer desorption peak, labelled \( \beta \), is visible for the 2 ML C/Au(111) surface (Fig. 8a). In addition, no distinct second layer desorption peak can be observed. The multilayer desorption energy of 2.2 ± 0.1 eV/molecule, which has been determined for the 7 nm thick film in analogy to the above discussion, is similar to that obtained on the clean Au surface. The energy difference of 0.2 eV is just outside the measuring precision, which makes a clear decision somewhat difficult. But a changed crystal orientation of the films grown on Au(111) + C compared to that on the clean surface may be the reason for the difference. Whereas in the latter case the bulk crystal orientation parallel to the surface is \((21 \bar{3})\), in the former case the (001) crystal plane is parallel to the surface \cite{25}.

For 6P films grown on the C covered Au(111) surface no LEED reflections can be observed as long as the film thickness is in the range of 0.4 nm, which is roughly the nominal thickness of a monolayer comprised of flat lying molecules. However, increasing the film thickness results in a distinct LEED pattern showing concentric rings around the 00 reflection. Fig. 9 shows a representative LEED image of a 2.4 nm 6P film grown on 2 ML C/Au(111) at 300 K, recorded at 16.6 V. This behaviour can be interpreted in terms of regular 6P domains with an arbitrary azimuthal orientation. Similar to the system 4P/C/Au(111) described in Ref. \cite{18} we attribute the ring-like LEED pattern to structural domains with 001 oriented 6P crystallites, i.e., standing molecules. The innermost visible ring corresponds to a value of \( d_{h0} = 0.936 \) nm. Such a periodicity can also be found in the (001) net plane of the 6P bulk structure \cite{31}.

### 3.5. Formation of a 6P intermediate regular overlayer

According to the proposed model for the 6P dehydrogenation on the clean Au(111) surface described in Ref. \cite{19}, an intermediate polycyclic aromatic hydrocarbon (PAH) molecular species \( \text{C}_{48}\text{H}_{22} \) is formed after the first reaction step at a surface temperature between 650 and 750 K, as indicated by the H\textsubscript{2} desorption peak labelled A shown in

![Image](image1.png)

Fig. 8. TDS series of 6P on 2 ML C/Au(111) grown at 300 K. The desorption peaks are labelled \( \alpha \) for the multilayer and \( \beta \) for the monolayer, respectively.

![Image](image2.png)

Fig. 9. LEED image recorded at 19.3 V of a 2.4 nm 6P film grown on a 2 ML carbon covered Au(111) surface at 300 K.
Fig. 7b. Hence, annealing a 6P film grown on Au(111) at a temperature of 690 K (approximately the maximum of peak A) should enable the production of the PAH species on the gold surface. Due to the increased number of π-electrons the PAH molecules should bind stronger to the surface compared to the 6P molecules, while no intact 6P molecule will stay adsorbed on the surface at 690 K. Performing LEED experiments on such a film has clearly shown the existence of distinct diffraction spots, as depicted in Fig. 10 for an initially 2 ML thick 6P film that has been annealed at 690 K for several minutes. However, only one reflection order, presumably the 10 reflections, is observed. Nevertheless, the sixfold symmetric reflections can be attributed to the existence of a regular PAH overlayer.

The chemical structure of the proposed PAH species [19] is schematically illustrated in the lower part of Fig. 10. It should be emphasized here, that the reflections clearly do not stem from the Au surface. The radial distance of the reflections corresponds to a value of $d_{hk} = 0.78$ nm for the interrow distance of molecular rows $hk$. This distance corresponds quite well to the width of the PAH (0.6 nm).

The observed LEED reflections appear rather broad in the recorded LEED images. This may indicate that the size of the regular domains composed of the PAHs is still very small. The domain size can be approximately determined in terms of the number of scattering centres by the ratio of the radial distance of the 10 reflection and its full width at half maximum (FWHM) [35]. Such an analysis of the LEED spots in k-space yields a minimum domain size of about 3–4 nm, which equals a total number of only 4–5 coherent scattering centres equally distanced by about 0.78 nm.

4. Summary

The kinetics and energetics of thermal desorption of 6P thin films grown on clean and carbon pre-covered Au(111) have been determined. On clean gold, three different desorption regimes could be clearly distinguished corresponding to desorption of the first monolayer, second monolayer and multilayer, respectively. The activation energy for thermal desorption, $E_{\text{des}}$, has been experimentally determined for the 6P multilayer and monolayer regime. A significantly different desorption kinetics of the 6P monolayer has been obtained on a Au(111) surface pre-covered by two monolayers of carbon. In particular, only one monolayer desorption peak is observed instead of two distinct monolayer peaks on the clean gold surface. This indicates a change of the molecular packing structure within the 6P monolayer. The latter has been determined with LEED, yielding a well-defined and highly regular 6P monolayer structure on clean Au(111) opposed to a disordered first layer on carbon pre-covered gold, respectively.

A high temperature dehydrogenation surface reaction of 6P adsorbed on Au(111) has been demonstrated. To explain the experimentally observed multi-peak desorption of molecular hydrogen as the only reaction product from the sample surface a multi-step reaction model is proposed. It is demonstrated that a stable and regular overlayer composed of a supermolecular polycyclic aromatic hydrocarbon species (“double 6P molecules”) can be prepared by applying proper annealing to a 6P monolayer film on Au(111).

Acknowledgements

This research project has been supported by the Austrian Science Fund (FWF), project no. P15625. We gladly acknowledge the valuable discussions with R. Resel.

References


Fig. 10. LEED image recorded for an overlayer of “double 6P” polycyclic aromatic hydrocarbon (PAH) intermediates prepared by thermal desorption of a 2 ML 6P film from a Au(111) surface at 690 K. The 00 and 10 reflections are labelled. Below is schematically illustrated the chemical structure of the proposed PAH species.