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The influence of carbon on the adsorption/desorption kinetics and monolayer formation of *p*-quaterphenyl on Au(1 1 1)

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Abstract

The influence of surface carbon on the formation of highly regular thin films of *p*-quaterphenyl (4P) grown on a Au(1 1 1) surface has been investigated in the mono- and multilayer regime by thermal desorption spectroscopy (TDS), X-ray photoelectron spectroscopy (XPS) and micro-channelplate low energy electron diffraction (MCP-LEED) under UHV conditions. A small carbon pre-coverage of 0.03 monolayers (ML) improves the surface mobility of adsorbed 4P molecules with respect to the clean surface by passivating Au surface defects. This enables a highly crystalline 4P film growth even at a low substrate temperature of 93 K. Otherwise, the thermodynamically stable monolayer structure is identical to that on the C-free surface, namely consisting of alternating edge/face packed, lying molecules. The structure of the first 4P monolayer grown on a 0.15 ML C covered Au(1 1 1) surface is different. Only edge-on oriented molecules accommodate in the corresponding surface unit cell. At a C coverage of 0.5 ML the first 4P monolayer is disordered, whereas for higher coverages a highly crystalline structure with upright standing molecules is adopted. Depending on the substrate temperature during film growth the surface carbon causes a different wetting behaviour of the 4P films, resulting in a different mesoscopic film morphology.

Keywords: Thermal desorption spectroscopy; Low energy electron diffraction (LEED); Adsorption kinetics; Quaterphenyl; Gold; Carbon, Surface structure, morphology, roughness, and topography

1. Introduction

Thin films (<1 μm) of conjugated organic materials prepared by vacuum-deposition techniques are still attracting both academic and technical

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interest. The application of such materials in organic (opto)electronic devices has been frequently demonstrated [1–3]. It has been shown, that the film structure strongly influences properties relevant for device fabrication, e.g. the charge carrier mobility [4]. In order to optimize such properties, the preparation of well-defined, highly crystalline organic films is of great importance [5,6]. A commonly used tool for the preparation of tailored organic thin films is the variation of fabrication parameters during film growth, such as the adsorption rate, substrate temperature, -geometry and -chemistry [7–10]. The latter can easily be influenced by applying an adequate adsorbate layer to the original substrate prior to the organic film deposition.

The present study focuses on the model system *p*-quaterphenyl (4P, $C_{24}H_{18}$) grown on a single crystalline Au(1 1 1) substrate. Several surface analytical methods have been applied such as thermal desorption spectroscopy (TDS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and micro-channelplate low energy electron diffraction (MCP-LEED). The influence of a changed substrate chemistry on the adsorption/desorption kinetics and growth of 4P thin films has been investigated in the monolayer (ML) and multilayer coverage regime. The substrate chemistry has been varied by preparing different carbon pre-coverages on the Au(1 1 1) substrate prior to the 4P film deposition. It has been demonstrated that the film morphology and in particular the structure of the interfacing first 4 P monolayer can be tailored by applying different C pre-coverages. Similar to previous findings of 4 P grown on a C-free Au(1 1 1) surface [11,12], the regular first 4P monolayer has been shown to act as a structural pre-stage for the following multilayer growth [13]. To the best knowledge of the authors no comparable investigation on the influence of surface carbon on the organic thin film growth is available in the literature so far. It should be emphasised that the tailoring of the metal/organic interface by surface carbon may have a considerable relevance for the fabrication of optimised contact electrode interfaces.

2. Experimental

All experiments were performed in an ultrahigh vacuum system at a base pressure of about 10^{-10} mbar. A high-purity Au(1 1 1) single crystal was cleaned by Ar^+ ion sputtering (5×10^{-5} mbar, 1 keV) and annealed at 870 K. After the cleaning procedure the Au surface was covered by different amounts of carbon. These C-covered Au(1 1 1) surfaces were used as substrates for the 4P thin film deposition. In particular, 4P films grown on three different C-covered Au(1 1 1) substrates were investigated: 0.03 ML C/Au(1 1 1), 0.15 ML C/Au(1 1 1) and 0.5 ML C/Au(1 1 1). The carbon coverages, which were determined by quantitative Auger spectroscopy, were established by either one of the following methods: (1) 4P dissociation during sample heating: Auger analysis reveals that after a few ML of 4P are adsorbed and thermally desorbed on/from a thoroughly cleaned and annealed Au(1 1 1) surface, small amounts of C remain on the surface. The origin of this C coverage is attributed to the dissociation of 4P molecules pinned to surface defects on the Au(1 1 1) surface. The C atoms partially passivate these defects and after applying several consecutive 4P adsorption/desorption cycles, in our case the C-coverage levels off at about 0.03 ML. This corresponds to a complete passivation of the Au surface defects. (2) Carbon coverages greater than 0.03 ML were prepared by means of X-ray induced dissociation of 4P molecules previously adsorbed on the Au surface: A 5 nm thick 4P film grown at 93 K on Au(1 1 1) was exposed to the MgK_α radiation of our XPS instrument for 30 and 90 min, respectively. Hereafter, the remaining intact 4P molecules were thermally desorbed by heating the sample up to 870 K. C-coverages of 0.15 and 0.50 ML were prepared in this way.

Thin films of 4P were evaporated onto the differently C-covered Au substrates from a home-made quartz glass Knudsen cell. The substrate temperature was 93 and 300 K, respectively, and the deposition rate was 1 ML/min. The total amount of 4P molecules adsorbed on the Au substrate was quantitatively measured in-situ during the deposition process by a quartz micro balance, as described in Ref. [14]. The desorption kinetics was investigated by TDS using an in-line quadrupole mass spectrometer (linear heating rate: 1 K/s, detected mass: 306 amu). Combined XPS and TDS experiments were performed for investigating structural changes of the 4P film upon sample heating prior to desorption. These measurements are denoted by "XPS vs. Temp"—measurements and details on this technique can be found in Ref. [14]. MCP-LEED experiments were performed at 93 K, applying very small electron beam currents (a few nA) and the positions of the diffraction spots were corrected for inherent image deformations caused by the LEED optics.

3. Results

3.1. Adsorption/desorption kinetics

The TDS results of 4P grown on a 0.03 ML C/Au(1 1 1) surface at 93 K are shown in Fig. 1a. To begin with the low coverage regime (curves a–d), the first desorption peak, labelled β_1, appears above 550 K. With increasing coverage the peak maximum shifts to lower temperatures until β_1 is saturated at a mean film thickness of about 0.15 nm. At even higher coverages a second peak, labelled β_2, appears around 380 K which saturates at about 0.3 nm (curve d). Both peaks β_1 and β_2 seem to comprise roughly the same amount of 4P molecules/cm^2. Since the adsorbed 4P molecules desorb intact from the 0.03 ML C/Au(1 1 1) surface these peaks are attributed to first-order desorption from the 4P monolayer. The shift of the peak maxima of both peaks to the low temperature side with increasing coverage indicates repulsive forces acting between neighbouring molecules within the monolayer [15]. At 4P coverages that exceed the saturation coverage of the first monolayer of 0.3 nm, a sharp desorption peak, labelled α, is observed that steadily increases with increasing coverage (see insert of Fig. 1a). Peak α is attributed to zero-order desorption from the multilayer. These TDS results are very similar to those obtained for 4P grown on a C-free Au(1 1 1) surface [12].

The 4P desorption kinetics in the monolayer regime is significantly different on the 0.15 ML C/

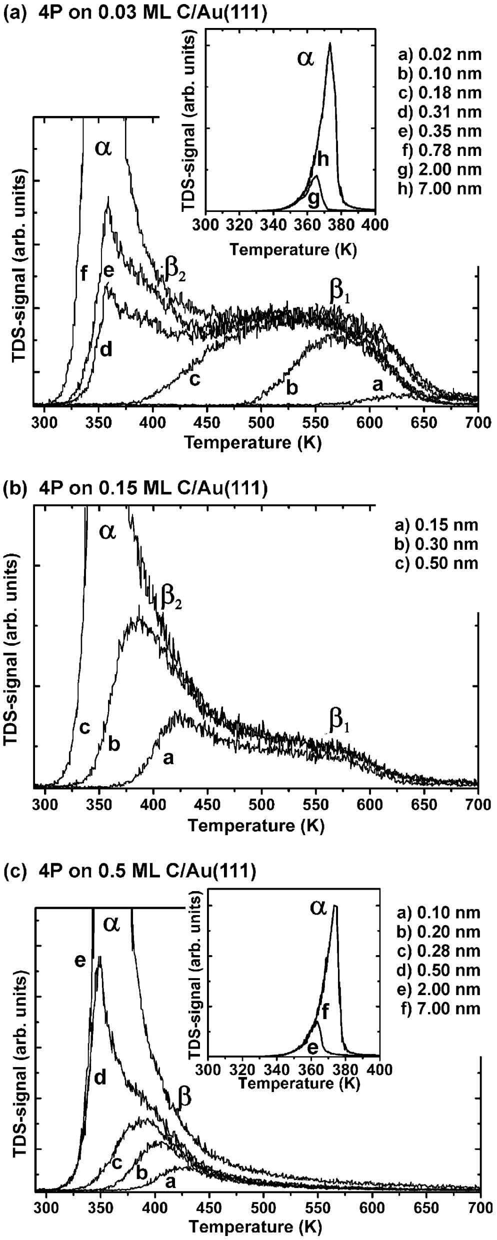

Fig. 1. Series of TD spectra of 4P grown on variably C covered Au(1 1 1) surfaces at 93 K. The monolayer and multilayer desorption peaks are denoted by β and α, respectively. The total amount of deposited 4P for each single TD spectrum is represented as the mean film thickness in nm. (a) TDS-series of 4P on 0.03 ML C/Au(1 1 1). Insert: large scale view at high coverages. On this scale, the monolayer desorption peaks are hardly visible. (b) TDS series of 4P on 0.15 ML C/Au(1 1 1). (c) TDS series of 4P on 0.5 ML C/Au(1 1 1). Insert: large scale view at high coverages.

Au(1 1 1) surface. The corresponding TDS series for 4P grown at 93 K is shown in Fig. 1b. Similar to the previous case, two monolayer desorption peaks, labelled β_1 and β_2, are observed. Although the peaks appear in the same temperature regime as on the 0.03 ML C/Au surface, their saturation coverages are changed. The high temperature monolayer peak, β_1, is significantly decreased in favour of an enhanced β_2 peak, yielding a ratio of β_2:$\beta_1 \approx$ 3:1. The saturation coverage of the full 4P monolayer, $\beta_1 + \beta_2$, however, is roughly the same as in the previous case. Again, the 4P ML saturates at about 0.3 nm of mean film thickness, which equals 8×10^{13} 4P molecules/cm^2.

The decrease of the β_1 peak with an increasing C pre-coverage of the Au(1 1 1) surface is even more pronounced on the 0.5 ML C/Au(1 1 1) surface. The corresponding TDS series is presented in Fig. 1c. At low coverages only a single desorption peak, β, arises in the temperature range between 350 and 450 K, similar to the β_2 peak found for the less C covered surfaces. No second, high temperature 4P monolayer desorption peak exists on the 0.5 ML C/Au surface. But again, the total coverage of the β peak corresponds to a mean 4P film thickness of 0.3 nm. Similar findings were made on a C-covered polycrystalline Au surface [14].

Whereas the desorption kinetics of the 4P monolayer strongly depends on the C pre-coverage, the multilayer desorption regime, α, remains nearly unchanged. Its onset occurs at about 310 K. Independent of the degree of C coverage, the α peaks exhibit a common leading edge, characteristic of zero-order desorption. According to the Polanyi-Wigner formalism a 4P multilayer desorption energy of E_{des} = 1.47 eV was calculated [16]. This is in good agreement to the literature value of 1.62 eV for the 4P sublimation enthalpy [17].

3.2. Multilayer growth kinetics

The growth kinetics of 4P films grown on differently C covered Au(1 1 1) surfaces at different substrate temperatures was investigated with XPS vs. temp. measurements. Fig. 2 shows the temperature dependence of the Au 4f$_{7/2}$ signal for four independently prepared 7 nm thick 4P films grown on 0.03 ML C/Au(1 1 1) and 0.5 ML C/Au(1 1 1) surfaces, respectively. The adsorption temperatures were 93 K for the curves (a) and (c) and 300 K for the curves (b) and (d), respectively. In addition, TD spectra were recorded for equivalently prepared 4P films in order to distinguish between a possible recrystallisation and 4P desorption. As the 4P multilayer TD spectra did not change significantly upon a variation of substrate chemistry or temperature, only one representative spectrum is shown (Fig. 2, curve (e)).

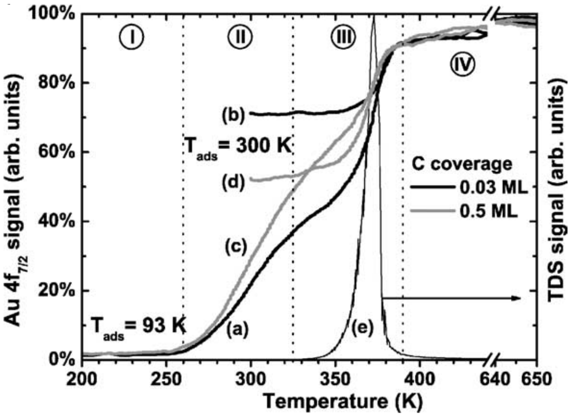

Fig. 2. (a–d) Temperature dependent XPS (Au 4f$_{7/2}$) measurement and (e) TDS measurement of 7 nm thick 4P films grown on variably C covered Au(1 1 1) surfaces at 93 and 300 K, respectively. The adsorption temperature and C pre-coverage of the Au(1 1 1) substrate during the 4P film deposition are (a) 93 K, 0.03 ML C, (b) 300 K, 0.03 ML C, (c) 93 K, 0.5 ML C and (d) 300 K, 0.5 ML C. The temperature range is divided into four regimes, labelled I–IV (see text).

The investigated temperature range can be divided into four regimes according to the degree of structural and/or coverage change of the 4P films. First, the case of adsorption at 93 K is described (curves (a) and (c)). Regime I (<260 K) shows neither a structural change (XPS signal) nor a coverage change (TDS signal). In regime II (260–325 K) the films (a) and (c) show a large change in the Au 4f$_{7/2}$ signal. This is attributed to a structural change (recrystallisation) within the 4P films, since no 4P desorption occurs in this temperature regime. The increasing Au signal indicates the formation of 4P islands, which are becoming higher and at the same time laterally smaller with increasing temperature, hence uncovering larger areas of the Au substrate. Within the temperature regime III (325–380 K) the 4P multilayer desorbs, which results in a further increase of the Au signal to about 90%. Finally, the regime IV (>380 K) covers the 4P monolayer desorption, where a slight and nearly linear increase of the XPS signal can be seen until it reaches 100% of the clean Au surface at about 650 K. In the case of adsorption at 300 K, both curves (b) and (d) exhibit a significantly higher XPS signal than in the previous case, after heating to the same temperature. Moreover, they show nearly no change of the XPS signal in regime II, whereas the qualitative trend within the regimes III and IV is similar to the former case.

3.3. Monolayer structure of 4P on 0.03 ML C/Au(111)

Fig. 3 shows two examples of LEED images obtained for a 0.5 ML (a) and 1 ML (b) thick 4P film recorded at 93 K. The substrate temperature during the film growth was also 93 K. Apparently, 4P forms highly regular (sub)monolayer structures on a 0.03 ML C/Au(111) surface already at low substrate temperatures. The obtained structures are identical to those found for 4P grown on a C-free Au(111) surface, as described in Refs. [11,12]. However, in that case the formation of a regular structure takes place only at room temperature, but not at 93 K.

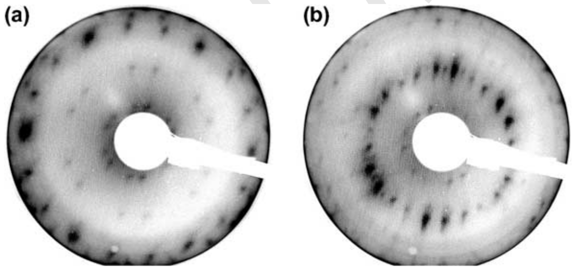

Fig. 3. LEED images recorded for (a) 0.5 ML 4P and (b) 1 ML 4P grown on a 0.03 ML C/Au(111) surface at 93 K. The corresponding beam voltages are 19.2 and 18.7 V, respectively.

3.4. Monolayer structure of 4P on 0.15 ML C/Au(111)

Fig. 4 illustrates the LEED results of the 4P monolayer grown on a 0.15 ML C/Au(111) surface at 300 K and recorded at 93 K. The same LEED patterns have also been observed for 4P films grown at 93 K, but with inferior quality. A deformation free representation of the LEED pattern was gained from extracting the spot positions from several LEED images at different voltages and is shown in Fig. 4c. The dimensions of the corresponding 4P real space surface unit cell are in absolute values: $a = 1.05$ nm, $b = 2.21$ nm, $\gamma = 71°$ and $\Phi = 11°$, where a and b denote the lengths of

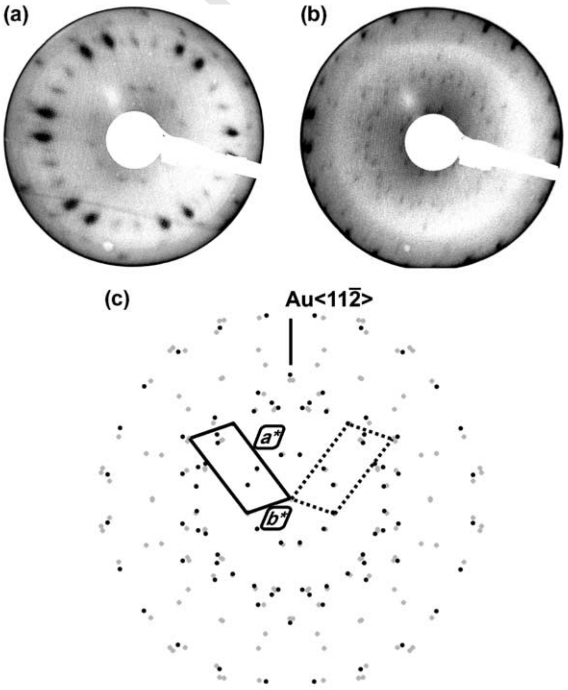

Fig. 4. LEED images of 1 ML 4P grown on a 0.15 ML C/Au(111) surface at 300 K, recorded at (a) 12.1 V and (b) 24.3 V. (c) Representation of the corresponding LEED pattern free of image deformations. Black dots correspond to experimental data, grey dots represent the simulated pattern. The reciprocal surface unit cell is indicated by a solid parallelogram and the reciprocal unit cell vectors are denoted by a^* and b^*, respectively. The dotted parallelogram represents a mirror equivalent of the reciprocal unit cell. The Au$\langle 11\bar{2}\rangle$ direction relative to the LEED pattern is indicated by a short line.

the real space unit cell vectors, γ is the cell angle and ϕ is the azimuthal rotation angle of the cell relative to the Au$\langle 1\bar{1}0\rangle$ direction. The matrix representation of this superstructure is

$$M = \begin{pmatrix} 4.09 & 0.83 \\ 5.61 & 9.03 \end{pmatrix} \approx \begin{pmatrix} 4 & 1 \\ 5.5 & 9 \end{pmatrix}. \quad (1)$$

3.5. Monolayer structure of 4P on 0.5 ML C/Au(111)

The 0.5 ML C/Au(111) surface exhibits the same LEED pattern as a C-free Au(111) surface. No extra spots were observed that could be attributed to a regular carbon superstructure. After the deposition of 1 ML 4P at 93 K or 300 K, no additional LEED spots could be observed, suggesting that 4P cannot form a regular monolayer structure on the 0.5 ML C/Au(111) surface. Instead, the 4P monolayer (wetting layer) seems to be amorphous. However, after increasing the 4P coverage, ring-like structures appear in LEED already at a nominal thickness of 0.6 nm and can be observed up to a mean film thickness of several nm. Fig. 5 shows two examples of LEED images at different beam voltages recorded for a 3 nm thick 4P film grown at 300 K. The origin of these rings is attributed to the existence of highly ordered 4P domains with an arbitrary azimuthal orientation. The lateral size of these regular 4P domains can be up to 700 nm, as observed in recent AFM experiments on a 30 nm thick 4P film grown on 0.5 ML C covered Au(111) [18]. A more detailed analysis of this structure is given below.

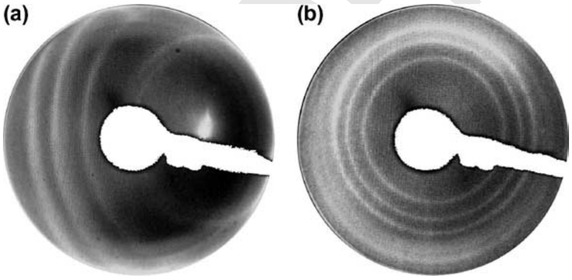

Fig. 5. LEED images of a 3 nm 4P film grown on a 0.5 ML C/Au(111) surface at 300 K. (a) was recorded at 16.6 V with a non-normal incident beam. The specular reflection is clearly visible on the right. (b) was recorded at 52.1 V with normal incidence.

4. Discussion

Before the influence of surface carbon on the 4P layer growth is discussed, we will briefly recapitulate the major results recently found for 4P grown on C-free Au(111) [11,12]. A regular 4P monolayer structure is established only above 270 K. The monolayer comprises two molecules per surface unit cell being oriented with their long molecular axes parallel to the Au surface. The aromatic planes of the molecules are oriented either nearly parallel or side-tilted with respect to the surface (edge-face packing). This overlayer packing is corroborated by TDS results exhibiting two distinct monolayer desorption peaks [12]. The 4P monolayer saturates at about 0.3 nm of nominal film thickness.

As far as the desorption kinetics of 4P is concerned, an additional 0.03 ML C pre-coverage of the Au(111) surface has no significant influence. The experimental results are similar to previous findings for 4P grown on a C-free Au(111) surface. However, the surface mobility of the 4P molecules is considerably enhanced. This can be deduced from the appearance of a regular 4P LEED pattern already at a low monolayer growth temperature of 93 K. Apparently, surface defects on the sputter cleaned and annealed Au(111) surface act as pinning centers for 4P surface diffusion. These defects can either be vacancies, adatoms, kinks, steps or reconstruction "elbows" of the reconstructed Au(111) surface. However, a specific determination of the type of defects was not possible with the applied methods. Small amounts of C can deactivate these defects, which results in a higher mobility of the 4P molecules. Indeed, such small amounts of C stem from dissociation of adsorbed 4P molecules during sample heating. Those 4P molecules pinned to surface defects are no longer able to desorb intact from the surface and thus do not contribute to the TD spectrum. In the case of 4P grown on C-free Au(111), a detailed analysis of the TD peak areas shows that a maximum amount of 2×10^{12} 4P molecules/cm^2 is constantly missing in the TD spectra. This amount corresponds to pinned 4P molecules that dissociate during sample heating. Hence, a C-coverage of about 5×10^{13} atoms/cm^2 remains on the formerly C-free Au(111) surface (surface density of Au(111): 1.4×10^{15} atoms/cm^2). This finding is in good agreement with the coverage of 0.03 ML C obtained by a quantitative Auger analysis after several 4P adsorption/desorption cycles without intermediate sputter cleaning of the surface, as described above. Apart from a different 4P surface mobility, LEED measurements show that on both the C-free Au(111) surface and the 0.03 ML C/Au(111) surface the structure of the 4P monolayer is identical. In that sense, the 0.03 ML C/Au(111) surface could as well be regarded as a "defect-free" Au(111) surface, where all pinning sites are passivated by C atoms and no longer hinder 4P surface diffusion.

Increasing the C pre-coverage to 0.15 ML induces a change of the 4P monolayer structure: the LEED results (see Fig. 4) show a slight change of the dimensions of the 4P monolayer unit cell. Whereas the lengths of the cell vectors, *a* and *b*, and the cell angle, γ, are only slightly changed compared to 4P grown on a C-free Au(111) surface, the azimuthal angle, ϕ, is significantly different. This indicates a new 4P structure. Although from the LEED experiments no proper information on the molecular packing within the 4P monolayer surface unit cell can be derived, a combination of the LEED and TDS data allows a further insight: the TDS monolayer spectrum can be interpreted by a superposition of two different types of 4P monolayer packing domains, denoted "type A" and "type B". The type A domains exhibit both flat and edge-on adsorbed 4P molecules (edge-face packing) similar to the structure found on the C-free Au(111) surface. The flat/edge-on adsorbed molecules contribute in equal shares to the β_1 and β_2 peak, respectively. Consequently, the β_2 peak in Fig. 1b, which correspond to edge-on adsorbed molecules, is attributed to a superposition of two peaks, i.e. $\beta_2 = \beta_{2,\mathrm{A}} + \beta_{2,\mathrm{B}}$. The $\beta_{2,\mathrm{B}}$ peak is attributed to the type B packing domains, which comprise only edge-on oriented 4P molecules. Apparently, this type of 4P domain is by far the dominating one. This is corroborated by the LEED images shown in Fig. 4, where all observed diffraction spots could be attributed to the type B domains. A real space representation of the type B domain structure is shown in Fig. 6. The long molecular axes are oriented nearly parallel to the surface with the aromatic plane being tilted by an angle δ with respect to the Au(111) plane (edge-on), as shown in Fig. 6a. Of course, no information on the tilt angle can be obtained from our experimental techniques. An alignment of the 4P molecules along the Au$\langle 11\bar{2}\rangle$ azimuthal direction similar to previous findings on a C-free Au(111) surface [11] has been proposed. As will be described in a forthcoming paper [13], the dominant type B domain structure typical for the 4P monolayer grown on a

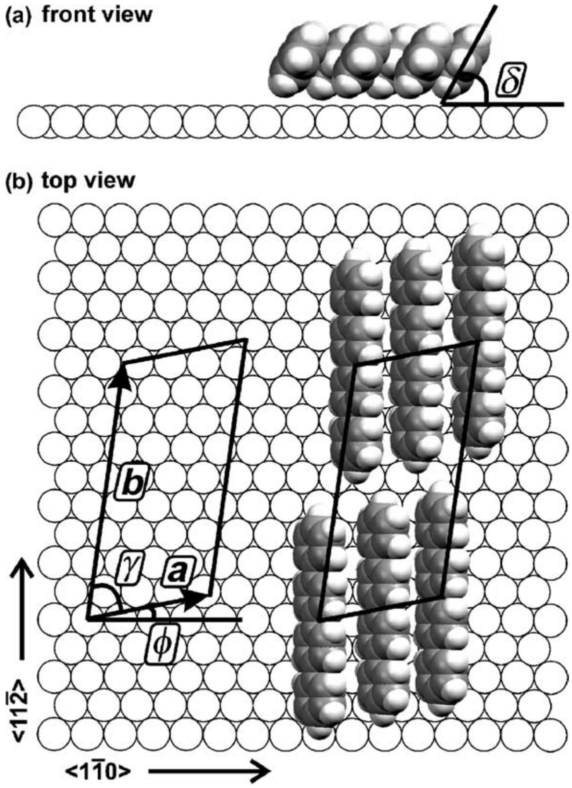

Fig. 6. Real space van der Waals representation of the 4P monolayer structure on a 0.15 ML C/Au(111) surface. The surface unit cell is characterised by the lengths of the unit cell vectors, *a* and *b*, the cell angle, γ, and the azimuthal angle, ϕ. The aromatic planes of the 4P molecules are side-tilted with respect to the Au(111) plane by an angle δ.

0.15 ML C/Au(1 1 1) surface causes thicker 4P films to adopt a crystal orientation with a similar molecular packing structure.

On the 0.5 ML C/Au(1 1 1) the saturation coverage of the full 4P monolayer, β, is again about 0.3 nm, similar to the less C covered Au surfaces. This suggests that the 4 P monolayer again consists of lying molecules, i.e. the long molecular axes are almost parallel to the Au(1 1 1) plane. From the obvious similarity of the shape and position of the β_2 peak on the C-free surface and the β peak on the 0.5 ML C/Au surface, it seems plausible to attribute the peak β to an edge-on adsorption geometry, similar to the former case. The total suppression of the β_1 peak suggests a 4P monolayer exhibiting exclusively edge-on adsorbed molecules. However, the LEED results show that the first 4P monolayer predominantly grows in a disordered manner on the 0.5 ML C/Au(1 1 1) surface. After the first monolayer is saturated, however, with increasing coverage regular 4P domains start to grow. These domains no longer show any preferential azimuthal orientation relative to the C/Au(1 1 1) surface. Hence, ring-like LEED structures are observed, as shown in Fig. 5. Although no complete determination of the corresponding real space surface unit cell is possible, an analysis of the inmost ring observable with LEED at a minimum beam voltage allows a further insight: This particular ring corresponds to the length, b, of the largest possible real space surface unit cell vector of a regular 4P overlayer structure. Assuming a rectangular surface unit cell for a first approximation, a length of $b = 1.1$ nm is obtained. This is significantly smaller than the van der Waals length of a 4P molecule. Therefore, the regular 4P domains responsible for the ring-like LEED structures cannot comprise lying 4P molecules, as found for the less C-covered surfaces. Instead, the 4P molecules are supposed to be nearly "standing upright" with respect to the C/Au surface, i.e. the long molecular axes are oriented roughly normal to the Au(1 1 1) plane. These findings are corroborated by preliminary results from X-ray diffraction experiments for a 30 nm thick 4P film grown on 0.5 ML C/Au(1 1 1), where an upright molecular orientation was found within 4P crystallites in the bulk phase [13]. On a 0.5 ML C/Au(1 1 1) surface the first regular 4P monolayer acts as a structural pre-stage for the further epitaxial growth of thicker 4P films again, similar to the findings on less C-covered Au surfaces.

So far it has been shown that the existence of a C pre-coverage influences the structure of the first 4P monolayer. Additionally, the particular monolayer structure influences the mesoscopic film morphology of several nm thick 4P films, as inferred from the combined XPS/TDS measurements shown in Fig. 2. Here, the influence of the adsorption temperature and/or the carbon pre-coverage on the 4P film morphology can be separately analyzed by comparing the corresponding curves: (1) Adsorption temperature: Both films grown at room temperature, (b) and (d), exhibit a significantly large Au signal at 300 K. The signals remain nearly unchanged upon a further heat treatment until desorption sets in. Hence, independent of the amount of C pre-coverage, a thermodynamically stable 4P island morphology is achieved already at 300 K. This is due to a high surface mobility of the 4P molecules in the multilayer. The 4P islands are highly crystalline, as determined by recent X-ray diffraction measurements [11]. In contrast to that, the surface diffusion is hindered at 93 K, resulting in continuous 4P films, (a) and (c), as indicated by the close to zero Au signal. During the recrystallisation both films (a) and (c) aspire a thermodynamically stable island morphology. However, the corresponding Au signals at 300 K are still significantly lower than for the films initially grown at 300 K, (b) and (d). This indicates a higher degree of wetting. Apparently, both kinetic and thermodynamic effects influence the 4P film morphology. (2) The influence of a C pre-coverage on the film morphology seems to be strongly dependent on the growth temperature. At 93 K the morphology of 4P films grown at 93 K is independent of a C pre-coverage. However, upon heat treatment (regime II) an improved de-wetting is observed in the case of a high C pre-coverage. This is indicated by curve (c) being higher than curve (a) within regime II. Different from that, films grown at 300 K exhibit an opposite trend. Here, a C pre-coverage causes an improved wetting, as indicated by a smaller Au signal of (d) compared to (b) at 300 K. This behaviour is most probably due to an interplay between kinetic and thermodynamic effects influencing the film morphology.

5. Summary

The possibility of tailoring the *p*-quaterphenyl (4P) monolayer structure on a Au(1 1 1) surface by applying different C pre-coverages has been demonstrated, which in turn enables a tailoring of the growth of several nm thick 4P films. Thin 4P films have been grown on various carbon pre-covered Au(1 1 1) surfaces. The C coverages were 0.03, 0.15 and 0.5 ML, respectively. With increasing C coverage a structural change of the 4P monolayer was observed, revealing different molecular packing modes compared to 4P grown on C-free Au(1 1 1). Simultaneously, a significant change of the 4P desorption kinetics was observed, reflecting the different adsorption situations of 4P molecules on variably C-covered Au(1 1 1) surfaces. A C pre-coverage as small as 0.03 ML passivates surface defects on the Au(1 1 1) surface, which significantly increases the surface mobility of 4P molecules in the monolayer. The 4P monolayer structure, however, is identical to that found on a C-free Au(1 1 1) surface. On the 0.15 ML C/Au(1 1 1) surface a coexistence of at least two different 4P monolayer structures has been identified. The predominant structure exhibits a different molecular packing (edge-on adsorbed molecules) compared to previously found structures. Furthermore, the molecular orientation changes from lying to standing upright on a 0.5 ML C/Au(1 1 1) surface. Combined XPS/TDS measurements revealed a strong temperature dependence of the morphology of thicker 4P films (up to 7 nm).

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