

## **ARTICLE IN PRESS**

#### 1 1. Introduction

3 Crystalline organic semiconductors show a huge anisotropy in charge transport as well as in their
5 optical characteristics [1]. Therefore, the performance of these materials in electronic and opto7 electronic devices (e.g. in thin film transistors) depends crucially on the utilization of this
9 anisotropy. Since most of the applications are based on thin films, detailed knowledge about the
11 thin film formation and of the involved growth parameters is essential [2].

13 Quaterphenyl (p-4P,  $C_{24}H_{18}$ ) is an aromatic molecule of the oligo-phenylene series and a

15 frequently studied model system for organic thin film studies [3–5]. Like other rod-like aromatic
17 molecules, p-4P crystallizes in layers of parallel molecules with a layer thickness of approximately
19 the length of one molecule. Within the layers the

aromatic planes are in herringbone arrangement [6]. Theoretical studies reveal that the herringbone

arrangement is formed by electrostatic quadrupole interactions between aromatic molecules which

exceed their van der Waals interactions [7].However, between the layers only van der Waals interactions are present.

27 Thin films of p-4P show a strong tendency to crystallize [3]. Crystallites with upright standing 29 molecules ("end-on") as well as with lying molecules ("edge-on" or "flat-on") are found [4]. 31 In the latter case typical needle-like morphology is observed [5]. Some work has already been done 33 with respect to p-4P thin films on Au(111): the epitaxial growth has been demonstrated [8] and the 35 growth and energetics in the monolayer and in the multilayer regime were also studied [9]. The 37 influence of a carbon layer to the monolayer properties was also investigated [10]. The present 39 work describes the role of the organic-substrate interface in thin film growth: the transition of the monolayer structure to the thin film bulk structure 41

### 43

#### 45 **2. Experimental techniques**

and final morphology.

47 Quaterphenyl thin films were prepared by organic molecular beam deposition (OMBD)

under UHV conditions on defined carbon pre-49 covered Au(111) surfaces [10]. The carbon coverage was 50%, 15% and 3%. Since a low carbon 51 coverage of 3% does not have any influence on the monolayer structure of the film, this surface was 53 treated as a clean Au(111) surface. During the thin film deposition the substrate was kept at a 55 temperature of 300 K and the deposition rate was 0.3 nm/min, controlled by a quartz microbalance. 57 The final film thicknesses were between 20 and 30 nm. 59

X-ray diffraction (XRD)  $\Theta/2\Theta$  investigations (specular scans) were performed partly by a 61 SIEMENS D501 diffractometer using CuKa radiation and a bent secondary graphite mono-63 chromator. Some  $\Theta/2\Theta$  investigations as well as the pole figures were taken on a PHILIPS X'PERT 65 system equipped with an ATC3 Eulerian cradle using CrKa radiation. A flat graphite monochro-67 mator was used on the secondary side which was transparent for  $\lambda = CrK\alpha$  and also for wave-69 lengths of  $\lambda/2$ ,  $\lambda/3$  ... (higher harmonics). In addition to the low scattering signal of the organic 71 film, scattering of higher harmonics on the gold single crystal substrate was observed, too. The X-73 ray diffraction pole figures were taken in Shultz reflective geometry. The pole figures were mea-75 sured in  $\psi/\phi$  steps of  $1^{\circ}/3^{\circ}$ , respectively; the measurement time for each  $\psi/\phi$  pair was 12 s. 77 The crystallographic software POWDERCELL was used to determine  $2\Theta$  values and intensities 79 of the diffraction peaks [11]. Spherical projections of the crystal structures and their comparison with 81 the experimental pole figures were performed by STEREOGRAM [12]. The simulations were per-83 formed on the basis of the room temperature structure of p-4P (a = 8.11 A, b = 5.61 A, 85  $c = 17.91 \text{ \AA}, \beta = 95.8^{\circ}$ ) which represents a flat molecular conformation (all four phenyl rings are 87 arranged in one plane) [13]. The crystal structure of Au is taken as face-centred cubic with 89  $a = 4.0784 \,\mathrm{A}.$ 

Atomic force microscopy (AFM) was performed 91 with a Digital Instruments Multimode IIIa scanning probe microscope equipped with a 93  $100 \,\mu\text{m} \times 100 \,\mu\text{m} \times 5 \,\mu\text{m}$  scanner. The measurements were performed in tapping mode under 95 ambient conditions. A low scan speed had to be

## **ARTICLE IN PRESS**

 applied to image the three-dimensional crystallite shape with high precision. To quantify the vertical
 film roughness, the rms roughness was calculated as the average of three independent images up to
 50 μm × 50 μm size.

7

#### 3. Experimental results

9 Specular scans have been performed on all 11 samples in order to detect the crystallographic planes of the p-4P crystallites which are parallel to the surface of the substrate. Additional to the 13 strong 111 reflection of gold, weak reflections of p-15 4P have been observed. Fig. 1 shows three specular scans of p-4P films prepared on differently carbon 17 covered Au(111) surfaces. For p-4P grown on the clean Au(111) surface, a single peak is observed at 19  $2\Theta = 42.23^{\circ}$  which corresponds to an interplanar distance of d = 3.18 A. This peak is identified as 21 the 211 reflection of p-4P (Fig. 1a). Based on the knowledge of the arrangement of the molecules 23 within the unit cell of the quaterphenyl crystal structure, it can be concluded that the (211) plane 25 represents molecules facing the aromatic plane parallel to  $(111)_{Au}$  (flat-on). The film grown on 27 the 15%C surface shows a dominant reflection at  $2\Theta = 34.67^{\circ}$  (Fig. 1b) which corresponds to 29 d = 3.84 A. This peak is assigned to the 201 reflection, and it represents crystallites which are 31 built by molecules which have "edge-on" orientation relative to the substrate. Additionally, this 33 sample shows a weak trace of 211 at  $2\Theta = 42.23^{\circ}$ . The specular scan of the film grown on the 50% carbon covered surface is shown in Fig. 1c. A peak 35 at  $2\Theta = 5.15^{\circ}$  (interplanar distance d = 17.8 A) 37 and higher order reflections of this peak are observed. This peak series is assigned to the 00L 39 reflections of p-4P crystallites, since the peak positions as well as the peak intensities (including 41 the missing 005 reflection) fit well to the calculated values. The observation of this peak series reveals that the orientation of the p-4P molecules within 43 the bulk of the film is "end-on" relative to the 45 substrate. In all three films the observed peaks can be identified unambiguously from the room 47 temperature structure of p-4P; no traces of other polymorph structures have been found.



Fig. 1. Specular scans of quaterphenyl films grown on (a)a clean Au(111) surface, (b) on the Au(111) surface which was covered by 15% with carbon (c) and on the Au(111) surface 50% covered by carbon. The scans depicted in (a) and (b) were measured with CrK $\alpha$  radiation; in case of (c) CuK $\alpha$  was used. 89

91

Pole figures were taken at the calculated  $2\Theta$ positions of the strongest reflections of the p-4P 93 crystal structure. Fig. 2 shows pole figures of the 110 reflection taken from the film grown on clean 95 Au(111) surface (Fig. 2a) and of the film grown on

### **ARTICLE IN PRESS**



Fig. 2. X-ray diffraction pole figures of the 110 reflection of quaterphenyl films prepared on a clean (a) and a carbon covered (15%) Au(111) surface (b) Full circles give the ψ-angle in steps of 15°, and dashed lines give the measurement limits. Enhanced pole densities are marked by black areas, and crosses denote intensity arising due to the Au(111) substrate.

- 39 15% C surface (Fig. 2b). High intensities arising due to diffraction of higher harmonics on the gold
- 41 single crystal substrate are marked by crosses. Fig. 2a shows individual areas of enhanced pole 43 densities (EPD) at  $\psi = 22^{\circ}$ . Pairs of EPD are
- clearly visible; one of these pairs is marked in Fig.
  2a by a dotted ellipse. The fact that individual spots
- are observed leads to the conclusion that an inplane alignment of the p-4P crystallites is present.
- In agreement with previous results [8] it is

concluded that the long axes of the p-4P molecules 49 are parallel to  $[1\bar{1}0]_{Au}$  and  $[11\bar{2}]_{Au}$  (and their symmetry equivalent directions). The alignment of 51 the molecules (in the bulk of the film) with respect to the clean Au(111) surface is shown in Fig. 3a. 53 The molecules are projected along their long axes; the arrow  $(\otimes)$  denotes the direction of the long 55 molecular axes. Due to the herringbone arrangement of the molecules within the bulk structure, 57 only every second molecule is oriented "flat-on". The second half of the molecules is oriented "edge-59 on" which results in an "edge-face" packing of the molecules within the epitaxially ordered film. Note 61



Fig. 3. Orientation of the molecules relative to the surface for the three observed cases: (a) the "flat-on" alignment on the clean Au(111) surface, (a) the arrow ( $\otimes$ ) denotes the long molecular axes aligned along  $\langle 110 \rangle_{Au}$  and  $\langle 112 \rangle_{Au}$ , (b); the "edge-on" alignment on a 15% carbon covered Au(111) surface and (c)the "end-on" alignment on a Au(111) surface covered 50% by carbon .

### **ARTICLE IN PRESS**

 that the 211 plane which is parallel to the surface of the substrate does not represent a densely packed
 crystal plane of the p-4P bulk structure.

The 110 pole figure of the sample prepared on 5 the 15% carbon covered surface reveals a ring-like structure of the EPD at  $\psi = 56^{\circ}$  (Fig. 2b). The 7 presence of a ring instead of spots of EPDs reveals the loss of in-plane alignment of the crystallites. 9 Fig. 3b gives the alignment of the molecules in the bulk as concluded from the specular scan: their 11 long molecular axes are parallel to the surface of the substrate and their aromatic planes are tilted by  $32^{\circ}$  relative to the surface of the substrate 13 ("edge-on"). The pole figure reveals that no 15 distinguishable directions of the long molecular axes along the surface of the substrate are present.

The experimental result on the babshute dre present.
The experimental result on the thin film grown on the 50% C surface reveals that the long axes of
the molecules are approximately perpendicular to the surface of the substrate ("end-on"); in detail
they enclose an angle of 17° to the surface normal of Au(1 1 1) as depicted in Fig. 3c. Since the strong
diffraction peaks of the p-4P structure are at *ψ* angles larger than 75°, no clear results have been obtained in the pole figure investigations.

In Fig. 4, representative 50 µm × 50 µm AFM
images of the film morphology as a function of the carbon coverage are shown. Fig. 4a gives the
morphology of the film grown on the clean Au(111) surface which had a nominal thickness
of 20 nm. The morphology is dominated by p-4P needles with widths from 500 nm up to 4 µm and

33

heights of up to 200 nm. This results in an rms 49 roughness of 51 nm. Although the needle growth is disturbed by scratches on the surface, there are 51 strong indications that only a limited number of needle orientations (at least 12 in this image) are 53 allowed. Fig. 4b shows the morphology of the film grown on the 15% C surface with an average film 55 thickness of 30 nm. The resulting morphology consists of needles and plate-like structures. The 57 typical width of the features is 1 µm for the needles and several µm for the plates. The height analysis 59 reveals a non-uniform height distribution with peaks at 60, 90 and 120 nm [14]. The rms rough-61 ness is reduced to about 43 nm.

The morphology of the film grown on the 50% 63 C surface is depicted in Fig. 4c, and the average film thickness is 30 nm. The Au surface is covered 65 by a smooth film of p-4P with an rms roughness of 8 nm. The corrugation of the film is caused by 67 small hillocks with an average separation of 800 nm. The relative height of these hills with 69 respect to the surrounding surface level is around 20 nm. Detailed scans reveal that the hillocks are 71 of terrace-like nature with a typical step height between the terraces of 1.7 nm corresponding to 73 one molecular length.

#### 75

77

81

#### 4. Discussion

In a previous surface science study it was found 79 that the clean Au(111) surface and the Au(111)



 $\frac{47}{15\%} \frac{\text{Fig. 4. 50 } \mu\text{m} \times 50 }{15\%} \text{ carbon covered Au} (111) \text{ surface and (c) on a 50\%} \text{ carbon covered Au} (111) \text{ surface . For (a), (b) and (c) the z-scale is 500, 300 and 150 nm; the nominal film thickness is 20, 30 and 20 nm, respectively.} 95$ 

### **ARTICLE IN PRESS**

- surface with 3% carbon coverage show different surface mobility of p-4P molecules but the same
   monolayer structure at room temperature [10].
- The proposed alignment of p-4P molecules on the 5 Au(111) surface fit excellently to our XRD results: the molecules are oriented "flat on" and
- 7 aligned along in-plane directions on the Au(111) surface:  $\langle 1 \bar{1} 0 \rangle_{Au}$  and  $\langle 1 1 \bar{2} \rangle_{Au}$ .
- 9 Also the experimental findings at the 15% carbon covered Au(111) surface fit well to our results. The "edge-on" orientation observed for molecules at the monolayer is confirmed in the bulk. However, the alignment of the long mole-
- cular axes with respect to the Au(11) surface is
- 15 less pronounced. While the LEED (low energy electron diffraction) studies reveal an in-plane
- alignment of the long molecular axes of p-4P,
  within our pole figures (Fig. 2b) a random
  orientation of the long molecular axes is formed.
- Despite the low intensity in the pole figure (Fig. 21 2b) the expected 24 distinct areas of EPDs for epitaxially aligned p-4P crystallites are not ob-23 served.
- The formation and structure of the first monolayer on the clean Au(111) and 15% carbon covered Au(111) surface reveals the same molecular orientation as it is received in this work from XRD investigations. This leads to the conclusion that the orientation of the molecules at the inorganic/organic interface determines the formation (and orientation) of p-4P crystallites within the bulk of the thin film.
- The observation of a needle-like morphology of the film grown on pure Au(111) and on the 15%
  carbon covered Au(111) surface can be explained
- by the molecular orientation within the first 37 monolayers in combination with the crystallographic properties of p-4P. Since it is known that
- the energy gain for a single aromatic molecule is highest by arranging itself within a herringbone
  laver, the herringbone laver of the p-4P crystallites
- 41 layer, the herringbone layer of the p-4P crystallites continues along the needle axis resulting in an
- 43 alignment of the long molecular axes of p-4P approximately perpendicular to the needle axis.
   45 Starting the growth of crystallites from the
- 45 Starting the growth of crystallites from the orientation of the molecules at the first monolayer,47 the herringbone layer grows in two dimensions:
- one dimension along the needle axis (along the

surface of the substrate) and the second dimension 49 perpendicular to the substrate surface. The anisotropic sticking of the p-4P molecules to already 51 existing crystallites results in a needle-like morphology. The needles are huge in length and show 53 considerable height. A similar feature is observed in sexiphenyl thin films [15]. p-4P films grown on a 55 50% carbon coated Au(111) surface show a crystalline orientation with "end-on" molecules 57 (compare Fig. 3c). This molecular orientation explains the morphology: the herringbone layers 59 grow in the two dimensions of the substrate surface. It results in a relatively smooth thin film 61 surface with a terrace-like structure with a typical step height of one molecular length [14,16]. 63

The growth of p-4P on the clean Au(111) surface can be classified as epitaxially ordered, 65 since the crystallites in the p-4P film show an inplane alignment with respect to distinguishable 67 crystallographic directions on the Au(111) surface. The monolayer structure of p-4P molecules 69 ("flat-on" orientation of the molecules and an alignment along  $\langle 1\bar{1}0 \rangle$  (and  $\langle 11\bar{2} \rangle$ ) acts as 71 template for the subsequent film growth. All possible crystal orientations (and alignments) 73 which could grow around such aligned molecules are present: for molecules aligned along one 75 direction, totally four crystal alignments are 77 observed.

The situation is different for the crystal growth 79 on the 15% and 50% carbon covered Au(111)surface. In these two cases the (201) and the (001)plane, respectively, are formed parallel to the 81 surface of the substrate. These planes are densely packed planes (cleavage planes) of p-4P crystal-83 lites. This is a clear hint that the intermolecular interactions dominate the formation of the crystal-85 lites on the 15% and 50% carbon covered surface. Obviously, the carbon coverage reduces the inter-87 action between the substrate and the p-4P molecules. In addition, the transition from three-89 dimensional crystallites to terrace-like hillocks caused by increasing the carbon coverage is 91 accompanied by a significant reduction in the films rms roughness (from about 50 nm for the 93 bare Au(111) surface to 8 nm for the 50% C 95 surface.

### **ARTICLE IN PRESS**

35

#### 1 5. Conclusion

- This work shows that small amounts of carbon on the Au(111) surface have drastic consequences
  to the orientation of the quaterphenyl (p-4P) crystallites as well as to the thin film morphology.
  Evaporation of p-4P on a clean Au(111) surface results in epitaxially oriented p-4P crystallites and molecules "flat-on" the surface of the substrate. A
- 15% carbon coverage of the Au(111) surface changes the orientation of the crystallites to the
- (201) plane parallel to the Au(111) surface with
   an orientation of the molecules "edge-on" within
- crystallites. The typical morphology of the p-4P films at these low carbon coverages at Au(111)
- surfaces is needle-like. The formation of needles is a consequence of anisotropic sticking of the
- molecules to the already existing p-4P crystallites.
  50% carbon coverage of the Au(111) surface leads to upright standing p-4P molecules ("end-
- 21 on") with the typical terrace-like morphology. Since the anisotropic sticking happens at the edges
- 23 of the terraces a quasi-two-dimensional growth appears with comparable smoother surface rough-
- 25

ness.

27

29

#### Acknowledgements

This work was supported by the Austrian 31 Science Foundation (FWF) within the project cluster "Highly Ordered Organic Epilayers".

33

#### References

- N. Karl, Charge carrier mobility in organic crystals in organic electronic meterials, In: R. Farchioni, G. Grosse (Eds.) Springer Series in Materials Science, Berlin, 2001.
- [2] S. Forrest, Chem. Rev. 97 (1997) 1793.
- [3] D.J. Gundlach, Y. -Y. Lin, T.N. Jackson, D.G. Schlom, 39
   Appl. Phys. Lett. 71 (1997) 3853.
- [4] L. Athouel, R. Resel, N. Koch, F. Meghdadi, G. Froyer, 41 G. Leising, Synth. Met. 101 (1999) 627.
- [5] F. Balzer, H. –G. Rubahn, Surf. Sci. 507–510 (2002) 588. [6] C. Davirnin, A. Crowaratti, Acta Crowtallogr, B 45 (1090).
- [6] G. Desiraju, A. Gravezzotti, Acta Crystallogr. B 45 (1989)
   473.
- [7] D.E. Williams, Y. Xiao, Acta Crystallogr. A 49 (1993) 1. 45
- [8] S. Müllegger, I. Salzmann, R. Resel, A. Winkler, Appl. Phys. Lett. 83 (2003) 4536.
   47
- [9] S. Müllegger, I. Salzmann, R. Resel, G. Hlawacek, C. Teichert, A. Winkler, J. Chem. Phys. 121 (2004) 2272.
  [10] S. Müllegger, A. Winkler, Surf. Sci. 574 (2005) 322.
  [49]
- [10] S. Müllegger, A. Winkler, Surf. Sci. 574 (2005) 322.
- [11] W. Kraus, G. Nolze, J. Appl. Crystallogr. 29 (1996) 301.
- [12] I. Salzmann, R. Resel, J. Appl. Crystallogr. 37 (2004) 1029. 51
- [13] Y. Delugeard, et al., Acta Crystallogr. B 32 (1976) 702.
- [14] G. Hlawacek, C. Teichert, S. Müllegger, R. Resel, A. Winkler, Synth. Met. 146 (2004) 383.
- [15] A. Thierry, J.C. Wittmann, B. Lotz, V. da Costa, J. Le Moigne, M. Campione, A. Borghesi, A. Sassella, H. Plank, 55
   R. Resel, Org. Electron. 5 (2004) 7.
- [16] T. Mikami, H. Yanagi, Appl. Phys. Lett. 73 (1998) 563. 57
  - 59