Substrate structure dependence of the growth modes of p-quaterphenyl thin films on gold

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Abstract

The variably oriented crystallite surfaces of a recrystallized polycrystalline gold sample served as substrates for the investigation of the structure dependence of p-quaterphenyl (4P) thin film growth. The films were prepared in ultrahigh vacuum by organic molecular beam evaporation. Optical microscopy, scanning electron microscopy, combined with laterally resolved electron backscatter diffraction and scanning tunnelling microscopy have been applied to determine the correlation between the substrate surface structure and 4P film morphology. Crystallite surfaces consisting of (110) terraces favour highly anisotropic needle like 4P growth with the needle orientation normal to the Au \(<1\bar{1}0>\) directions. Atomic steps on vicinal planes with narrow terraces (< 2 nm) can also induce anisotropy in the 4P thin film growth, in particular elongated 4P islands normal to the step direction. In contrast to that, a nearly isotropic distribution of the needle orientations is observed on Au grains terminated by highly symmetric (111) or (100) crystal planes. Additionally, patches of continuous 4P layers can be found on these surfaces. There is strong evidence that the 4P molecules within the needle like crystallites are oriented parallel to the Au surface, whereas for the continuous layers the 4P molecules are oriented nearly upright on the surface.

Keywords: Organic substances; Evaporation; Scanning electron microscopy; Surface structure
1. Introduction

The application of thin organic films for electronic and opto-electronic devices has attracted considerable interest in the recent past [1]. The growth of organic semiconductors on different surfaces is a widespread topic of recent investigations [2]. The large number of organic compounds available provides the opportunity to tailor the specific device properties. An important issue in this context is the ability to manipulate the thin film structure and morphology. This has been pointed out frequently in the literature [1,3,4], however only little systematic work has been done so far in this context. Among the multitude of organic materials available p-phenylene oligomers are promising candidates for optoelectronic applications [5]. In this work we have focused on the thin film morphology of p-quaterphenyl (4P, C_{24}H_{18}) on gold surfaces as function of the substrate structure. Gold is commonly used for contact electrodes in organic semiconductor devices. In order to figure out the importance of the substrate structure on the layer growth, well defined single crystal surfaces are frequently used as substrates. Experiments of this type are typically carried out under ultra-high vacuum (UHV) conditions. To investigate the surface structure dependence of the organic layer growth on the orientation of a large number of various low indexed and/or vicinal planes is a very time consuming task. Therefore we have chosen a different method to obtain a large amount of information on the substrate/film structure dependence in a comparably short time: Proper sputtering/annealing of a thin polycrystalline gold foil in UHV results in a microcrystalline sample with a great variety of differently oriented, but well defined crystallite surfaces. Evaporation of the organic film on this sample surface reveals immediately the pronounced crystallite surface dependence of the film growth. Measurement of the orientation of the individual substrate crystallites by electron backscatter diffraction
EBSD) provides the correlation between the substrate structure and the 4P film morphology for a large number of different Au crystallites simultaneously. A great variety of 4P film morphologies on gold has been observed: Highly anisotropic needle like islands, less anisotropic islands but with even longer needles, continuous films with high wetting character and crystal surfaces with very little coating with the organic film. These results should contribute to a better understanding of the layer growth of 4P on gold in particular and on the tailoring of organic thin films in general.

2. Experimental

The formation of thin 4P films on the gold surface was carried out under ultra-high vacuum (UHV) conditions, using organic molecular beam evaporation (OMBE) [6]. A recrystallized gold foil (10 x 10 x 0.1 mm$^3$) at room temperature was used as substrate. For proper recrystallization the foil was repeatedly annealed at 1000 K in ultra-high vacuum by Ohmic heating and sputtered by Argon ions (1 kV, 5x10$^{-5}$ mbar) until an atomically clean surface was obtained. Auger electron spectroscopy was used to verify the purity of the sample surface. Optical microscopy (OM) revealed the development of a microcrystalline Au substrate with grain diameters ranging from 50 µm to 200 µm. 4P was evaporated onto the sample surface from a home made quartz glass Knudsen cell at room temperature. The evaporation rate was 0.3 nm/min. The amount of evaporated material was measured in-situ by a quartz microbalance.

The morphology of the sample surface and the thin film morphology were investigated ex-situ at room temperature with different microscopic techniques. An MZ12 (Leica Inc.) optical stereo microscope with coaxial sample illumination, a JSPM-4500S (JEOL Inc.) combined scanning tunnelling and scanning electron microscope (STM/SEM) and a Gemini DSM 982
(Zeiss Inc.) scanning electron microscope were applied. The STM images have been recorded with W tips in constant current mode under ultra-high vacuum conditions. The Gemini SEM was equipped with an EBS (electron backscatter) detector which allowed the determination of the crystal orientation of the individual Au grains with respect to the macroscopic sample surface. Except for the STM, these measurements have been performed on the already coated samples. But since the electron backscatter coefficient increases strongly with the atomic number of the material and the information depth of the EBS is much larger than the thickness of the organic film, nevertheless the orientations of the crystalline gold grains have been measured. The signal from the organic film contributes only to the background of the EBSD patterns.

3. Results and discussion

The morphology of a nominally 30 nm thick 4P film evaporated on the recrystallized gold sample was investigated in detail. An optical micrograph of this film which already contains the main features of the film morphology is depicted in Fig. 1a. The dark areas represent the 4P crystallites. Apparently, the 4P thin film growth proceeds in quite different ways on the individual Au grains. Only in a few instances the 4P film covers smoothly the gold surface. In the case of elongated 4P island formation a strong azimuthal alignment can be seen. The uncovered areas of individual Au grains show the same brightness in OM, demonstrating that the terminating surface planes of all grains are nearly parallel to the macroscopic sample surface. Fig. 1b shows an SEM image of a selected section of the same film at higher magnification. In the area labelled A several μm long needle like 4P crystallites are visible. Their azimuthal alignment is not pronounced, although several preferential orientations seem to exist. The crystallites are not uniformly distributed over the surface. Instead, bunches of several tens of 4P crystallites exist. These bunches are separated by rather wide “denuded” areas (several μm) which are not covered by crystallites. Only about 40 % of the type A grain
surface is covered with 4P crystallites. In area B a highly anisotropic island growth is observed, where the individual crystallite needles are aligned along a single preferential direction. No pronounced bunching of the crystallites is observed. Roughly 60% of the type B grain surface is covered by 4P. In contrast to that, in area C more than 90% of the surface is covered by a continuous 4P film. The growth of discrete crystallite needles seems to be suppressed on this Au grain surface.

In order to gain a more detailed understanding of the shapes of 4P crystallites formed on individual Au grains, high resolution SEM images were recorded. In Figs. 2a and 2b two SEM images with different magnifications are depicted, which correspond to area A in Fig. 1b. It turns out that the needle like islands actually consist of individual 4P crystallites which are connected and aligned along a preferential direction. The regular shape and strict azimuthal alignment of those individual 4P crystallites indicates a highly regular orientation of the 4P molecules within the 4P crystallites. Furthermore, all the individual needles have roughly the same width of 0.5 - 1 µm and are of similar height, as observed in previous AFM investigations [8]. A closer inspection of Fig. 2a reveals that several predominant needle orientations exist, which differ roughly by integer multiples of 15°. This strongly indicates that the single crystal surface of the gold grain acts as template for the 4P crystal growth. The strong azimuthal dependence of the 4P crystallites indicates that those needle like 4P crystallites consist of regularly arranged 4P molecules aligned with their long axes parallel to the substrate surface. Indeed, recent investigations by low energy electron diffraction (LEED) and X-ray diffraction (XRD) of 4P thin films grown on Au(111) have shown that the 4P molecules in the needle like crystallites are oriented with their long axes parallel to the substrate surface [7]. Furthermore, it has been shown that the molecules can either arrange parallel to the Au $<1\overline{1}0>$ or $<1\overline{1}2>$ direction, respectively.
The quite different behaviour of film growth in area C of Fig. 1b (continuous film) is more
clearly represented in the high resolution SEM images of the Figs. 2c and d. In this case a
small amount of needle shaped 4P islands coexists with large areas covered by continuous
layers resembling 4P terraces (see Fig. 2c). These terraces are of arbitrary shape and seem to
be very flat. A close-up picture shown in Fig. 2d reveals the characteristic terrace steps, as
indicated by the arrow. Although we cannot determine the step height with SEM, recent
atomic force microscopy (AFM) investigations have shown that these terrace steps are about
1.8 nm high [8]. This is in good agreement to the long side of the 4P crystal unit cell (c = 1.79
nm) [9], indicating that the 4P terraces consist of nearly upright standing molecules, i.e. the
4P (001) plane is parallel to the substrate surface. In contrast to that, the needle like 4P
crystallites are mainly composed of flat lying molecules (see Fig. 2a and 2b), as described
above. Actually, recent XRD investigations of 4P films grown on a carbon covered Au(111)
surface have yielded a crystal structure with 4P molecules oriented nearly normal to the
surface [10]. This demonstrates that not only the surface crystal structure but also the
chemical composition of the surface is of considerable importance for the layer growth.
Therefore, the continuous 4P terraces observed on some areas could be caused by some
amount of segregated carbon at the substrate surface, which could not be totally removed by
the cleaning procedure.

The most important challenge in this context is to find out the relationship between the
substrate crystallography and the correlated 4P film growth modes. For this purpose we have
carried out laterally resolved electron backscatter diffraction measurements on the same film.
The results for a small section of the sample surface are depicted in Figs. 3a and 3b. In Fig. 3a
again the SEM image shows individual gold grains, which are covered with characteristically
shaped 4P islands/terraces. Fig. 3b represents an orientation map (inverse pole figure map,
[001]) of the individual substrate grains of the same surface area with respect to the
macroscopic sample surface. Firstly, each individual Au grain (numbered from 1 through 13) appears as one homogeneous single-crystalline entity of uniform crystal orientation. Sharp grain boundaries can be observed between the Au grains. Secondly, a distinct correlation between the individual Au grains with their specific grain orientation (orientation map) and the corresponding 4P film morphology (SEM image) can be clearly observed. For the determination of the absolute Au grain orientation a reference frame was chosen by calibration with a Si single crystal reference specimen. Accordingly, the fcc(100) plane is parallel to the macroscopic sample surface and the [100] direction is parallel to the vertical axis of Fig. 3a. From EBSD one directly obtains the orientations of the individual Au grains relative to the reference frame, which are represented by their Euler angles \([11]\). For a given set of Euler angles the corresponding Miller indices \((hkl)\) of the characteristic set of crystal planes of the Au grain, which are oriented parallel to the sample surface, can be calculated \([11]\). Those are either in close vicinity to or even identical to the actual terminating surface planes of the Au grains. In table 1 the Euler angles, \(\varphi_1, \phi, \varphi_2\), the corresponding Miller indices, \((hkl)\), of the crystal planes parallel to the surface and the azimuthal directions, \([uvw]\), parallel to the [100] direction of the reference frame are compiled for the individual Au grains 1 through 13. The colouring of the grains in Fig. 3b shows the orientation of the respective grains according to the associated colour triangle in Fig. 3c. In Fig. 3a white bars indicate the azimuthal orientations of the dense packed \(<1\bar{1}\bar{0}>\) directions for each individual Au grain.

We will start the discussion of the relationship between the orientation of the individual Au grains and the corresponding 4P morphologies with the grains #2 and #8. The corresponding Miller indices of these two grain surfaces parallel to the macroscopic sample surface are quite different, i.e. \((0\ 10\ 9)\) for grain #2 and \((\overline{3}\ \overline{2}\ 10)\) for grain #8, respectively. However, the 4P film morphology on both grains is very similar, as shown in Fig. 3a. Both grains exhibit a
growth of long needle-like 4P islands aligned along a single direction. The common feature of these grain surfaces is that the Au $<1\bar{1}0>$ direction is oriented in nearly the same way. On both grains the orientation of the 4P islands is preferentially perpendicular to the $<1\bar{1}0>$ direction. Figs. 4a and 4c show sphere models of these two surface orientations. The $(0\ 10\ 9)$ plane consists of 2.4 nm wide (011) terraces where the step edge orientation is normal to the $<1\bar{1}0>$ direction. Apparently, this configuration is an ideal template for the oriented growth of 4P molecules. The Van der Waals dimensions of a 4P molecule are 2.04 x 0.67 x 0.35 nm$^3$. Therefore, the 4P molecules can easily accommodate on a terrace when oriented with their long axis along the dense packed $<1\bar{1}0>$ direction. It has been demonstrated for the system 4P/Au(111) that the orientation of the first monolayer determines the arrangement of the molecules in the multilayer and hence the morphology of the multilayer [12]. The sphere model of the surface plane of grain #8, which exhibits a similar 4P morphology as grain #2, is depicted in Fig. 4c. The $(\bar{3}\ 10\ 2)$ plane dominating this structure does not exhibit a clear step-terrace structure, but again the dense packed Au $<1\bar{1}0>$ rows act as a template for the monolayer growth of 4P. Grain #4, with a surface orientation $(2\ 2\ 5)$, also shows a pronounced anisotropic 4P growth. Again, the 4P needle directions are normal to the Au $<1\bar{1}0>$ direction (compare Figs. 3a and 4b). In this particular case the Au $<1\bar{1}0>$ direction is identical to the step direction of this vicinal plane. The terrace width is only 0.5 nm, which is quite small to accommodate the short axis of a flat lying 4P molecule. This might lead to a larger strain within the 4P film resulting in shorter needles compared to the former case.

A quite different behaviour of the 4P film morphology is observed for the grains #5, #11 and #12. The surfaces of these crystallites are mainly composed of (111) or (100) terraces. The sphere models corresponding to grain #5 ($(\bar{7}\ 10\ 8)$ orientation), #11 ($(2\ \bar{1}0\ 10)$ orientation) and #12 ($(9\ 10\ 8)$ orientation) are compiled in Fig. 5a-c, respectively. In the case of the
exposed (111) planes (#5, #12), where three equivalent $<1\bar{1}0>$ directions exist and the widths of the (111) terraces are comparable to the Van der Waals length of the 4P molecule, no single preferential orientation for the macroscopic alignment of the 4P needles can be seen. Instead, at least 6 different but equal orientations exist, reflecting the high symmetry of these grain surfaces. Apparently, the potential energy surface of these planes is not corrugated enough to act as a template for highly anisotropic, oriented layer growth. In addition to the needle like structures patches of continuous 4P film exist within this layer. There is evidence that in this case the 4P molecules are standing upright relative to the surface [10]. The grain #11 exposes terraces of (100) orientation with a terrace width of about 0.9 nm. In the corresponding 4P film only a weak preference for elongated island growth can be observed. The 4P needle orientation on this grain is roughly perpendicular to the step edge direction, indicating that the 4P molecules are aligned parallel to the step edges. Different from all the other grains analyzed above, the $<1\bar{1}0>$ direction is not characteristic for this particular surface and the 4P molecules align along the step edges, instead.

In addition to the SEM/EBSD measurements, combined STM/SEM experiments have been performed. With the help of a combined STM/SEM instrument, the position of the STM tip relative to the substrate surface could be monitored in-situ with SEM. This is shown in Fig. 6a, where the position of the STM tip is visible together with the surface of the plain Au substrate. The two Au grains involved are labelled A and B, accordingly. In particular, STM measurements of the plain Au substrate prior to the film deposition clearly reveal the stepped surfaces of the Au grains. Fig. 6b presents a 30 nm x 30 nm STM image of the plain Au surface, which has been recorded at the same position as shown in Fig. 6a, i.e. on grain A left of the grain boundary. Almost parallel rows of bunched steps are visible, with an inter-row distance of 1-1.5 nm. This can be seen from the height profile (line scan) presented below, which has been taken along the straight line indicated in Fig. 6b. After deposition of the 4P
film, SEM measurements with higher resolution have been made at the same sample position as shown in Fig. 6a. This is presented in Fig. 6c, where elongated 4P aggregates can be observed. On the grain labelled A the 4P aggregates are aligned along a single preferential direction, which is perpendicular to the direction of the corresponding step bunch rows of the Au surface underneath. Obviously, the width of the step bunched terraces (about 1 nm) is small enough to hinder an isotropic distribution of the crystallite orientations. Instead, a highly anisotropic growth of 4P is observed. This corroborates the results of the EBSD experiments.

4. Conclusions

A recrystallized polycrystalline gold foil was successfully applied to study the growth modes of p-quaterphenyl (4P) thin films on a large number of single crystal gold surfaces with different orientations at the same time. Needle like islands with a more or less anisotropic alignment, strongly wetting continuous films and surface areas with very little wetting ability could be observed simultaneously as function of the substrate surface structure. Those crystallite surfaces which consist mainly of (110) terraces tend to favour needle like 4P growth with the needle orientation perpendicular to the \(<1\overline{1}0>\) direction. Furthermore, steps on vicinal planes with narrow terraces also act as templates for 4P layer growth to induce elongated layer growth normal to the step direction. In all these cases the 4P molecules are oriented with their long axes parallel to the surface. In contrast, an isotropic distribution of needle orientations is observed on the highly symmetric (111) and (100) crystal planes of the gold surface. In addition to that, patches of continuous 4P films do exist on these surfaces. They may be caused by impurities (carbon) on the substrate surface. There is strong evidence that these continuous films consist of 4P molecules standing upright on the surface.

Acknowledgements
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References


List of Figure and Table Captions

Table 1

Euler angles ($\varphi_1, \varphi_2$), Miller indices (hkl) and azimuthal directions [uvw] for the measured orientations of the individual gold grains #1 through #13 of Fig. 4b.

Fig. 1 a, b

(a) Optical micrograph of a recrystallized gold surface covered with a 30 nm thick film (mean thickness) of p-quaterphenyl. (b) SEM micrograph (secondary electrons) of the same film/substrate system. Three different film morphologies can be observed on the three grain surfaces labelled A, B and C.

Fig. 2 a-d

(a) and (b) SEM images with different magnifications of the 4P film morphology of sections chosen from the area A in Fig. 1b. The dotted rectangle defines the area for the image (b) of higher resolution. (c) and (d) SEM images of the film morphology, of sections chosen from area C in Fig. 1b. The dotted rectangle in (c) defines the area with higher magnification in image (d).

Fig. 3 a,b,c

(a) SEM image of a 30 nm thick 4P film on the recrystallized Au surface. (b) Corresponding inverse pole figure map ([001]) as obtained by EBSD, with the Au grain orientations according to the colour code of the colour triangle shown in (c). The Au grains are labelled by 1 through 13. The white bars in (a) indicate either the $<1\bar{1}0>$ directions or the directions of
the step edges of the Au grains as obtained from the EBSD measurements. The growth of needle like 4P islands normal to the $<1\bar{1}0>$ directions can clearly be seen on most grains.

Fig. 4 a,b,c
Sphere models of the Au grain surfaces for (a) grain #2: (0 10 9) orientation, (b) grain #4: (2 2 5) orientation and (c) grain #8: (3 2 10) orientation. The area coloured in red indicates the (001) reference plane. The [100] reference direction runs parallel to the vertical direction of the Au grain as indicated in each image. The Au $<1\bar{1}0>$ direction is also shown.

Fig. 5 a,b,c
Sphere models of the crystallite surfaces for (a) grain #5: (7 10 8) orientation, (b) grain #11: (2 10 10) orientation and (c) grain #12: (9 10 8) orientation. The area coloured in green indicates the (001) reference plane. The [100] reference direction runs parallel to the vertical direction of the Au grain as indicated in each image. The Au $<1\bar{1}0>$ direction is also shown.

Fig. 6 a,b,c
(a) SEM image showing the position of the STM tip relative to the Au surface for the combined STM/SEM measurements. Two neighbouring grains are labelled A and B, respectively. (b) 30 nm x 30 nm STM image ($U_{\text{Sample}} = 2.0$ V, $I = 2.0$ nA) taken on grain A at the tip position shown in (a). The height profile (line scan) shown below is taken across the straight line as indicated. (c) SEM image at higher resolution after deposition of a 20 nm 4P film taken at a position next to the STM tip shown in (a).
| Grain # | EULER angles | (hkl) || (001)$_{Ref}$ | [uvw] || [100]$_{Ref}$ |
|---------|--------------|-----------------|--------------------------|
|         | $\varphi_1$ | $\Phi$ | $\varphi_2$ | $h$ | $k$ | $l$ | $u$ | $v$ | $w$ |
| 1       | 80.3         | 67.7     | 44.6       | 5   | 5   | 3   | -1  | -2  | 5   |
| 2       | 137.9        | 47.1     | 359.4      | 0   | 10  | 9   | -10 | -6  | 7   |
| 3       | 42.2         | 25.8     | 50.2       | 4   | 3   | 10  | 0   | -10 | 3   |
| 4       | 81.9         | 29.5     | 43.4       | 2   | 2   | 5   | -7  | -10 | 7   |
| 5       | 101.0        | 57.9     | 326.2      | -7  | 10  | 8   | 1   | -3  | 5   |
| 6       | 151.4        | 22.3     | 273.0      | -2  | 0   | 5   | 2   | -5  | 1   |
| 7       | 57.7         | 43.8     | 33.2       | 5   | 8   | 10  | 1   | -10 | 7   |
| 8       | 215.7        | 20.8     | 235.6      | -3  | -2  | 10  | 0   | -10 | -2  |
| 9       | 39.5         | 25.2     | 53.2       | 4   | 3   | 10  | 0   | -10 | 3   |
| 10      | 49.1         | 50.5     | 41.0       | 8   | 9   | 10  | 2   | -10 | 7   |
| 11      | 291.1        | 11.7     | 130.3      | 2   | -1  | 10  | 5   | -10 | -2  |
| 12      | 47.0         | 58.7     | 43.3       | 9   | 10  | 8   | 3   | -10 | 8   |
| 13      | 130.9        | 42.5     | 8.1        | 1   | 9   | 10  | -10 | -6  | 7   |

Table. 1 – Müllegger et al, Thin Solid Films 2004
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Fig. 5 – Müllegger et al, Thin Solid Films 2004
Fig. 6 – Müllegger et al, Thin Solid Films 2004