Crystal growth of \textit{para}-sexiphenyl on clean and oxygen reconstructed Cu(110) surfaces

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The formation of crystalline \textit{para}-sexiphenyl (6P) films on Cu(110) and Cu(110)-(2 \times 1)O (Cu–O) has been studied by low energy electron diffraction, X-ray absorption spectroscopy and both \textit{in situ} and \textit{ex situ} X-ray diffraction methods to elucidate the transition from the initial monolayers to crystalline thin films. It is found that, for Cu–O, a single and, for Cu(110), a double wetting layer is formed which then acts as a template for the subsequent 3D crystal growth. For both substrates the orientation of the long molecular axes of the 6P molecules in the first layers is conserved for the molecules in the bulk crystals growing on them. The main difference between both systems is that on Cu–O the first monolayer assembles in a form close to that of a 6P bulk plane which can be easily continued by crystallites grown upon them, while on the Cu(110) surface the 6P mono- and bi-layers differ substantially from the bulk structure. The bi-layer forms a complex periodically striped phase. Thin 6P films grow with the 6P(20\overline{3}) crystal plane parallel to the Cu–O substrate surface. For this orientation, the 6P molecules are stacked in layers and the molecules demonstrate only one tilt of the mean molecular plane with respect to the sample surface. On clean Cu(110), a more complex 6P(629) plane is parallel to the substrate surface and this orientation is likely a consequence of the super-molecular long-range periodicity of the second molecular layer striped phase.

1 Introduction

Thin films of conjugated molecules have been extensively studied due to their potential applicability as electronic devices.\textsuperscript{1–4} Molecular orientation, crystallinity and morphology of thin films of conjugated molecules are key determinants for the function of devices.\textsuperscript{5,6} Like for all thin film devices, interfaces play a major role in their function and are closely related to their geometric structure.\textsuperscript{7,8} This is particularly important for organic molecules, as their geometric and closely related optoelectronic properties are highly anisotropic.\textsuperscript{9} Therefore a detailed knowledge of the interface is a prerequisite to understand the intrinsic properties of these devices.

To exploit the highly anisotropic properties of organic crystals it is necessary to steer the orientation of the molecules in a certain direction. One way to achieve a certain degree of control is to evaporate rod-like molecules on anisotropic single crystal substrates. In previous studies of rod-like molecules adsorbed on e.g., Cu(110), a uniaxial molecular orientation was observed.\textsuperscript{9–16}

In general, the crystallographic structure of a thin organic film depends on the surface structure of the substrate, the substrate–molecule interaction, and the final film thickness.\textsuperscript{17} Depending on the interaction strength of the molecules with a particular substrate, several cases have been observed. On weakly interacting substrates, molecules assemble in their bulk structure already in the first layers, with low index crystal planes parallel to the substrate surface.\textsuperscript{18–20} On strongly interacting surfaces, molecules tend to form wetting layers with a structure far from their native bulk crystal structure. On top of the first layer(s) the molecules grow in their bulk structure.\textsuperscript{10–12,21,22} However, some strongly interacting surfaces force the molecules of the wetting layer to a structure close to their bulk. If these surfaces are anisotropic and have a low symmetry, rod-like molecules can be efficiently forced to a certain direction. Then, uni- or bi-axially oriented crystals can be obtained.\textsuperscript{9–16} As we will illustrate here, a wetting layer of uniaxially oriented molecules, ordered close to a bulk plane, can serve as an excellent template for the 3D growth of organic molecular crystals with a higher index termination of lying molecules.\textsuperscript{9,16,23}
Previous studies of rod-like molecules on Cu(110) and Cu(110)-(2 × 1)O have shown that these substrates are very suitable to align the molecules and result in layers of uniaxially oriented molecules. In this article we focus on the relationship of the structure of the first layers with the crystal structure of 6P thin films grown on these surfaces.

2 Experimental

Sexiphenyl (6P, Tokyo Chemical Industry Co., Ltd., without further purification) thin films were prepared by molecular beam epitaxy (MBE) in ultra-high vacuum (UHV). Prior to the 6P film deposition, the Cu(110) substrate was cleaned by several cycles of Ar+ ion sputtering and thermal annealing at 800 K. The surface of Cu(110) is anisotropic and has densely packed copper rows along the [1 1 0]_Cu azimuthal direction. The mutually perpendicular surface lattice vectors are directed along the [1 1 0]_Cu and [0 0 1]_Cu crystallographic directions and their lengths are equal to the nearest neighbour atom distances in the copper rows and the row-to-row distances, 0.255 nm and 0.36 nm, respectively (see Fig. 1). The Cu(110)-(2 × 1)O reconstructed surface was formed by dosing 20 L (1 langmuir = 1 × 10⁻⁶ Torr s) of oxygen on the previously cleaned Cu(110) surface. Rows of copper–oxygen are formed along [0 0 1]_Cu with a row-to-row lateral distance of 0.51 nm. The direction of the densely packed oxygen rows on Cu(110)-(2 × 1)O is perpendicular to the rows of copper on the clean Cu(110) surface.25,26 (Fig. 1). Sexiphenyl was deposited from a degassed Knudsen-cell onto a substrate held at a temperature of about 300 K. The nominal film thickness was measured with a quartz micro-balance assuming a density of 1.3 g cm⁻³. The growth rate was around 0.3 nm min⁻¹. The final film thickness for samples measured ex situ was 30 nm.

Low energy electron diffraction (LEED) measurements were performed using an Omicron multi-channel plate MCP-LEED at sample temperatures of 100 K after room temperature deposition in an ultra-high vacuum (UHV) chamber (base pressure 1 × 10⁻¹⁰ mbar). For the reported measurements, the energy of the primary electron beam was \( E_0 = 20 \) eV. Scanning tunnelling microscopy (STM) was performed in situ using an Omicron combined STM/atomic force microscope system.

Near-edge X-ray absorption fine structure (NEXAFS) measurements were performed at the Russian–German beamline at the BESSY II synchrotron facility in the MUSTANG end station. The carbon Auger electron yield was recorded using a SPECS 150 hemispherical analyzer. The overall photon energy resolution was better than <0.3 eV.

Grazing incidence X-ray diffraction (GI-XRD) measurements were performed in situ at the ESRF Grenoble at the beam-line BM32.27 The end-station of this beam-line combines an UHV chamber with a high precision goniometer in z-axis geometry.28 A photon energy of 18 keV and a grazing incidence angle of \( \alpha_1 = 0.178^\circ \) were used. A pair of slits in front of a point detector was used to adjust angular resolution at the detector side. While letting slits to be widely opened along the vertical direction, X-rays with an exit out-of-plane angle \( \alpha_2 \) from 0° to 0.7° were detected. The angular resolution in the horizontal direction was restricted to \( \Delta(2\theta) = 0.05^\circ \) (see Fig. 2), to be sensitive to lattice spacing of the film crystal planes perpendicular or nearly perpendicular to the sample surface. The main advantage of the grazing incidence geometry compared to other X-ray diffraction geometries is the high surface sensitivity that allows the measurement of organic layers of monolayer or even sub-monolayer coverage.24 For the ex situ X-ray diffraction measurements a Philips X’Pert diffractometer equipped with an ATC3 texture cradle, the wavelength of CrKα and a flat graphite monochromator were used. To calculate the peak positions and the corresponding intensities the software Powdercell29 was used. The simulation of single crystal pole densities was done with the Stereopole software package. In all measured X-ray patterns the so-called β-phase of sexiphenyl31 (\( a = 0.8091 \) nm, \( b = 0.5568 \) nm, \( c = 2.6241 \) nm, \( \beta = 98.17^\circ \)) was observed.

The final film morphology was investigated ex situ with Atomic Force Microscopy (AFM). The data were acquired with a Digital Instruments Multimode Nanoscope IIIa microscope in tapping mode. A low scanning speed together with a sharp tip allowed to image high islands.

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![Fig. 1](image1.png) Structure of substrates surface lattice. On the left the bare copper (110) surface is depicted while on the right the reconstructed Cu(110)-(2 × 1)O (Cu–O) surface is shown. The black dots represent the oxygen in the Cu–O rows in the latter.

![Fig. 2](image2.png) Scheme of the experimental set-up for grazing incidence X-ray diffraction. The angular acceptances at the detector side were in the in- and out-of-plane directions \( \Delta(2\theta) = 0.05^\circ \) and \( \Delta\alpha_2 \approx 0.7^\circ \) respectively.
3 Results and discussion

3.1 Sexiphenyl on Cu(110)-(2 × 1)O

The geometric structure of a 6P monolayer on Cu–(2 × 1)O has been investigated by LEED. At a coverage of 0.3 nm (i.e. the nominal thickness of a 6P monolayer), a weak LEED pattern can be observed at room temperature. On cooling to 100 K, the LEED shows sharp spots, as shown in Fig. 3(a), and a monolayer structure can be determined. A surface unit cell with \( b_1 = 5.8 \, \text{nm} \) and \( b_2 = 1.02 \, \text{nm} \) along the substrate principle azimuths fits well to the observed LEED pattern. These values imply a periodicity equal to a distance of two oxygen rows in the [1\(1\),0]\(_{\text{Cu}}\) direction and two lengths of a 6P molecule in the [001] direction. The LEED is in agreement with LT-STM data of ref. 9 and 15. The periodicity of 5.8 nm spans two molecules along the long molecular axis due to alternating tilt angles of the average phenyl plane about the long axis that leads to alternating sideways shift in adjacent rows of molecules (see schematics of Fig. 3(c) and (d)).

As can be observed in the LEED image of the monolayer (Fig. 3(a)), certain groups of spots have an enhanced intensity, two of which are marked by arrows originating at the 0,0 reflex. These arrows describe the reciprocal space vectors corresponding to the diagonal ring-to-ring distance of two adjacent molecules in this direction, as indicated by the two thin arrows in the monolayer schematic (Fig. 3(c)). The neighbouring phenyl rings of a 6P molecule alternate back and forth their tilt with respect to the average molecular plane in a twisting fashion, in both the solid state and the gas phase. The alternation is shifted by one ring on neighbouring molecules. The sites of nearest neighbour equivalent phenyl ring inclination would be described by the two inter-ring vectors shown by thin diagonal arrows in Fig. 3(c). Therefore, we suggest that the greater intensity of certain groups of LEED reflexes arises from a structure factor modulation of reflex intensities due to this phenyl ring tilt periodicity. Alternating torsional directions on neighbouring molecules explain the two-molecule periodicity in the direction perpendicular to the long molecular axis.

To explore the transition from the monolayer to thin film growth in situ GI-XRD measurements were carried out for a monolayer and thicker 6P films. As the structure of the two-dimensional unit cell is already known from above discussed LEED images and STM measurements, we have probed the 6P reciprocal lattice along the [001]\(_{\text{Cu}}\) and [1\(1\),0]\(_{\text{Cu}}\) directions of the copper substrate. GI-XRD measurements along the [001]\(_{\text{Cu}}\) direction of thin in situ grown 6P films are shown in Fig. 4. The diffraction pattern shows lattice planes that are perpendicular (or almost perpendicular) to the substrate surface and have a normal vector along the [001]\(_{\text{Cu}}\) direction. Thus, the lattice planes perpendicular to the long molecular axis are probed. The diffraction pattern of a 6P layer with a nominal thickness of 0.39 nm (approximately one monolayer) shows two weak peaks located at \((2.1 \pm 0.1) \, \text{nm}^{-1}\) and \((4.39 \pm 0.07) \, \text{nm}^{-1}\). These peaks can be indexed as 001 and 002 and arise from an inter-planar distance of \((2.90 \pm 0.02) \, \text{nm}\). The GI-XRD measurement along [001]\(_{\text{Cu}}\)
is sensitive to the organic film electron density modulation along the scan direction, i.e. molecule-to-molecule distance along this direction, and non-sensitive to the alternate tilt of two neighbouring molecules lying in the monolayer surface unit cell along [001]$_{\text{Cu}}$. The molecule-to-molecule distance (2.90 ± 0.02) nm obtained from GI-XRD fits well the distance of eight O atoms, 2.88 nm, on the Cu–O (110) surface, i.e. a half of the 6P unit cell length along the [001]$_{\text{Cu}}$ determined from LEED. In the perpendicular direction (i.e. along [110]$_{\text{Cu}}$), X-rays probe again the molecule-to-molecule distance, which is the same as the distance of oxygen rows running perpendicular to this direction. Thus, the diffraction peaks of 6P and the Cu–O (110) surface occur at the same reciprocal space positions. The sexiphenyl peaks are overwhelmed by those of the oxygen decorated substrate.

In contrast to LEED, the X-ray diffraction measurement is not sensitive to the alternating twist of phenyl rings as no additional peaks are visible in the diffraction pattern. This fact can be attributed to the differences in the scattering of X-rays compared to low energy electrons. While X-rays scatter from the entire electron density, the low energy electrons are sensitive to the molecular orbitals of the valence band and not to the 1s and 2s core levels. In the case of LEED, all true periodicities are observed and the pattern can be understood in terms of the internal phenyl ring periodicity along [110]$_{\text{Cu}}$ resulting from the phenyl ring twist within the molecules, and the average molecular plane tilt periodicity along the [001]$_{\text{Cu}}$ direction, which is twice the interlayer spacing (i.e. 5.8 nm), arising from the molecules alternate tilt to opposite sides of the grooves formed by the oxygen rows. Therefore, the GI-XRD measurements confirm the commensurability of the monolayer lattice with the Cu–O substrate and the 6P monolayer surface unit cell dimensions observed in LEED.

Capturing the transition from the sub-monolayer to the thin film, the diffraction peaks (see Fig. 4) for a film with a nominal thickness of 0.54 nm (above one monolayer) show more pronounced peaks that are shifted to larger values of $q_{[001]_{\text{Cu}}}$ (2.29 ± 0.01) nm$^{-1}$ and (4.59 ± 0.01) nm$^{-1}$). Additionally, peaks of higher order appear as well (only peaks up to the 3rd order are plotted in Fig. 4). As shown in the next paragraphs, after a full determination of the 6P layer crystal orientation with respect to the substrate, the peaks in Fig. 4 can be identified as the 00l Bragg peaks of the bulk structure of 6P,31 At all larger film thicknesses up to 1.2 nm, the positions of these peaks do not change any more. Thus, the equilibrium crystallographic orientation in the 6P film is established during the growth of the second layer. The peak positions yield a surface periodicity of the film along the [001]$_{\text{Cu}}$ direction of (2.739 ± 0.001) nm. Due to the high diffraction intensity of thicker films compared to the monolayer signal (note that the intensity scale of Fig. 4 is plotted logarithmically) no clear conclusions can be drawn whether the first monolayer structure remains unchanged at thicker films or not. A LEED image of a thin 6P multilayer film is shown in Fig. 3(b). It is overlaid by circles, indicating the monolayer diffraction structure obtained above. Although the diffraction image is blurred, it reflects the structure of the monolayer but with a relaxation to the bulk periodicity, as indicated by a slight vertical offset of the reflexes towards the center of the image (cf. the dashed lines intersecting ±1k diffraction peaks of the monolayer). Moreover, it is clear that the internal structure, attributed to twisted molecules, is maintained in the bulk. Twisted 6P molecules have been previously concluded from the electron structure measurements of 6P(203) films grown at room temperature.9,32

Thick 6P films grown on Cu–O were also studied using ex situ specular (i.e. coplanar) and out-of-plane XRD with lab equipment. Specular scans reveal net planes parallel to the substrate surface, while pole figures display the orientational distribution of net planes in the whole orientation space. With these measurements and by the knowledge of the crystal structure of the film, the crystallographic orientation of the 6P crystallites and therewith the molecular alignment with respect to the Cu–O substrate can be fully determined. Ex situ specular diffraction measurements of a 30 nm thick film reveal only one dominant peak at $q_z = 16.3$ nm$^{-1}$. This peak can be identified as 203 reflection of the 6P bulk structure, which means that sexiphenyl {203} net planes of the grown crystallites are oriented parallel to the substrate surface. Molecules within the {203} planes are packed similarly to the ones observed by STM15 and implied by the LEED measurements: all long molecular axes are parallel to the sample surface and stacked in rows. The mean molecular planes within the rows are side tilted by 33°. This tilt angle alternates between neighbouring planes of molecular rows (see also Fig. 5(a)). The in-plane azimuthal orientation of the 6P crystallites can be determined by a set of pole figures. Fig. 6 shows pole figures for the {213} and {111} net planes, measured at scattering momentum transfers of $q = 19.85$ nm$^{-1}$ and $q = 13.76$ nm$^{-1}$.

**Fig. 5** Crystallographic orientation and molecular packing for thick sexiphenyl films on a Cu(110)–O surface derived from XRD. Views along [001]$_{\text{Cu}}$ (a), [110]$_{\text{Cu}}$ (b), and [110]$_{\text{Cu}}$ (c) directions. Orientations of (203) {213} and (001) sexiphenyl net planes are indicated.
respectively. The twofold symmetry of enhanced pole densities (EPD) in both pole figures arises from the twofold symmetry of the oxygen decorated Cu surface, which drives the azimuthal orientation of the 6P crystallites (i.e. molecules therein). Two classes of crystallites with their lattices mutually rotated by 180° around the reciprocal space vector \( \mathbf{G}_{2,0,3} \) (i.e. around the sample normal) are present. Their reflexes in Fig. 6 are distinguished from each other by a superscript ‘r’. The orientation of the 6P thin film with respect to the Cu–O substrate, based on the pole figures and a specular scan, is shown in Fig. 5. Similarly to the monolayer, the 6P molecules are aligned with their long molecular axis parallel to the oxygen rows on the Cu(110) surface lattice. Although weakly bound, the monolayer is commensurate with the substrate. The lattice spacing of 5.76 nm and 1.02 nm, along the [001]\(_{\text{Cu}}\) lattice directions, corresponds to the measured series of lattice planes was well to the spacing of bulk 6P (001) planes \( d(001) = 2.597 \) nm. Thus, the transition to the bulk phase of 6P during the growth of the second layer was deduced.

In Fig. 7, an AFM image of sexiphenyl on Cu(110)–(2 \( \times \) 1)O with the final film thickness of 30 nm is shown. The film is homogeneously tiled with crystallites that are all elongated along the [1\( \bar{1} \)0] direction with all molecules lying perpendicular to it. These structures are between 250 and 400 nm long and have an average width of 120 nm. The average island height is very homogeneous with a variation of only 5 nm. This morphology is a direct consequence of the [20\( \bar{3} \)] orientation in combination with the monoclinic 6P crystal structure. The two dimensional unit cell of [20\( \bar{3} \)] is rectangular, but the next layer of molecules is shifted by about \( \frac{1}{2} \) of a phenyl ring size in the direction of the long molecular axis (equivalently the [001]\(_{\text{Cu}}\) direction, see also Fig. 5). The two possible shift directions result in two symmetric crystal orientations that can be distinguished by pole figure measurements (compare Fig. 6(b), where EPDs from orientations [20\( \bar{3} \)] and [20\( \bar{3} \)] are identified). As these two orientations are equally likely it is not surprising that multiple crystallites with limited sizes are formed as seen in the AFM. The elongation of crystallites along the [1\( \bar{1} \)0]\(_{\text{Cu}}\) direction is induced by the preferential herringbone (i.e. side-by-side) stacking of the molecules. A similar morphology has been previously observed for 6P thin films grown on TiO\(_2\)(110).\(^{16}\)

To summarize, XRD, LEED, and AFM provide a coherent picture of 6P thin films grown on Cu(110)–O. For the monolayer, 6P completely wets the substrate at a thickness of around 0.3 nm\(^{14}\) and forms a two-dimensional rectangular lattice. Although weakly bound, the monolayer is commensurate with the substrate. The lattice spacing of 5.76 nm and 1.02 nm, along the [001]\(_{\text{Cu}}\) and [1\( \bar{1} \)0]\(_{\text{Cu}}\) lattice directions, respectively, corresponds to a commensurate structure with an epitaxial matrix of \( M = (0 \ 16;4 \ 0) \) with respect to the Cu(110) surface lattice. The long molecular axes of all 6P molecules are oriented along the [001]\(_{\text{Cu}}\) direction of the copper substrate, i.e. parallel to the oxygen rows, whereby the molecules organize in rows in the perpendicular direction.
(see Fig. 3(c)). The nearest neighbour molecules along the \([001]_{\text{Cu}}\) direction have an alternate tilt of the average molecular plane with respect to the sample surface, while in the \([1\overline{1}0]_{\text{Cu}}\) direction they have the same tilt\(^{15}\) but the phase of the phenyl ring twist directions is shifted by one phenyl ring. Thus the surface unit cell spans two molecules along both translational directions. After completion of the monolayer, the diffraction pattern of the bulk crystal structure is observed both in GI-XRD and LEED. The in-plane lattice spacing relaxes to 5.46 nm (i.e. contracts by \(e_{\text{[001]Cu}} = 5.2\%\)) and 1.114 nm (i.e. expands by \(e_{\text{[1\overline{1}0]Cu}} = 9.2\%\)), along the \([001]_{\text{Cu}}\) and \([1\overline{1}0]_{\text{Cu}}\) lattice directions, respectively. The 6P crystallites grow with the (20\overline{3}) crystal planes, which contain the long molecular axes of 6P molecules, parallel to the substrate surface (see Fig. 5(a)). The azimuthal orientation of the long molecular axes of the 6P molecules in the bulk crystallites copies the orientation of the molecules in the first monolayer and, thus, is dictated by the direction of the oxygen rows. The molecular planes are tilted by \(33^\circ\) with respect to the (20\overline{3}) plane. Two possible directions of shifts of molecules in subsequent layers of molecules along the \([001]_{\text{Cu}}\) direction (see Fig. 5(c)), i.e. two nonequivalent orientations of the 6P monoclinic unit cell keeping (20\overline{3}) crystal planes parallel to the sample surface and 6P molecules parallel to \([001]_{\text{Cu}}\), result in relatively small crystallites observed in the AFM.

### 3.2 Sexiphenyl on Cu(110)

The geometric structures of a monolayer coverage of 6P on Cu(110) have been determined by LEED measurements. The diffraction pattern for a coverage of 0.3 nm is shown in Fig. 8(a). At this full monolayer coverage, sharp diffraction spots appear which suggest a highly ordered surface lattice with unit cell translation vectors of lengths \(b_1 = 2.83\) nm and \(b_2 = 0.72\) nm spanning an angle of \(\phi = 82.7^\circ\) (see the model in Fig. 8(c)). This results in an epitaxial matrix \(M = (11 \, 1, 0)\) with respect to the Cu(110) surface lattice \(a_1 = 0.255\) nm and \(a_2 = 0.36\) nm. The image of Fig. 8(a) was collected at a substrate temperature of 100 K but does not change up to room temperature. This monolayer structure is in agreement with STM measurements shown in Fig. 8(b).

C1s-NEXAFS measurements provide information on the average phenyl plane tilt angle and the orientation of the molecules in the first few layers. The NEXAFS spectra of the completed monolayer (nominal thickness 0.3 nm) depicted in Fig. 9(a) show strong C1s \(\rightarrow \pi^*\) resonance intensities at glancing incidence \((\theta = 80^\circ)\) at \(E = 285\) eV, while no absorption \(\pi^*\) peak is observed for normally incident X-rays \((\theta = 0^\circ)\) in both azimuths. This can only be the case if the phenyl rings, and hence the molecular planes, are lying flat on the Cu(110) surface. In this situation, NEXAFS cannot reveal...
the azimuthal orientation of the long molecular axis. However, the LEED results suggest and the STM image (Fig. 8(b)) clearly shows the long axes parallel to the [110] direction. The registry of the molecules in this monolayer as determined by STM can be found in ref. 15.

When the nominal coverage is doubled from the monolayer to a bi-layer with a nominal thickness of 0.6 nm, a new LEED pattern (Fig. 8(d)) starts to emerge which is then completed at 0.8 nm (Fig. 8(e)), while the monolayer pattern disappears.

The amount of material deposited and both STM as well as NEXAFS measurements shown below suggest that the new structure covers the monolayer. In the LEED pattern of a 0.8 nm thick layer, the reflexes are split. We attribute this splitting to domains occurring in the second layer with an estimated periodicity of 3.5 nm containing molecules with a lateral spacing of 0.64 nm. The domains can be seen in a RT-STM image shown in Fig. 8(f) as bright areas separated by dark bands, running in the [110] surface direction. The distance of the domains along [001]Cu ranges from 30 to 40 nm. The domains can be resolved within each domain, which correspond to individual molecules therein.

NEXAFS measurements for a 0.8 nm thick film are shown in Fig. 9. The C1s → π* transition remains strong for glancing incidence angles. However, the absorption peak appears for normal incidence as well in the [001]Cu direction, indicating that the molecular planes of the additional molecules are no longer flat on the surface. An analysis (for the theory see ref. 36) of the π* resonance intensities measured as a function of the incidence angle (see inset of Fig. 9(b)) reveals an average molecular plane tilt angle of (30 ± 3°). The absorption peak is weak for the measurements at normal incidence for polarization along the [110]Cu direction. This implies that the long molecular axes of the 6P molecules are still preferentially oriented along [110]Cu in the bilayer. The determined tilt of the molecules in the second layer is consistent with the coverage dependence of the LEED. Nearly twice the material sufficient to grow a monolayer is needed to cover the monolayer of flat lying molecules (nominal thickness of 0.3 nm) with a new layer of tilted molecules, which is completed at a nominal thickness of 0.8 nm (see Fig. 8(e)).

The combined results from LEED, STM and NEXAFS measurements suggest that the bi-layer at 0.8 nm forms a one-dimensional strain pattern, as represented in the schematic of Fig. 10(b). As the coverage is increased above 0.8 nm, the LEED pattern no longer changes its structure but only gets weaker.

To determine the crystal alignment of 6P that grows on this complex bi-layer, a 30 nm thick film was grown and investigated by XRD. The specular XRD pattern did not reveal any diffraction peak originating from the organic layer. This is already an unusual result because in general films grown on single crystals have a cleavage plane (i.e., a plane with relatively low surface energy) parallel to the substrate. Nevertheless, the orientation of the crystallites can be determined by the pole-figure technique. In Fig. 11(a) and (b) the pole figures for {213} and {111} net planes, respectively, are shown.
6P crystallites with \{629\} net planes parallel to the surface can fully describe the positions of all measured EPDs. This high index plane that has a negligible structure factor explains the absence of peaks in the specular diffraction pattern.

In Fig. 11(a) the EPDs for the \{213\} net planes are depicted. In contrast to 6P on Cu–O (Fig. 6(a)), now, corresponding EPDs are aligned along the [001]_{Cu}. This is consistent with the orientation of the long axes of 6P molecules parallel to the \{1\overline{1}0\}_{Cu} direction, which is the same as for the bi-layer structure. Crystallographic and molecular orientations of 6P grown on Cu(110) are depicted in Fig. 10(b). For comparison the structure of 6P on Cu–O is shown in Fig. 10(a).

A doubling of the number of EPDs can be noticed when comparing corresponding pole diagrams for the two different substrates shown in Fig. 6 and 11, respectively. While the mirroring with respect to the (20\overline{3}) plane combined with a rotation by 180° around the \{001\}_{Cu} reciprocal space vector is a symmetry operation for the 6P monoclinic unit cell, it is not the case for the \{629\} contact plane for 6P/Cu(110). Thus, crystallites grown with \{001\}_{Cu} parallel and anti-parallel to the outer sample surface normal give rise to two different sets of EPDs, which, in a general case, do not merge together. The EPDs from crystallites with \{001\}_{Cu} anti-parallel to the sample surface outer normal are marked with an asterisk (*) in Fig. 11. Still, the pole figure for 6P/Cu is twofold symmetric due to the twofold symmetry of the Cu(110) surface (see the discussion of 6P/Cu–O above).

To summarize the XRD results, the pole figures of 6P/Cu(110) for reflections on \{213\} and \{11\overline{1}\} reveal that the 6P molecules within the \{629\} net planes are all oriented in the \{1\overline{1}0\}_{Cu} direction. In contrast to what was observed for 6P grown on Cu(110)–O, the molecular planes within one layer have two different orientations with respect to the substrate, i.e. 9° and 57° (see also Fig. 10(b)). This observation is also dissimilar from growth on other metal surfaces at room temperature. For example, 6P is flat on Al(111) and Au(111) in the first monolayer, however, after the completion of the first molecular layer, crystallites with the \{213\} net planes parallel to the surface are formed with the epitaxial symmetries related to the metal substrate.21 Nevertheless, PEEM for 6P/Cu(110) suggests that \{213\} terminated crystallites are obtained for elevated temperatures.37

An AFM image of a 30 nm thick 6P film grown on Cu(110) is shown in Fig. 12. The 6P crystallites do not tile the whole surface, which results in a crystallite height of around 60 nm. This is considerably higher than in the Cu–O case with the same amount of molecules deposited (compare Fig. 7). Crystallites are observed to organize in larger agglomerates. The open areas between the crystallites are probably covered with two 6P layers (see LEED discussion above). The shapes of the crystallites within the larger clusters on Cu are less regular than on Cu–O, as could be expected from the high index termination 6P(629).

Summarizing the growth of 6P on Cu(110), we should note that the situation on Cu(110) is not as straightforward as in the Cu(110)–O case. In the monolayer regime the 6P molecules adsorb flat on the surface and orient in the \{1\overline{1}0\}_{Cu} direction. After the monolayer is completed, a tilted second wetting layer forms with two clear periodicities. A long-range domain periodicity of 3.5 nm is observed with stripes running in the \{1\overline{1}0\} direction (i.e. along the molecular axis) with a periodicity of the molecules within the domain of 0.64 nm. We suggest that molecules with a negligibly small tilt of their average molecular plane with respect to the substrate surface sit in the sites between the bright domains (see STM in Fig. 8(f) and the model in Fig. 10(b)). For the multilayer at room temperature, on top of this bilayer, crystallites grow with the \{629\} contact plane. The molecules in the next layers are still uniaxially aligned following the direction of the molecules in the monolayer. Although different in their details, structural similarities

![Fig. 11](https://example.com/fig11.png) Pole figures of a 30 nm thick sexiphenyl film grown on a clean Cu(110) substrate taken at \(q = 19.85\ \text{nm}^{-1}\) (a) and \(q = 13.76\ \text{nm}^{-1}\) (b), corresponding to 213 and 11\overline{1} diffractions of 6P, respectively.

![Fig. 12](https://example.com/fig12.png) Atomic force microscopy image of a 30 nm thick sexiphenyl film on Cu(110). The z-scale ranges from 0 nm to 100 nm. The principal substrate directions are indicated by arrows in the figure.
between the second layer structure and the $\{629\}$ termination (see Fig. 10(b)) can be found. Both have alternating molecular tilt angles with a larger in-plane periodicity encompassing several molecular widths.

We suggest that a possible explanation for the non-facile ($629$) orientation obtained for the multilayer film is the strained structure observed in the second layer of molecules. A model of a 6P layer with ($629$) termination plane shown in Fig. 10(b), where an in-plane molecular arrangement periodicity of 1.86 nm can be seen in the $\{001\}_{Cu}$ substrate direction. A doubling of this periodicity to 3.7 nm is close to the 3 nm to 4 nm domain periodicity observed in STM and LEED of the 0.8 nm film ($i.e.$ double-layer) along the $\{001\}_{Cu}$ direction. Only a small strain would exist between the second monolayer and the multilayer crystallites, suggesting that the second layer strain pattern is the cause of the ($629$) orientation of the multilayer film.

4 Conclusion

In the present study we have focused on the transition of the 2D to the 3D structure of 6P grown on Cu(110) and Cu(110)-(2 × 1)O. In both cases, the orientation of the molecules in the first monolayer is imposed on the molecules within the crystallites that grow upon them, $i.e.$ molecular axes are parallel to the close packed atomic rows of the substrate. For Cu–O, the monolayer assembles in a structure close to a bulk crystalline plane with a similar herring bone arrangement (see Fig. 3(c)). Here, the first monolayer templates the further film growth. The 6P $\{203\}$ termination on the Cu–O substrate results in a morphology of rectangular crystallites in accordance with the rectangular two dimensional unit cell in the 6P($203$) termination plane. The relaxation to the bulk in-plane lattice structure appears already during the growth of the second 6P layer, leading to a contraction of the lattice by −5.2% and its expansion by 9.2% along the [001]$_{Cu}$ and [110]$_{Cu}$ direction, respectively.

In contrast to 6P on Cu–O, the interface between Cu(110) and 6P is more complex. The monolayer on clean Cu(110) is a well ordered structure consisting of flat lying molecules that are oriented in the [110]$_{Cu}$ direction. It is totally different from any possible plane of bulk 6P. On the first monolayer, a second layer grows with a complex structure containing a large super-molecular periodicity. This larger bi-layer periodicity is similar to a double of the periodicity in the $\{629\}$ crystallites termination plane (see Fig. 10), which is observed for thicker films. Therefore, we conclude that the strain conditions that exist at this interface lead to this high index plane orientation in the bulk crystallites. The $\{629\}$ terminated crystallites on the pure Cu substrate have a less regular shape and are clustered together, incompletely covering the surface.

We have shown that the first one or two molecular layers can be crucial for organic thin film growth. The different interfacial structures obtained due to different molecule-surface interactions are directly responsible not only for the orientation of the molecules in a thin film but also for the resulting thin film crystallite orientation. Further, the particular 6P crystal orientations on these two surfaces clearly lead to rather different morphologies in the thin film. By a careful choice of a particular substrate template, the controlled growth of different crystalline orientations and morphologies is possible.

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