ESRF	**Experiment title:** **In-situ growth studies of sexiphenyl on TiO2(110) surfaces**	**Experiment number:** **32-03/625**
Beamline: **BM32**	**Date of experiment: from: July 28th to:August 4th, 2004**	**Date of report:** **10:12:2004**
Shifts:30	**Local contact(s): Tobias Schülli**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

* **Annette Thierry,** Institute Charles Sadron, Strasbourg, France

* **Martin Oehzelt,** Institute of Solid State Physics, Graz University of Technology, Austria

* **Roland Resel,** Institute of Solid State Physics, Graz University of Technology, Austria

* **Georg Koller,** Institute of Experimental Physics, University Graz, Austria

* **Michael Ramsey,** Institute of Experimental Physics, University Graz, Austria

* **Tobias Schülli,** Commisariat à l'Énergie Atomique, Centre de Grenoble, Grenoble, France

Report:

Sexiphenyl (p-6P: $C_{36}H_{26}$) is not only a promising molecule for LED and photo-voltaic applications it is also a useful model molecule for studying the growth of aromatic based organic semiconductors. During the last years the experimental team has investigated the growth of sexiphenyl on $TiO_2(110)$ and Al(111) surfaces with in-situ surface science techniques including LEED, STM and NEXAFS from monolayer thickness up to the multilayer regime. The morphology and crystallographic structure of in situ (UHV) prepared and characterised film have also been investigated ex-situ by AFM, TEM/TED and laboratory XRD. These laboratory techniques showed that epitaxial growth with unique morphologies and p-6P crystallite/molecular orientations could be achieved by controlling the inorganic substrate conditions. The aim of the experiments reported here was to perform in-situ structural studies on sexiphenyl films and follow the evolution of the crystallographic structure and epitaxy starting from the first monolayer (< 3Å) up to device relevant thickness (~300 Å). The initial stages of growth are particularly interesting because of the large lattice mismatch of the bulk 6P structure (monoclinic with a = 8.091Å, b = 5.568Å, c= 26.241Å and ß = 98.17°) to the substrates $TiO_2(110)$ (tetragonal with a = 4.594Å, c = 2.959Å) and Al(111) (cubic with a = 4.0414 Å). As well as the specific scientific goals the beamtime was also a test of BM 32 and its end-station for investigating the initial stages of organic film growth. *Despite both the molecule and the substrates being challenging* (a low structure factor on the one hand and reactive surfaces on the other) *the beamtime was very successful.*

Two particular p-6P morphologies were concentrated upon, these will be called needle-like and terrace-like in the following. Needle-like: For p-6P film deposition at a low rate (~2 Å/min.) at room temperature on the 1x1 reconstructed $TiO_2(110)$ surface (2.96 x 6.497 Å) an island growth mode (Volmer-Weber) occurs forming needles up to 10 µm in length. The needles of p-6P are aligned along $[1\text{-}10]_{TiO2}$, the crystallographic p-6P(20-3) plane is parallel to the TiO2(110) surfaces and all the molecules are parallel to the oxygen rows of the substrate surface ($[001]_{TiO2}$). There is often a small fraction of defective areas with a terrace like morphology. Terrace-like: Preparation of a p-6P films at elevated substrate temperature (>100° C) leads to films with exclusively terrace like morphology. The terraces are formed by molecules which are oriented near up-right on the TiO2(110) surface (p-6P(001) orientation). It is known that the growth mode is rather layer + island type (Stranski-Krastanov) than of island type (Volmer-Weber). The nominal quantity for an up-right monolayer is 27 Å and at this exposure around 60% of the molecules are in very large first layer islands.

Needle-like growth: The TiO2(110) (1x1) substrate was prepared by Ar sputtering and annealing cycles and p-6P films from (sub-)monolayer (2.3 Å) to multilayer (30 Å) coverages were grown in-situ with the substrate at RT or at elevated temperatures. The films were grown at a rate of ~2 Å/min and the nominal film thickness was determined from micro-balance measurements assuming the mass density of p-6P ($\rho = 1.3$ g/cm^3). In addition two crystals with thick (> 300 Å) needle-like and terrace morphologies prepared in Graz were also investigated.

It could be confirmed that the ultra-thin films grown in-situ show the same epitaxial orientation as the thicker films grown in Graz. Concerning the whole growth series, it could be concluded that the epitaxial orientation of p-6P on TiO2(110) is independent on the film thickness. *The in-situ growth together with the high resolution of beamline BM32 made it possible to identify p-6P polymorphs*.

In the region of the (00-6) reflection a second peak of comparable intensity was discovered. Investigations of this new peak and its higher orders yields an interplanar distance of 26.24Å which agrees exactly with an interplanar distance of the γ–phase of sexiphenyl. Till now the γ–phase has only been found for very thick films grown on amorphous substrates at elevated temperature where the molecules are in an essentially upright geometry. It is not fully crystallographically solved making further analysis difficult. *However, the presence of an additional epitaxial ordered γ–phase where the molecules are parallel to the surface observed here from 4.6 to 300 Å is a significant result important to any discussion of the film formation processes and growth dynamics of epitaxially ordered films of p-6P.*

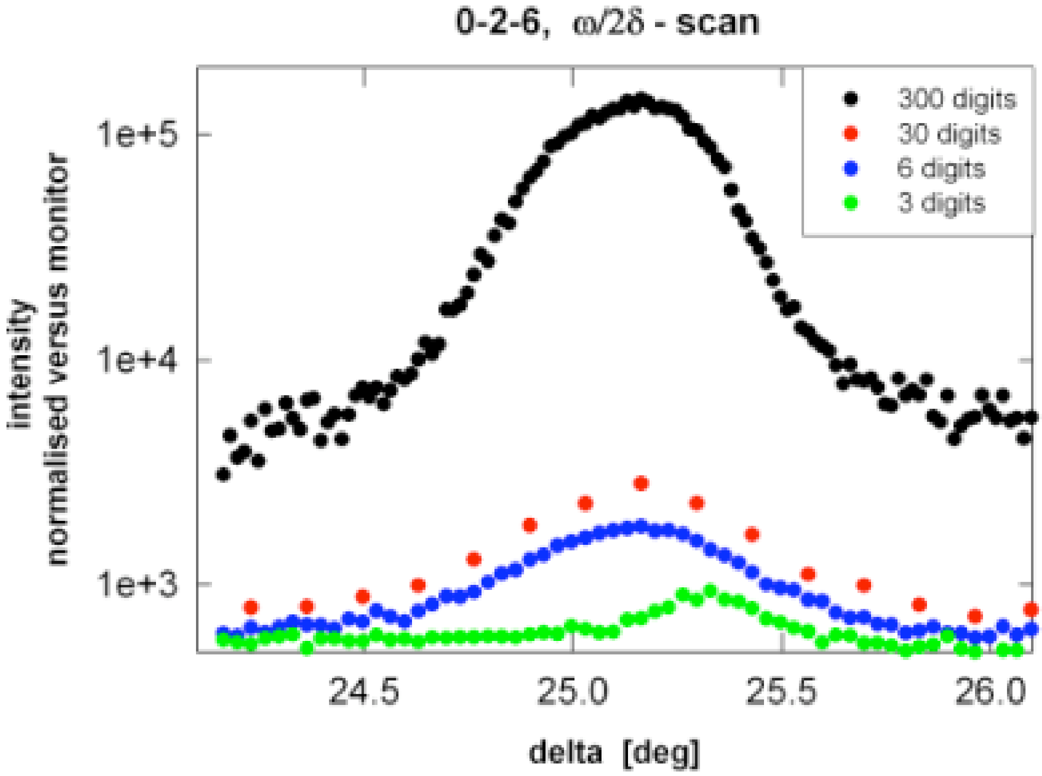

Figure 1: ω/2δ scan of the 0-2-6 peak as a function of the film thickness. The observed peak positions are 25.15° for the 300, 30 and 6 digit film, while the position changes to 25.32° in the film with thickness of about one monolayer. Remarkable is the small FWHM at the 3 digit films which increases to larger values at thicker films, an opposite behaviour would be expected.

Figure 1 gives the omega/2delta scan (comparable with a theta/2theta scan) of the 0-2-6 reflection of samples with different thickness. The 0-2-6 peak could be observed in all samples, even in the film with a thickness of 2.3Å. The fact that a clear diffraction peak is observable at an average film thickness of one monolayer suggests that pure island growth is present in the system p-6P on TiO_2(110)and consequently no wetting layer is present. A further remarkable result is the observation of an apparent peak shift of the 0-2-6 reflection. For coverages of 4.6Å and above the centre of mass of the peak corresponds to that of the accepted structure of p-6P however at 2.3Å coverage it is not only shifted but also much sharper. Relating this change to a lattice deformation of [010]p-6P along the [1-10]TiO2 a total strain of 0.045Å would result along the b-axis (b_strain = 5.523Å). This value is considerably smaller than the lattice mismatch of the TiO_2(110) surface (distances between the oxygen rows 6.497Å) and the repeating distances of the sexiphenyl contact plane (distance between neighbouring sexiphenyl molecules 5.568Å). It is probably more appropriate to consider that the lattice mismatch for the organic films is manifested in terms of polmorphism. The behaviour observed in figure 1 suggests the formation of a particular structure at very low coverages which grows together with the known bulk structure at moderate exposures.

Terrace-like growth: The results clearly indicated that the known bulk structure of p-6P, with an (001) orientation, grows even in a single layer of upright p-6P on the TiO2 substrate. Figure 2 presents a full range omega scan of the 20-3 reflection from a monolayer of p-6P (23Å at HT) in comparison to that obtained from the defective areas of 23 and 300 Å films grown at RT. These results in combination with those from the 11-1 reflection allowed the determination of the in plane alignment of the 6p crystallites unambiguously. By far the most intense features (note log scale) appear at 34°, 142°, 213° and 322°. These are due to four symmetry equivalent domains arising from the 17° tilt of the molecules from the surface normal whose projection onto the substrate makes an angle of 50° to the oxygen rows ([001) azimuth) of the substrate. *Presently we are trying to understand why this particular epitaxial relationship occurs.*

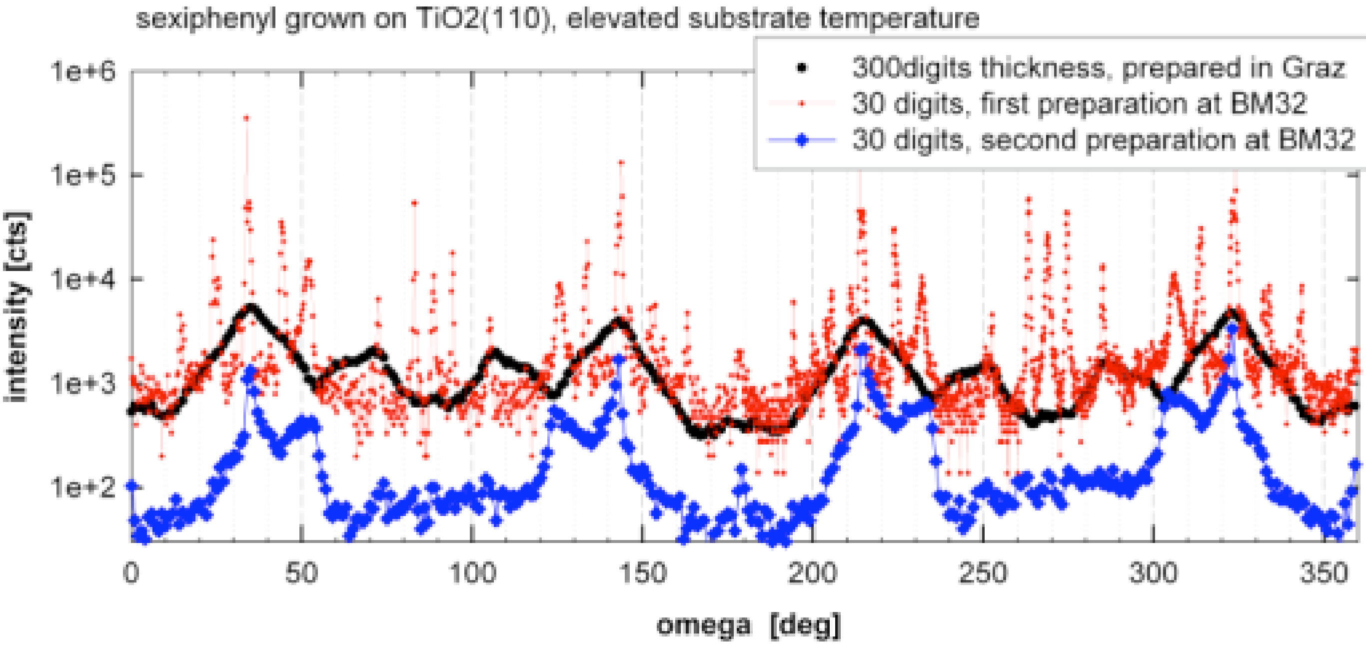

Figure 2: Omega scans for the 20-3 reflection in the whole angular range to probe the in-plane alignment of p-6P crystallites which forms the terrace like morphology. Two films are prepared at room temperature (filled circle, filled diamond) with different thickness (300 digits, 30 digits); one film was prepared at a substrate temperature of 373K (small symbols). Please note, the intensities are given in a logarithmic scale.

Layer growth on Al(111): During the beamtime we also made preliminary investigations of the 6P wetting monolayer and 5 layers of p-6P on clean Al(111). The data has yet to be fully analysed, however it is clear that epitaxial (21-3) oriented p-6P grows at RT even for ultra-thin layers. *Significant for our future experimental plans is the fact that the experimental set-up at BM 32 was not only well suited for investigating monolayers of poorly scattering organics but also allows the preparation of challenging substrates such as clean Al single crystal surfaces.*

Perspective: Although not yet fully analysed the results of this highly successful beamtime clearly showed that the structural studies of organic growth performed at BM 32 are not only possible without beam damage but also provide information not accessible by other techniques. This opens up a host of novel experiments.