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The epitaxial sexiphenyl (0 0 1) monolayer on TiO_2(1 1 0): A grazing incidence X-ray diffraction study

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Abstract

A para-sexiphenyl monolayer of near up-right standing molecules (nominal thickness of 30 Å) is investigated *in-situ* by X-ray diffraction using synchrotron radiation and *ex-situ* by atomic force microscopy. A terrace like morphology is observed, the step height between the terraces is approximately one molecular length. The monolayer terraces, larger than 20 μm in size, are extended along the [0 0 1] direction of the TiO_2(1 1 0) substrate i.e. along the Ti–O rows of the reconstructed substrate surface. The structure of the monolayer and its epitaxial relationship to the substrate is determined by grazing incidence X-ray diffraction. Extremely sharp diffraction peaks reveal high crystalline order within the monolayer, which was found to have the bulk structure of sexiphenyl. The monolayer terraces are epitaxially oriented with the (0 0 1) plane parallel to the substrate surface (out-of-plane order). Four epitaxial relationships are observed. This in-plane alignment is determined by the arrangement of the terminal phenyl rings of the sexiphenyl molecules parallel to the oxygen rows of the substrate.

Keywords: Organic epitaxy; Thin film structure; Grazing incidence X-ray diffraction; Atomic force microscopy

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1. Introduction

Oligophenylenes-like sexiphenyl ($C_{36}H_{26}$) are technologically relevant molecules with intense blue light emission, high quantum yield and acceptable chemical stability making them useful in display technology [1,2] and for photovoltaic applications [3]. The molecular alignment, crystal order and morphology within thin films is a key parameter for device performance [4]. Generally, for conjugated molecules with rod-like shape (e.g. sexiphenyl, sexithiophene, pentacene, a.o.) a terrace like morphology made up of near-upright oriented molecules gives good characteristics in organic thin film transistors (oTFT) [5]. Since the charge transport in oTFT happens exclusively within the first monolayers, the crystal order within these monolayers is of crucial importance [6].

Both needle and terrace like morphologies, where the sexiphenyl molecules are near parallel or perpendicular to the surface, respectively, have been reported on mica(0 0 1) and alkali halide(1 0 0) surfaces [7–9]. On well ordered TiO_2(1 1 0) surfaces growth at room temperature or below leads to films where the molecules are exclusively oriented parallel to the surface and the raised oxygen rows of the surface, in needle like morphologies [10]. For growth on TiO_2(1 1 0) at elevated temperatures the molecules adopt a near upright orientation [11]. For pentacene huge efforts are being made to evaluate the crystallographic order within

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the first upright standing monolayers, particularly on the amorphous silicon oxide [12–14]. An interfacial structure, different to the equilibrium bulk structure, with the molecules almost perfectly perpendicular to the substrates has been found. Here it is shown that these results cannot be generalized. The present work describes the morphology and the crystallographic order of a sexiphenyl thin film of near up-right molecules with monolayer thickness on a well ordered $TiO_2(1\,1\,0)$ 1×1 reconstructed surface. It is shown that the bulk crystal structure exists even in the first monolayers with a 6P(0 0 1) surface orientation where the molecules are at 17° to the surface normal. Moreover these monolayer crystallites have an epitaxial relationship to the substrate with the epitaxial alignment related to the periodicity of the substrate surface corrugations.

2. Experimental

Thin films of para-sexiphenyl (6P) are prepared under ultra high vacuum (UHV, 10^{-10} mbar) in the so-called SUV chamber at the beamline 32, ESRF Grenoble. The $TiO_2(1\,1\,0)$ single crystal substrates are cleaned by Ar^+-ion bombardment and subsequent annealing at 900 K. 6P is deposited from a degassed Knudsen cell on the $TiO_2(1\,1\,0)$ surface at a substrate temperature of about 370 K. A quartz microbalance is used to calibrate the growth rate assuming a density of 1.3 g/cm^3. The deposition rate was determined as 0.1 Å/s.

Atomic Force Microscopy (AFM) is performed with a DIGITAL INSTRUMENTS MULTIMODE IIIa scanning probe microscope. The measurements are performed *ex-situ* in tapping mode under ambient conditions. Conventional silicon carbide tips are used, a low scan speed is applied.

In-situ investigations of the 30 Å film are performed by Grazing Incidence X-ray Diffraction (GI-XRD) at the *z*-axis goniometer at BM32, ESRF Grenoble [15]. A wavelength of 1.0325 Å (12.0 keV) is used to minimize the generation of photoelectrons and thus to reduce the beam damage of the organic film. Beam damage was monitored on 6P diffraction peaks over a period of 24 h and no degradation was detectable under these UHV conditions. The incidence angle of the primary beam relative to the substrate is chosen at 0.15°, slightly below the total reflection angle of the substrate. The detector angle for in-plane scattering (δ) determines the surface parallel component of the scattering vector ($q_\|$). The detector angle for out-of-plane scattering (β) gives the *z*-component of the scattering vector (q_z). The total scattering angle 2θ is obtained by $\cos 2\theta = \cos\delta \times \cos\beta$. The variation of the scattering vector relative to the sample is performed by rotating the sample around the surface normal by an angle ω. Both detector angles are required to observe diffraction peaks of 6P crystallites, since no intense in-plane peaks are present. Complementary to GI-XRD studies at the synchrotron source, standard *ex-situ* XRD specular scans ($\Theta/2\Theta$-scans) on films with a nominal thickness of 300 Å are performed on the laboratory equipment SIEMENS D501 using CuK_α radiation in Bragg Brentano geometry.

The software POWDERCELL was used to calculate 2θ positions and peak intensities, based on the tetragonal structure of TiO_2 with $a = 4.594$ Å and $c = 2.959$ Å and the β-phase of 6P with $a = 8.091$ Å, $b = 5.568$ Å, $c = 26.24$ Å and ß = 98.17° [16,17]. The software STEREOPOLE is used for the determination of the epitaxial relation between 6P crystallites and the $TiO_2(1\,1\,0)$ substrate [18]. Crystallographic size/strain analysis is performed by a modified Williamson–Hall formalism using following equations [19,20]:

$$\delta\omega = \sqrt{M^2 + \left(\left(\frac{\delta q_\Delta}{q}\right)^2\right)}, \qquad \delta q_r = \sqrt{(\delta q_\Delta)^2 + \left(q\frac{\delta d}{d}\right)^2}$$

with q the length of the scattering vector, $\delta\omega$ as the experimentally observed width of the in-plane rocking curves, δq_r the experimentally observed variation of the length of the scattering vector in radial direction (from $\omega/2\delta$ scans), M as the in-plane mosaicity, δq_Δ the variation of the scattering vector due to crystalline size effects (with $\delta q_\Delta = 2\pi/L$, with L as the crystallite size) and $\delta d/d$ the microstrains. The integral breadth of the diffraction peaks is determined by fitting Gauss peaks for ω/2delta-scans and Lorentzian functions for ω-scans.

3. Experimental results

Fig. 1 shows a typical AFM micrograph of a 6P film with a nominal thickness of 30 Å grown at elevated substrate temperature (approximately 370 K). The majority of the surface is covered by extremely large terraces (≈40 μm × 6 μm) elongated in the [0 0 1] azimuthal direction of the $TiO_2(1\,1\,0)$ substrate with step heights of 25 Å.

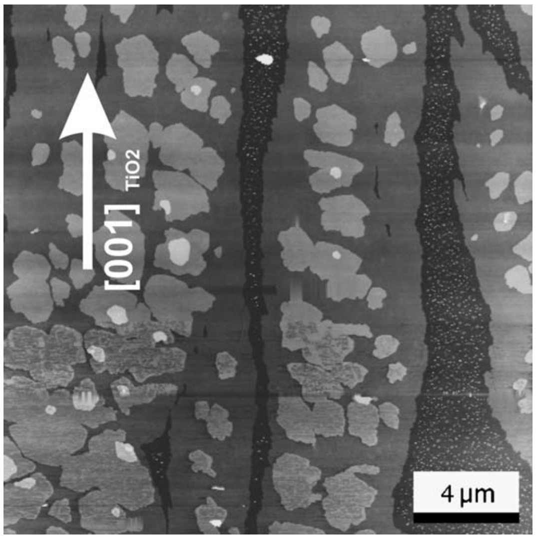

Fig. 1. An atomic force microscopy micrograph of a sexiphenyl film with a nominal thickness of 30 Å grown on a $TiO_2(1\,1\,0)$ surface. The *z*-scale is 100 Å.