

Highly ordered anisotropic nano-needles in para-sexiphenyl films

A. Andreev^{a,*}, H. Sitter^b, N.S. Sariciftci^a, C.J. Brabec^a, G. Springholz^b, P. Hinterdorfer^c, H. Plank^d,
R. Resel^d, A. Thierry^e, B. Lotz^e

^aLinz Institute for Organic Solar Cells (LIOS), Physical Chemistry, University Linz, Austria

^bInstitute for Semiconductor and Solid State Physics, University Linz, A-4040 Linz, Austria

^cInstitute of Biophysics, University Linz, A-4040 Linz, Austria

^dInstitute of Solid State Physics, Graz University of Technology, Graz, Austria

^eInstitute Charles Sadron, Strasbourg, France

Abstract

Atomic force microscopy (AFM) was used to investigate the early growth stage of highly ordered para-sexiphenyl thin films deposited by hot wall epitaxy on mica, in order to find the process controlling parameters. It was shown that the growth time and surface type are important parameters for controlling of the film morphology, in terms of the degree of anisotropy and long range order. X-Ray diffraction pole figure technique and transmission electron diffraction was also used to characterize the crystallographic structure of the thicker films. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Para-sexiphenyl (PSP) is a very interesting model compound for studying the basic physical properties of conjugated organic semiconductors. Practical interest in well-ordered PSP structures originates from the potential of such structures for the application in blue light-emitting diodes (OLED) with polarized emitting properties [1]. Thin films of PSP have been grown on oxidized and non-oxidized GaAs, KCl, glass and ITO substrates using conventional physical vapor deposition [1–3] and organic molecular beam epitaxy (OMBE) [4]. It was shown that the nature of the substrate, substrate temperature and the deposition rate are determining parameters for molecular packing. Recently, we reported that highly ordered crystalline films of PSP could be grown by hot wall epitaxy (HWE) on crystalline mica [5]. Self-organization of PSP molecules occurred during HWE growth resulting in large scale ordered needle-like

structures with a length to width ratio up to 500. However, the growth regularities of such high anisotropic structures and their relationship to the mica substrate were not clear yet, although this is important for achieving highly ordered PSP films on other substrates.

In this paper the early growth stages of the PSP films on mica were investigated using atomic force microscopy (AFM), in order to find the process controlling parameters. X-Ray diffraction pole figure technique (XRDPFT) and transmission electron diffraction (TED) were also used to determine the orientation of the PSP molecules with respect to the mica surface.

2. Experiment

PSP, obtained from Tokyo Chemical Industries, was purified by threefold sublimation under a dynamical vacuum. The used substrates were freshly cleaved (001)-oriented mica. The vacuum during growth was approximately 6×10^{-6} mbar and the PSP source temperature was fixed at 240°C. The substrate temperature was fixed at 90°C, growth time was in a range from 14 s to 60 min. These growth parameters resulted in a low depo-

* Corresponding author. Tel.: +43-732-2468-9658; fax: +43-2468-8770.

E-mail address: andrei.andreev@jk.uni-linz.ac.at (A. Andreev).

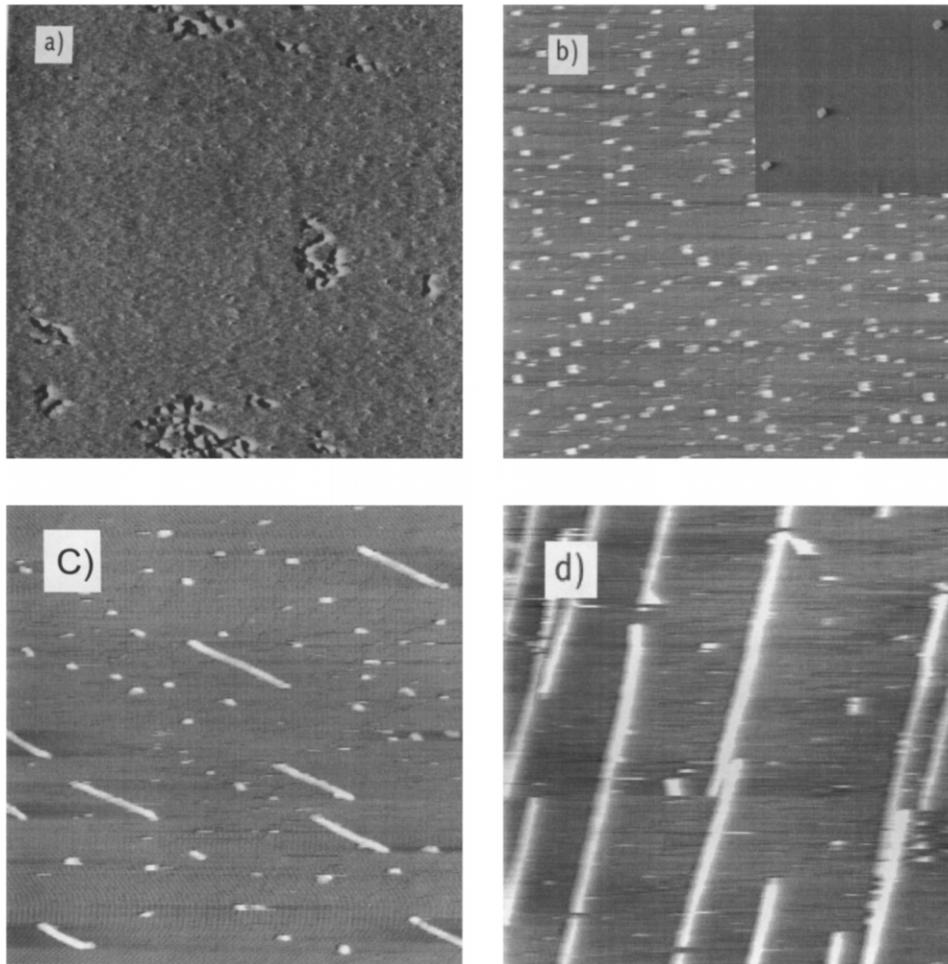


Fig. 1. The $5 \times 5\text{-}\mu\text{m}$ AFM images of the PSP films grown at a time (a) 14 s, (b) 25 s — insert shows also the island shapes ($1 \times 1\text{-}\mu\text{m}$ deflection image of the same sample) and (c) 46 s, (d) 94 s.

sition rate of approximately 2 nm/min. Further growth details can be also found in Andreev et al. [5]. The film morphology was imaged by AFM using AutoProbe CP PCI or NanoScope IIIa Microscopes. Selected area TED measurements were employed with a Philips CM12 electron microscope. A Philips X'Pert system with an ATC3 texture cradle was utilized for the pole figure measurements performed in Schultz reflection geometry using Cr-K_{α} radiation and a secondary graphite monochromator. The software packages Powder Cell 2.3 [6] and Stereogramm [7] were used for XRD data analysis.

3. Results and discussion

The PSP film morphology with increasing growth time in the range from 14 to 94 s is shown in the AFM images of Fig. 1. As depicted in Fig. 1 a smooth film surface with many pin-holes can be detected for the sample grown within 14 s. AFM line profile measurements show that their depth varies approximately from 10 to 30 Å. The surface morphology changes drastically

if growth time is varied from 14 to 25 s: uniformly distributed small 3D-islands with a compact shape (see insert on Fig. 1b) and average height of ≈ 9 nm appear. This behavior can be interpreted as evidence that PSP grows on mica in the Stranski–Krastanov (layer by layer + 3D-islands) growth mode. Further increase of the coverage leads to an island shape transition resulting in typical needle-like structures with longer 3D-islands [4,5]. Fig. 1c,d clearly shows that the islands become progressively elongated, quickly reaching a fixed asymptotic width while their height remains much smaller than their length and width, as quantitatively depicted for the whole time scale in Fig. 2. AFM analysis showed also that the islands grow quickly from ≈ 17 to $\approx 4\text{ }\mu\text{m}$ between 25 and 94 s and reach a length of more than $100\text{ }\mu\text{m}$ at approximately 60 min.

We think (see also [4]) that these extraordinary features can be qualitatively explained in terms of strain-induced heteroepitaxial island growth. Tersoff and Tromp [8] have theoretically predicted a strain-induced, spontaneous shape transition from compact square

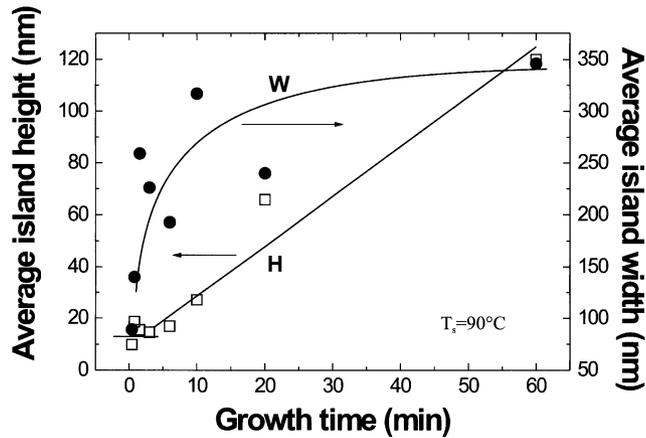


Fig. 2. Quantitative analysis of three-dimensional PSP islands (needles) grown on mica.

islands to elongated ones of asymptotic constant width. This means that compact 3D-islands grow to a critical size in their width and length, which are considerably larger than their height (nearly constant). Above the critical size, the islands grow only in length, but not in width, which converges towards an asymptotic value. Generally, our results agree with these theoretical predictions very well. However, experimentally we also observe (see Fig. 2) from a certain time point an increase of the islands in height, not only in length, which is not considered in the theoretical model.

The influence of substrate type on the growth behavior of PSP by HWE is demonstrated in Fig. 3. In this case the films were grown at the same conditions on different crystalline substrates: (001)-oriented mica (Fig. 3a) and (111)-oriented C_{60} (Fig. 3b). For the growth of the C_{60} layer, which acts then as 'substrate', the optimized growth parameters given in [9] were used resulting in perfect crystalline films. Note that the PSP layer was grown on top of the C_{60} just by changing the position of the substrate in the chamber from C_{60} -source to PSP-source. We can see that in contrast to mica PSP on C_{60} forms big unoriented lamellae and no large scale ordered needles-structures.

XRPDFT and TED were used to characterize the crystallographic structure of the thicker PSP films grown on mica. The growth time of all investigated films was set to 60 min, resulting in an average islands height of 130 nm. Fig. 4a gives a typical defocused electron microscopy image of the PSP film revealing the typical needle-like morphology. The diffraction patterns in Fig. 4b are taken from the darker spot in Fig. 4a. Their analysis reveals that the $(11\bar{1})$ crystallographic plane of PSP is parallel to the substrate surface, which confirms our earlier X-ray data [5]. The incident electron beam was parallel to the $[\bar{1}20]$ zone axis of crystalline PSP within an accuracy of $\pm 5^\circ$. The intensities and the positions of the reflections are in excellent agreement

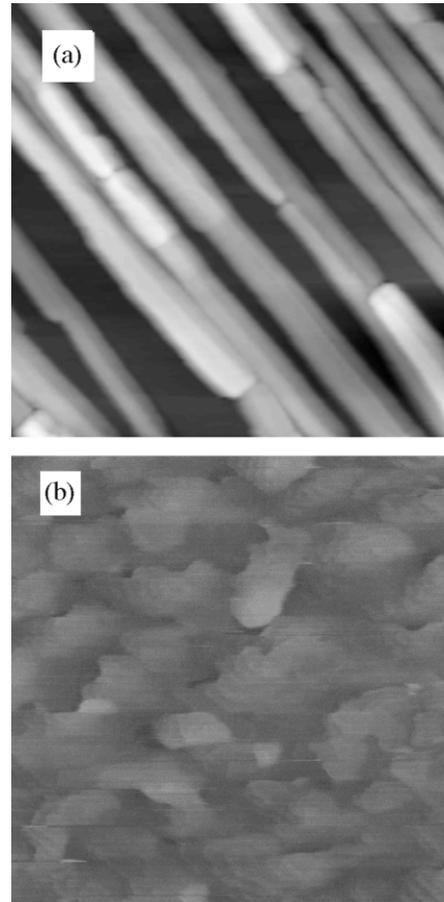


Fig. 3. The $3 \times 3\text{-}\mu\text{m}$ topographical images characterizing the PSP film grown on different crystalline substrates: (a) on (001) mica; and (b) on crystalline (111) C_{60} layer grown immediately before.

with a calculated diffraction pattern based on the β structure of PSP [10]. Therefore, further crystallographic analysis was performed on this structure.

XRD pole figures were collected at 2θ positions corresponding to the interplanar distances of the $(11\bar{1})$, $(11\bar{2})$, $(20\bar{3})$ and $(21\bar{3})$ crystallographic planes of PSP. The results are depicted in Fig. 5. Enhanced pole

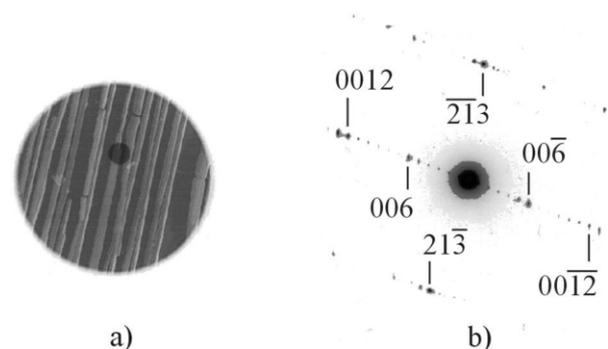


Fig. 4. TED studies on PSP films. (a) The defocused image. (b) The diffraction patterns, which were taken from the darker spot in (a).

densities are reflected by different gray scales, the inner circle indicates the measurement limit of $\psi = 75^\circ$. The strong maxima of poles indicate that the PSP layer was highly ordered. Problems in the beam geometry and the very similar lattice spacing between the $(11\bar{1})$ and $(11\bar{2})$ crystallographic planes of PSP are responsible for the elongated shape of pole figures at higher ψ angles. The detailed analysis of the whole set of the pole figures reveals two crystallographic orientations of PSP crystallites on mica: the $(11\bar{1})$, which was slightly preferred and the $(11\bar{2})$ crystallographic plane parallel to the substrate surface. The epitaxial relationships between the mica substrate and the organic layer are: (i) $\text{PSP}(11\bar{1}) \parallel \text{mica}(001)$ and $\text{PSP}[1\bar{2}\bar{1}] \parallel \text{mica}[\bar{3}40]$; (ii) $\text{PSP}(11\bar{2}) \parallel \text{mica}(001)$ and $\text{PSP}[2\bar{0}\bar{1}] \parallel \text{mica}[\bar{3}10]$. Based on the TED and XRDPT studies we can propose a model for the orientation of PSP molecules on the mica surface, which is schematically depicted in Fig. 6. Please note that both crystallographic orientations — $(11\bar{1})$ and $(11\bar{2}) \parallel \text{mica}(001)$ — show nearly the same alignment of the molecules relative to the substrate surface. Hence, we show only one of them. For both orientations the long molecular axes are tilted by $\sim 5^\circ$ with respect to

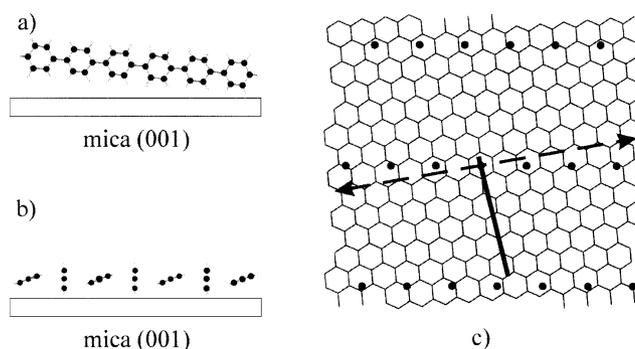


Fig. 6. Orientation of PSP in respect of the (001) mica surface: (a) Alignment of a single contact molecule in a side view; (b) parallel view; and (c) contact point lattice of the PSP molecules for the $(11\bar{1})$ orientation on an idealized hexagonal mica surface.

the surface. This finding is also in excellent agreement with our previous optical studies [5]. Therefore, only the lowest aromatic rings of the molecules are in contact with the substrate surface, as depicted in Fig. 6a. These contact molecules are oriented with their molecular plane perpendicular to the substrate surface. The inter-

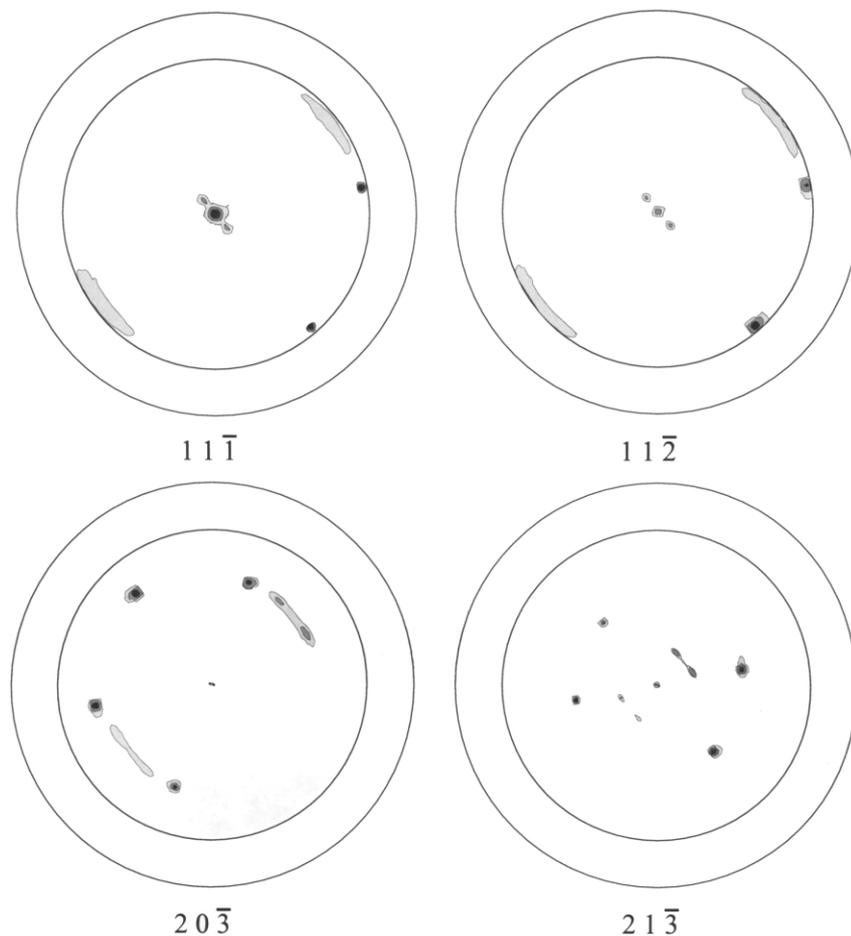


Fig. 5. X-Ray diffraction pole figures of the $(11\bar{1})$, $(11\bar{2})$, $(20\bar{3})$ and $(21\bar{3})$ reflections of PSP.

mediate molecules do not touch the substrate surface. This fact can be clearly seen in Fig. 6b — the cleavage plane character is also evident. Since the contact molecules touch the mica surface only at a single point, a contact point lattice can be generated. In Fig. 6c, the contact point lattice for the $(11\bar{1})$ orientation (marked with black points) is drawn on the mica surface (represented by a hexagonal net). The thick line represents a contact molecule projected in the direction of the molecular plane. The dashed line indicates the needle direction obtained by the TED measurements with an accuracy of $\pm 5^\circ$. Note that in the line with [5] the needles are perpendicular to the molecular axes. The two directions within each orientation lead to no change in the point lattice due to the antiparallel arrangement of the molecules.

From Fig. 6 we also infer that the specific interface configurations of (001) mica and $(11\bar{1})$ and $(11\bar{2})$ PSP are incommensurable. This type of growth, also referred to as quasi-epitaxy [11], is dominantly found for organic materials, in which intermolecular interactions are much stronger than substrate-molecule interactions. This is, at least in the initial growth stage, in certain conflict with the growth mechanism discussed above, because the latter suggests a strong epitaxial interaction between mica and PSP molecules. Therefore, additional studies (especially, X-ray investigations of thinner layers) are needed to refine the proposed growth model.

4. Conclusions

The growth of PSP thin films on crystalline mica substrates using HWE was investigated. A self-organization of PSP molecules occurs during HWE resulting in needle-like structures. AFM studies of the earlier

stage of the growth have shown that this self-organization can be presumably explained in terms of strain-induced epitaxial island growth. A possible arrangement of PSP molecules on the mica surface relative to the ‘needles’ is proposed from analysis of X-ray and transmission electron diffraction results.

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