

## Organic thin films grown by hot wall epitaxy on inorganic substrates

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In this work we use Atomic Force Microscopy and X-ray diffraction to study the morphology and the growth kinetics of *para-sexiphenyl* layers deposited by hot wall epitaxy on crystalline mica (001) and KCl(001) substrates. It is shown that *para-sexiphenyl* forms on mica very long parallel oriented crystalline needles with one preferential direction. In contrast, on KCl (001) the growth is characterized by a co-existence of long needles (“laying” molecules) and terrace structured islands (“standing” molecules). The former belong to the initial growth stage of the films, generating a rectangular network in accordance with the surface symmetry of the substrate.

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### 1 Introduction

$\pi$ -conjugated small molecules and oligomers have already been successfully used as active layers in field effect transistors, light emitting diodes and in solar cells [1–8]. These molecules are thermally stable up to 300–400 °C, can be obtained as pure materials and can be processed as thin films in high-vacuum conditions. The morphology, molecular packing and structural properties of these thin films are essential for their optical properties and charge transport through the active layer [1–3, 6, 9].

The present work focuses on *para-sexiphenyl* (PSP, C<sub>36</sub>H<sub>26</sub>), a six units oligomer of *para-phenylene*. PSP crystallizes monoclinic with the space group P2<sub>1</sub>/a and the lattice constants  $a = 8.09$  Å,  $b = 5.56$  Å,  $c = 26.24$  Å,  $\beta = 98.17^\circ$  [10]. The long molecular axes of all molecules within the unit cell are oriented parallel to each other, whereas adjacent molecular planes are tilted about 66°, which form the typical herringbone structure of PSP. PSP films are very promising for the application in blue organic light-emitting diodes (OLED) [3, 6, 11] and have been grown previously on different substrates using conventional physical vapor deposition [3, 6, 11, 12] or organic molecular beam epitaxy (OMBE) [13, 14]. It was generally shown that the nature of the substrate, substrate temperature and the deposition rate are the determining parameters for molecular packing. In particular, depending on substrate temperature and growth rate, films of predominantly standing or lying molecules can be obtained [3, 6, 12, 14–18].

Hot wall epitaxy (HWE), working close to thermodynamic equilibrium, is well known as very appropriate technique to grow highly ordered epitaxial organic films with improved optical properties [19–

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21]. In this paper we performed comparative atomic force microscopy (AFM) and X-ray diffraction (XRD) investigations of HWE deposition of PSP on mica and KCl substrates, in order to clarify the growth mechanism of these films.

## 2 Experimental

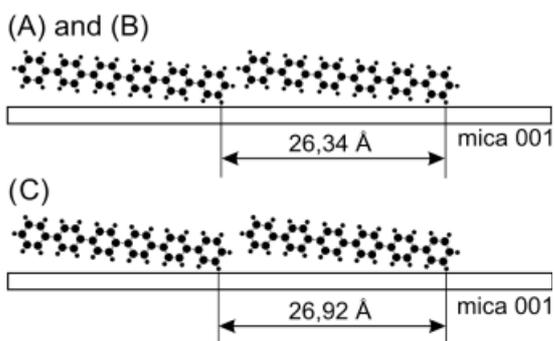
PSP was purified by three-fold sublimation under dynamic vacuum. As substrates we used crystalline freshly cleaved mica (001) and KCl (001). The base pressure during growth was about  $6 \times 10^{-6}$  mbar and the PSP source temperature was fixed at 240 °C. The substrate temperature was 80–90 °C. The growth time was varied between 5 sec and 60 min. The film morphology was imaged by AFM operated in tapping mode in air. XRD studies were performed at the Cornell High Energy Synchrotron Source (CHESS, Ithaca, USA).

## 3 Results and discussion

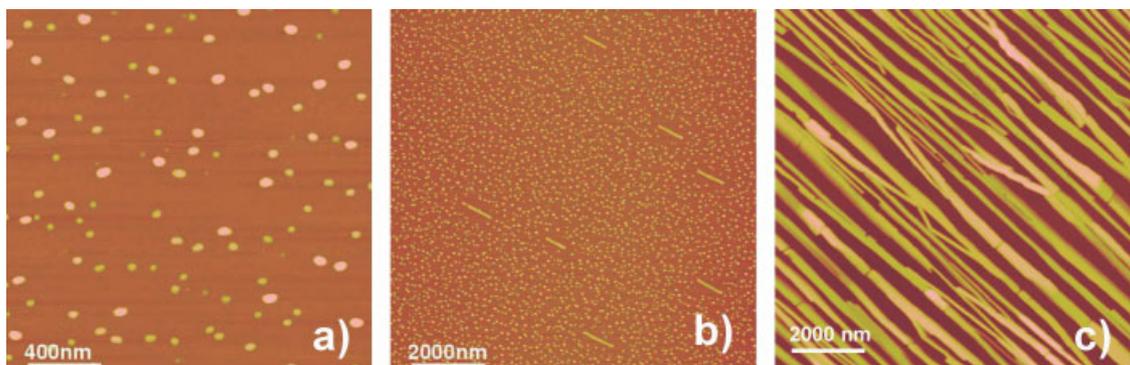
As we reported earlier a self-organization of PSP occurs during HWE on single crystalline mica substrates [19, 20], resulting in large scale (up to 1 mm range) ordered needle-like structures with only one preferential direction. Such structures show high optical anisotropy with dichroic ratios up to 15 [19]. Systematic crystallographic studies (combination of XRD, Pole Figures XRD and transmission electron diffraction) revealed three similar crystallographic orientations of PSP on mica:  $(11\bar{1})\text{PSP} \parallel (001)\text{mica}$  &  $[12\bar{1}]\text{PSP} \parallel [\bar{3}40]\text{mica}$  (orientation (A));  $(\bar{1}\bar{1}1)\text{PSP} \parallel (001)\text{mica}$  &  $[\bar{1}10]\text{PSP} \parallel [\bar{3}40]\text{mica}$  (orientation (B)) and  $(11\bar{2})\text{PSP} \parallel (001)\text{mica}$  &  $[\bar{2}0\bar{1}]\text{PSP} \parallel [\bar{3}10]\text{mica}$  (orientation (C)) [20, 22]. These three orientations of the molecules relative to the substrate are shown in Fig. 1. In all three cases the alignment of the long molecular axes relative to the substrate is approximately the same. Nevertheless, a high degree of epitaxial alignment was observed by rocking curves with a FWHM as low as  $0.06^\circ$  [23].

The surface morphology of PSP films prepared on mica with increasing growth time in the range from 10 sec to 40 min are shown in the AFM images of Fig. 2. As depicted in Fig. 2a only small uniformly distributed islands with a typical size of approximately  $100 \times 50 \times 20 \text{ nm}^3$  can be detected for the samples grown within 5–30 seconds. The surface morphology changes drastically if a critical density of islands is reached: a rearrangement of islands occurs resulting in self-organized needles with micrometer length (Fig. 2b). With increasing time these needles become progressively longer, quickly reaching a fixed asymptotic width, as already described in Ref. [24]. At least after 5 min of growth nearly no small islands could be found on the surface (Fig. 2c), while the needles become closer to each other. Interestingly, the same self-organized behavior was also found for the samples grown at 150 °C, however, in this case the islands rearrangement occurs earlier – between 10 and 25 seconds of growth time.

As is evident from Fig. 2b–c, all needles from the very beginning are strictly parallel to each other having the same preferential orientation relative to the substrate. Detailed AFM investigations showed that this orientation as well as PSP island nucleation is not controlled by step edges on the mica surface. As already shown in Fig. 1 the long axis of PSP molecules within the needles and islands are nearly parallel to the substrate and perpendicular to the needles direction [19, 20, 22].



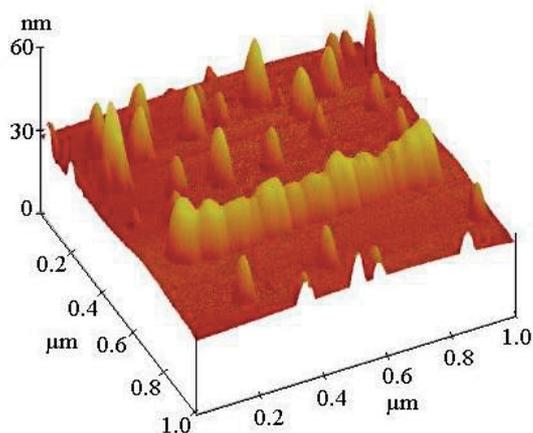
**Fig. 1** Side view of PSP molecules relative to the mica (001) substrate as they are oriented within their epitaxial orientations. Top part: orientations (A) & (B) with the same intermolecular distance of  $a = 26.34 \text{ \AA}$ . Bottom part: orientation (C) with another distance of  $a = 26.92 \text{ \AA}$ .



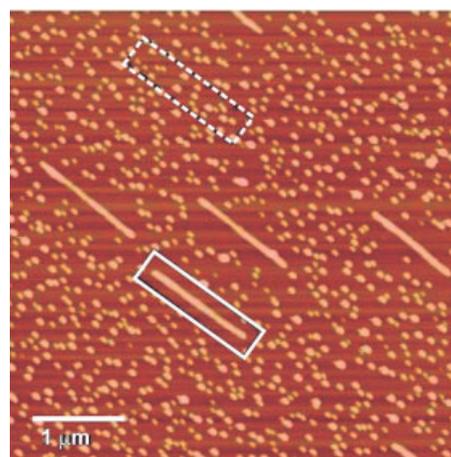
**Fig. 2** (online colour at: [www.pss-b.com](http://www.pss-b.com)) AFM images of the PSP films grown within a) 10 sec, b) 35 sec and c) 40 min. Z-scale is 0–25 nm in (a), 0–50 nm in (b) and 0–100 nm in (c).

Some of the extraordinary features shown in Fig. 2 can be explained qualitatively (see also [23, 24]) in terms of strain-induced heteroepitaxial island growth, well known in inorganic heteroepitaxy. For example, Tersoff and Tromp [25] have predicted theoretically a strain-induced, spontaneous shape transition from compact square islands to elongated ones of asymptotic constant width. This means that compact 3D-islands grow to a critical size in width and length considerably larger than their height (which remains nearly constant). Above the critical size, the islands grow only in length, but not in width, which converges towards an asymptotic value. Generally, our main results agree well with these theoretical predictions.

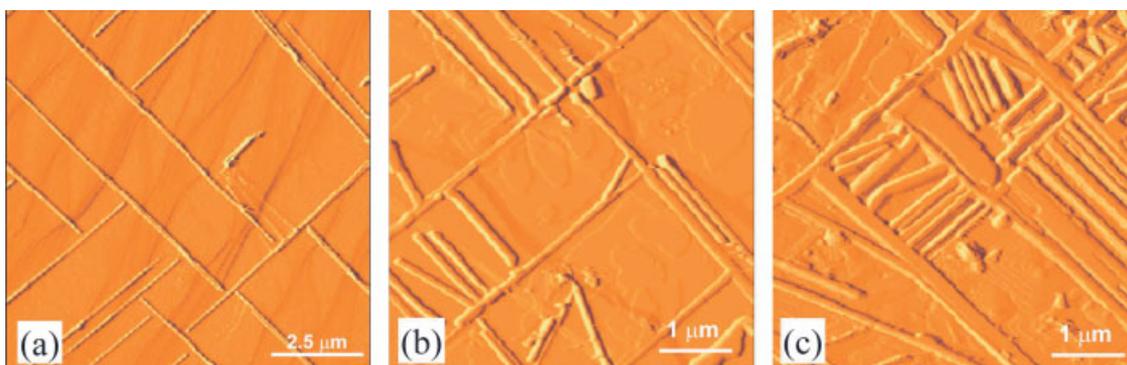
Figure 3 shows a 3D-AFM image of a single PSP nano-needle surrounded by small PSP islands in the earlier growth stage ( $t \approx 35$  sec, Fig. 2b). The image clearly reveals that the roughly 850 nm long needle is not homogenous and consists of about 15 small blocks with approximately the same size as free standing PSP islands. This result indicates that self-organized PSP needles on mica are formed really by re-grouping of mobile individual islands originating from earlier growth stages. This thesis is well supported by the observation of denuded zones (free of islands) around the needles as shown in Fig. 4. One can clearly see that the 75 nm wide and 1.25  $\mu\text{m}$  long needle has a denuded zone of about  $0.4 \times 1.5 \mu\text{m}$



**Fig. 3** (online colour at: [www.pss-b.com](http://www.pss-b.com)) High resolution three-dimensional AFM image showing individual PSP islands as well as a single needle.



**Fig. 4** (online colour at: [www.pss-b.com](http://www.pss-b.com)) AFM image ( $5 \times 5 \mu\text{m}$ ) showing a denuded zone (marked by the solid rectangle) around the PSP needle. The dashed rectangle marks the same surface area in a region far away from this needle.



**Fig. 5** AFM images of the PSP films grown within a) 45 s; b) 10 min; c) 40 min.

(marked by the solid rectangle). Note, that in the same surface area in a region far away from this needle (marked by dashed rectangle) you can find about 20 islands, which corresponds to the same surface coverage as the area covered by the compact needle. Further investigations concerning the details of the needles formation and their structure are in progress.

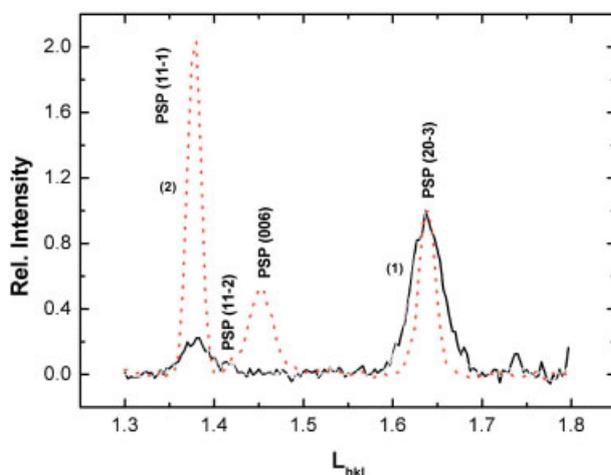
In order to compare the results obtained for PSP on mica substrates we perform the same kinetic studies on KCl (001). The films were grown on KCl (001) at the same growth temperature within growth times in the range from 45 s to 40 min. Corresponding surface morphologies are shown in the AFM images of Fig. 5. It is evident that under HWE conditions PSP can form needles (Fig. 5a) and plate-like crystallites (Fig. 5 b, c) at the same time, as well as during simple vapor-deposition [15]. This is in contrast to PSP growth on mica, where only PSP needles are formed. On the other hand, as shown in Fig. 5a, the needles are clearly the initial growth stage of the films on KCl. They start to grow direct on the substrate surface, generating a rectangular network in accordance with the surface symmetry of KCl [15, 16]. In this stage the needles are already in average of  $\approx 10$  nm in height,  $\approx 100$  nm in width and  $\approx 3-4$   $\mu\text{m}$  in length. After a few minutes of deposition time terrace structured islands develop between the needles, as depicted in Fig. 5b. The terraces are in average  $\approx 2.6$  nm high, which corresponds to one monolayer of standing molecules of PSP. Further growth (Fig. 5b, c) is characterized by a coexistence of the constantly growing needles and islands, whereby the last ones are clearly bordered by the rectangular network of the needles. The number of terraces on layered islands tends to increase with increasing surface coverage: at most 2, 5 and 9 terraces were observed in the films deposited for 5, 10 and 40 min, respectively. After 40 min of deposition almost the whole surface between the needles is covered with layered crystals (Fig. 5c). Nevertheless, we have not observed the overgrowth of the needles across the islands, or vice versa.

In accordance with Refs. [15, 16], the AFM images show, that the needles mainly grow along two orthogonal KCl [110] directions. This bidirectional epitaxial orientation seems to originate from an interaction between the linear PSP molecules and the ionic rows along KCl [110] and  $[1\bar{1}0]$  directions, as previously reported for PSP films grown by simple vapor deposition [15]. The epitaxial orientation of the needles is almost perfect for thin PSP layers (see Fig. 5a), but the amount of misaligned needles clearly increased with increasing of the growth time (see Fig. 5b, c). One can assume that this is caused by the islands, which after some time hamper the free extension of the needles.

The molecular orientation in PSP films grown on KCl (001) were proven by X-ray diffraction (XRD) measurements using synchrotron radiation, which allows to measure even weak intensities as those from thin organic layers. In order to get scans where the peak positions of the films are not dependent on the equipment and the energy of synchrotron beam, we have used so called  $L$ -scans [26]. In principle  $L$ -scan is a  $\theta/2\theta$ -scan, where you measure the intensity not versus  $2\theta$ , but as a function of the multiple of the lattice constant  $L_{\text{KCl}} = 6.2917$   $\text{\AA}$  of the substrate.  $L(hkl)$  value can be than calculated as:

$$L_{hkl} = L_{\text{KCl}} / d_{hkl},$$

where  $h$ ,  $k$  and  $l$  are the corresponding Miller indices and  $d$  – the net plane distance of the PSP planes.



**Fig. 6**  $L$ -scans for PSP films on KCl (001) corresponding to standard  $\theta/2\theta$ -scans. PSP films were grown for 45 s (1) and 40 min (2).

Figure 6 shows typical  $L$ -scans for PSP films grown within 45 s and 40 min at 80 °C. Note that the AFM morphologies of these films are depicted in Figs. 5a and 5c. The scans reveal at least four different growth orientations parallel to the surface of the substrate:  $(11\bar{1})$ ,  $(11\bar{2})$  and  $(20\bar{3})$  reflections are due to laying molecules, whereas (006) reflection is due to standing molecules [12, 20, 26]. In full agreement with results of AFM investigations, the (006) reflection appears only for thicker films which contain terrace shaped island consisted of standing molecules. Correspondingly, the needles consist of the other three epitaxial orientations, where the long molecular axes are approximately parallel to the KCl (001) surface.

Further investigations concerning the kinetics of the needles/islands formation and their crystallographic quality are in progress.

## 4 Conclusions

The HWE growth of PSP thin films on crystalline mica (001) and KCl (001) substrates was investigated using AFM and XRD techniques. AFM studies clearly show that self-organization of PSP molecules occurs during HWE on both substrates, resulting in well ordered films. On mica PSP forms very long parallel oriented crystalline needles with one preferential orientation. In contrast, on KCl (001) the growth is characterized by co-existence of long needles (“laying” molecules) and terraces structured islands (“standing” molecules). The former are the initial growth stage of the films, generating a rectangular network in accordance with the surface symmetry of the substrate. The islands, co-existing with the needles, are observed only at a later growth stage. XRD studies confirmed these AFM results and revealed the epitaxial order for both types of crystallites. The needles are build up of molecules aligned with their long molecular axes approximately parallel to the surface and the islands consist of standing molecules. It is also shown (at least for mica) that the growth process is very complex and involves not only molecules but also small PSP islands as migrating species.

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