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Morphology and growth kinetics of organic thin films deposited by hot wall epitaxy

A.Yu. Andreev [a,c,*], C. Teichert [b], G. Hlawacek [b], H. Hoppe [c], R. Resel [d], D.-M. Smilgies [e], H. Sitter [a], N.S. Sariciftci [c]

[a] Institute of Semiconductor and Solid State Physics, University Linz, A-4040 Linz, Austria
[b] Department of Physics, University of Leoben, A-8700 Leoben, Austria
[c] Physical Chemistry and LIOS, University Linz, A-4040 Linz, Austria
[d] Institute of Solid State Physics, Graz University of Technology, A-8010 Graz, Austria
[e] CHESS G-line, Cornell University, Ithaca, NY 14853, USA

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Abstract

In this work we have used atomic force microscopy and X-ray diffraction by synchrotron radiation to investigate the growth kinetics and morphology of para-sexiphenyl layers. The results of our investigations can be summarized as follows: (a) para-sexiphenyl grows on mica epitaxialy; (b) a rearrangement from randomly distributed small para-sexiphenyl islands with compact shape to elongated islands occurs during the growth if the critical island density is reached; (c) with further increase of the growth time the islands become elongated, quickly reaching a fixed asymptotic width while their height remains much smaller than their length and width.
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1. Introduction

π-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), a six units oligomer of *para-phenylene*. PSP crystallizes monoclinic with the space group $P2_1/a$ and the lattice constants $a = 8.09$ Å, $b = 5.56$ Å, $c = 26.24$ Å, $\beta = 98.17°$ [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

* Corresponding author. Address: Institute of Semiconductor and Solid State Physics, University Linz, A-4040 Linz, Austria. Tel.: +43-732-2468-9658; fax: +43-732-2468-9696.
E-mail address: andrei.andreev@jku.at (A.Yu. Andreev).

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the typical herringbone structure of PSP. PSP films are very interesting for the application in blue organic light-emitting diodes (OLED) [3,6,11] and have been grown previously using conventional physical vapor deposition [3,6,11,12] or organic molecular beam epitaxy (OMBE) [13,14]. Recently, we reported that a self-organization of PSP occurs during hot wall epitaxy (HWE) on single crystalline mica substrates [15,16], resulting in large scale ordered needle-like structures. Crystallographic studies revealed three similar crystallographic orientations of PSP on mica: dominant is (1 1 −1) plane and much weaker are the (1 1 −2) and (−1 −1 1) planes of PSP parallel to mica (0 0 1) [16–18]. However, the growth regularities of such highly anisotropic films are not clear yet. In this paper we performed atomic force microscopy (AFM) and X-ray diffraction (XRD) investigations of the early growth stage of PSP on mica, in order to clarify the growth mechanism of these films.

2. Experimental

PSP was purified by threefold sublimation under dynamic vacuum. HWE was used as evaporation technique. As substrates we used freshly cleaved (0 0 1)-oriented mica which shows a monoclinic crystal structure with $a = 5.20$ Å, $b = 9.03$ Å, $c = 20.11$ Å, $\beta = 95.78°$. The base pressure during growth was about 6×10^{-6} mbar and the PSP source temperature was fixed at 240 °C. The substrate temperature was 90 °C. The growth rate was 1–2 nm/min, as measured after growth for very thick PSP films [15]. The growth time was varied between 5 s 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) using monochromatic radiation with $\lambda = 1.23985$ Å.

3. Results and discussion

The PSP film morphologies of films prepared with increasing growth times in the range from 10 s to 40 min are shown in the AFM images of Fig. 1. As depicted in Fig. 1(a) and (b) only small uniformly distributed islands with a typical size of approximately $100 \times 50 \times 20$ nm^3 can be detected for the samples grown within 5–30 s. The surface morphology changes drastically if a critical density of islands is reached between 30 and 35 s of growth time: a rearrangement of islands occurs resulting in self-organized needles with micrometer length (Fig. 1(c)). As shown in Fig. 1(c)–(f), with increasing time these needles become progressively longer, quickly reaching a fixed asymptotic width, as already described in Ref. [19]. Further growth (Fig. 1(c) and (d)) is characterized by a coexistence of these constantly growing needles and small islands, whereby the last ones stay at roughly constant surface density and size. At least after 5 min of growth nearly no small islands could be found on the surface (Fig. 1(e) and (f)), while the needles become closer to each other.

As is evident from Fig. 1(c)–(f) from the very beginning all needles are strictly parallel to each other having the same preferential orientation relative to the substrate. Detailed AFM investigations shown, that this orientation as well as PSP island nucleation is not controlled by step edges on the mica surface. Moreover, XRD and transmission electron diffraction studies [16,17] revealed that the needle axis are oriented 24° relative to [1 0 0] zone axis of the mica substrate within an accuracy of ±5°. The long axis of PSP molecules within the needles and islands are nearly parallel to the substrate and perpendicular to the needles direction [14–17].

The spontaneous formation of elongated islands with asymptotic constant width could be explained in terms of strain-induced epitaxial growth, as well known from inorganic heteroepitaxy [20]. In order to check this idea we performed XRD measurements in $\Theta/2\Theta$ mode using a synchrotron source. From the peak positions in $\Theta/2\Theta$-scans we were able to infer the distance $d(hkl)$ between the lattice planes in the growth direction.

Fig. 2 shows the measured $d(1\,1\,-1)$ values for the strongest PSP reflex perpendicular to the substrate surface in dependence on the growth time. One can see that for a growth time less than 5 min

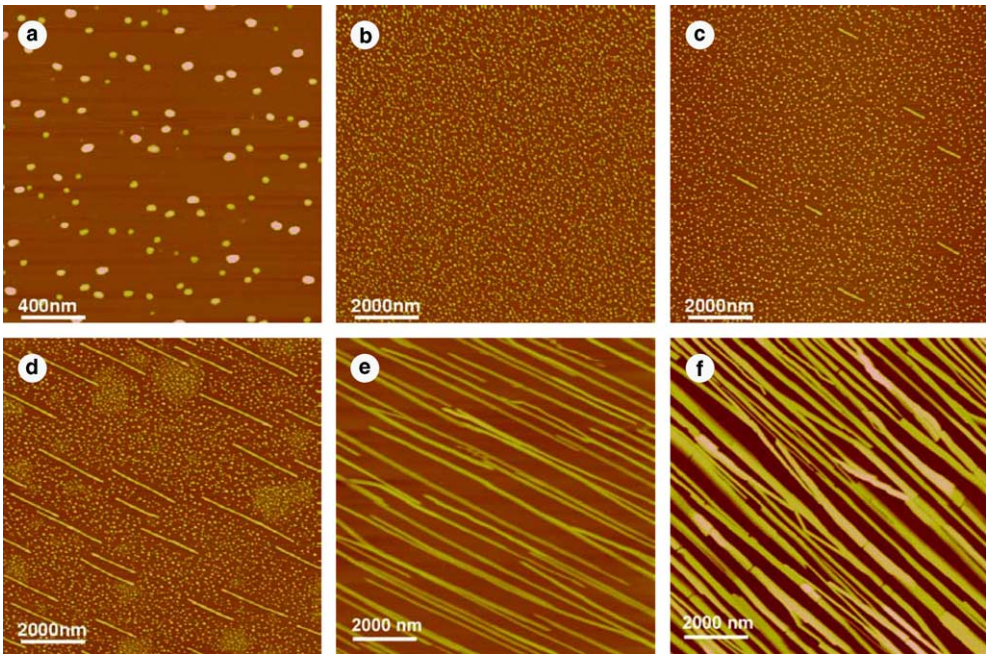

Fig. 1. AFM images of the PSP films grown within (a) 10 s; (b) 30 s; (c) 35 s; (d) 50 s; (e) 5 min; (f) 40 min. The growth temperature was 90 °C. *Z*-scale is 0–25 nm in (a), 0–50 nm in (d) and 0–100 nm in (e) and (f).

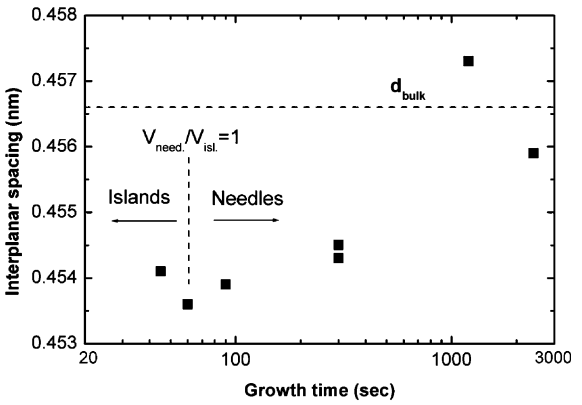

Fig. 2. Dependence of the interplane spacing $d(1\,1\,-1)$ on the growth time.

the values of $d(1\,1\,-1)$ deviate from the equlibrium value for bulk material, indicating residual strain in the PSP films [20,21]. For growth times larger than 5 min $d(1\,1\,-1)$ approaches rapidly the equilibrium value, what can be interpreted that the strain is released by forming dislocation network at the interface.

From AFM data we evaluated the amount of material deposited on mica in the form of islands (V_{isl}) and in the form of needles (V_{need}). For the growth times less than 60 s the ratio $V_{\mathrm{need}}/V_{\mathrm{isl}}$ is smaller than one, while for $t > 60$ s this ratio becomes larger than one. In particular, for $t = 5$ min the ratio is $\approx$1000, indicating that most of the material has the shape of the needles. However, the value of $d(1\,1\,-1)$ for this time is still far of the bulk value, which means that the islands and the needles are strained in the early stage of the growth. Only when the needles overcome a critical thickness of roughly 25–30 nm (corresponds to $\approx$20 min of the growth time) the strain is released.

Fig. 3 shows a 3D-AFM image of a single PSP nano-needle surrounded by small PSP islands in the earlier growth stage ($t \cong 35$ s). 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 by regrouping of mobile individual islands originating

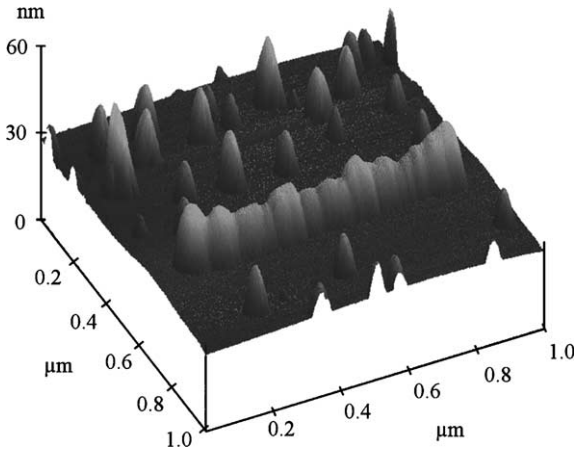

Fig. 3. High resolution three-dimensional AFM image showing individual PSP islands as well as a single needle.

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 μm long needle has a denuded zone of about 0.4×1.5 μm (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.

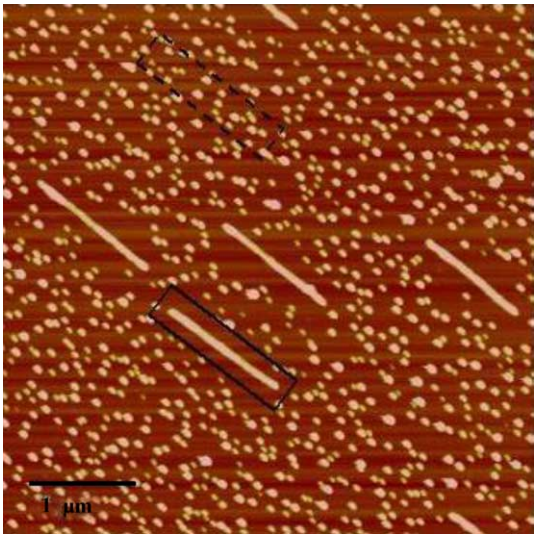

Fig. 4. High resolution AFM image (5×5 μm) showing a denuded zone (marked by the solid rectangle) around the PSP needle. The dashed rectangle marks the same surface area in a region far away from this needle.

4. Conclusions

The HWE growth of PSP thin films on crystalline mica substrates was investigated using AFM and XRD techniques. AFM studies of the early stages of growth clearly show that self-organization of PSP molecules occurs during HWE, resulting in well ordered needle-like structures. It is also shown that the growth process is very complex and involves not only molecules but also small PSP islands as migrating species. XRD investigations reveal the presence of lattice deformation within the first ≈20 min of the film growth (corresponds to ≈25–30 nm of the needles height).

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