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Journal of Crystal Growth 275 (2005) e2037–e2042
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

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

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Available online 15 December 2004

Abstract

In this work we use atomic force microscopy and X-ray diffraction to study morphology and growth kinetics of *para-sexiphenyl* layers deposited by hot wall epitaxy on crystalline KCl(0 0 1) substrates. It is shown that the growth on KCl(0 0 1) 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 surface symmetry of the substrate. It is in contrast to mica substrates, where *para-sexiphenyl* forms only needles with one preferential direction.

PACS: 81.15.Ef; 61.66.Hq; 68.37.Ps; 68.55.Ac

Keywords: A1. Atomic force microscopy; A1. Nanostructures; A1. X-ray diffraction; A3. Hot wall epitaxy; B1. Organic compounds

1. Introduction

The growth of thin films of organic semiconductor *para-sexiphenyl* (PSP), also known as *p*-6*P*, has recently received a lot of attention, because of excellent luminescence properties of PSP, making it very promising for the applications in organic blue light-emitting diodes (OLED) or lasers [1–16]. PSP films have been previously grown on glass [1–3], native oxide covered wafers [1,4], alkali halides [5–9], GaAs(0 0 1) [10] and mica [11–16] using different growth techniques. It was generally shown that the nature of the substrate, substrate temperature and the deposition rate are determining parameters for molecular packing.

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doi:10.1016/j.jcrysgro.2004.11.263

PSP crystallizes monoclinic with the space group $P2_1/a$ and the lattice constants $a = 8.09\,\text{Å}$, $b = 5.56\,\text{Å}$, $c = 26.24\,\text{Å}$, $\beta = 98.17^\circ$ [17]. Depending on substrate temperature and growth rate, films of predominantly standing or lying molecules can be obtained [5–9,11–16].

KCl crystals with its well-defined (0 0 1)-oriented surface are known as versatile model substrates for organic thin film deposition [5–9,18,19]. PSP films were previously grown on fresh cleaved KCl(0 0 1) using physical vapor deposition [5,6], mask-shadowing vapor deposition [7] and hot wall epitaxy-like [20] techniques. These studies were primarily concerned with the growth of films with sufficiently high thickness to take advantage of the luminescent property of PSP molecules. The grown films were investigated by means of optical microscopy (transmission/fluorescence), atomic force microscopy (AFM) and X-ray diffraction (XRD) [21] for a few randomly selected thicknesses and growth temperatures. It was shown that during vapor deposition the PSP molecules form very long needle-like crystallites and at the same time small plate-like islands [6,7,20,21]. Recently, it was also demonstrated that epitaxial growth of PSP on KCl(0 0 1) and optical properties of the grown films can be sufficiently promoted by using the hot wall epitaxy-like growth technique [20]. However, this study was again limited to very few selected thicknesses and growth temperatures.

In this paper we report on the application of the hot wall technique (HWE), which is fully developed in our laboratory, to produce highly ordered thin films of PSP on KCl(0 0 1). Based on our earlier results [11–14], we performed a systematic investigation of the growth morphology and kinetics using AFM measurements, in order to find the process controlling parameter. To obtain a complete picture of the growth kinetics of PSP films on KCl(0 0 1), AFM was complemented by XRD to define the molecular orientation in the films.

2. Experiment

PSP was purified by threefold sublimation under dynamic vacuum. HWE was used as the evaporation technique [11–14]. PSP films were grown under a vacuum about 6×10^{-6} mbar after preheating at 150 °C for 30 min. The substrate temperature was 80–90 °C and the PSP source temperature was fixed at 240 °C. We used freshly cleaved crystalline dielectric substrates KCl(0 0 1). The growth time was varied between 45 s and 40 min. The film morphology was imaged by AFM operated in air in contact mode. Test measurements done both in contact and in tapping modes reveal that PSP films were not damaged if the contact mode was used. XRD studies were performed at the Cornell High Energy Synchrotron Source (CHESS, Ithaca, USA) using monochromatic radiation with $\lambda \cong 1.25\,\text{Å}$.

3. Results and discussion

Since potassium halides are quite hygroscopic, preheat treatment of the surface in vacuum before deposition significantly affects the epitaxial growth of the PSP film. Figs. 1a,b show typical optical images of two PSP films grown on KCl(0 0 1) surface after preheating at 150 °C for 30 min and 10 h, respectively. One can see that longer preheat time causes clearly the 'scaling-up' of PSP needles together with the reduction of their surface density. Similar, but not so well-expressed scaling behavior was also observed for PSP layers preheated for different times at 90 °C. The reason for this effect is probably the longer diffusion length of PSP molecules on the better preheated KCl surface. Because very long preheating times are not practical, preheating conditions were fixed for the following growth experiments at $T_{\text{preh.}} = 150\,^\circ\text{C}$ and $t_{\text{preh.}} = 30\,\text{min}$.

The PSP surface morphologies for the films prepared with increasing growth times in the range from 45 s to 40 min are shown in the AFM images of Fig. 2. It is evident that under HWE conditions PSP can form needle-like ('needles', Fig. 2a) and plate-like crystallites (Figs. 2b,c) at the same time, as well as during simple vapor deposition [6]. This is in contrast to HWE growth on mica, where only PSP needles are formed [11–14]. On the other hand, as shown in Fig. 2a, the needles are clearly the initial growth stage of the films. They start to grow most probably direct

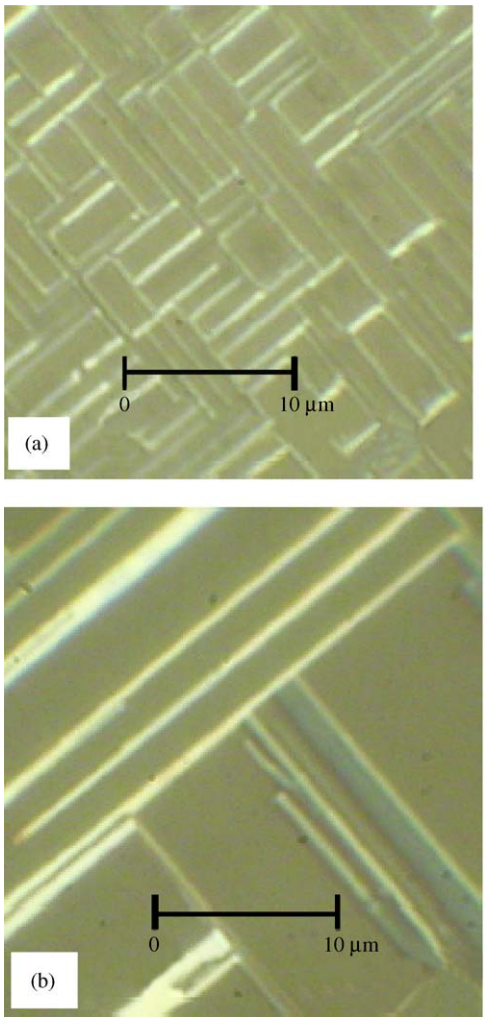

Fig. 1. Optical microscope images of two PSP films grown on KCl(0 0 1) within 10 min. Substrates were preheated at 150 °C for 30 min (a) and 10 h (b), respectively.

on KCl surface (the background of Fig. 1a is very similar to typical AFM images of bare KCl substrate after cleavage), generating a rectangular network in accordance with surface symmetry of the substrate [6,7]. In this stage the needles are already in average of ≈10 nm in height, ≈100 nm in width and ≈3–4 μm in length. After a few minutes of deposition time, terrace-structured islands develop between needles, as depicted in Fig. 2b. The terraces are in average of ≈2.6 nm, which corresponds to one monolayer of standing molecules of PSP. Further growth (Figs. 2b,c) is characterized by a co-existence 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 of 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 needles is covered with layered crystals (Fig. 2c). Nevertheless, we have not observed the growth of the needles across the islands, or vice versa.

In accordance with Refs. [6,7,20], AFM images show that the needles mainly grow along two orthogonal KCl [1 1 0] directions, referring to the KCl [1 0 0] edge. This bidirectional epitaxial orientation seems to be originating from an interaction between the linear PSP molecules and the ionic rows along KCl [1 1 0] and [1 $\bar{1}$ 0] directions, as previously reported for PSP films grown by simple vapor deposition [6]. The epitaxial orientation of the needles is almost perfect for thin PSP layers (see Fig. 2a), but the amount of misaligned needles clearly increased with increasing of the growth time (see Figs. 2b,c). One can assume that this is because of the islands, which after some time hamper the free extension of the needles.

It is worth mentioning that no needles crossing is observed (independent from growth time), in agreement with optical investigations done in Refs. [6,7,20]. The needles always terminate when a needle comes to another orthogonal oriented one (see, for example, Fig. 3). This T-end shaped growth was explained in Refs. [6,20] by assuming that the needles nucleate at the step edges of KCl and then extend along that. In contrast, our AFM investigations do not indicate that surface steps are nucleation centers for the formation of the needles. Moreover, we found that PSP needles can grow over the surface steps, at least if the step height is below 100 nm (see, for example, Fig. 4).

Molecular orientations in PSP films grown on KCl(0 0 1) were proven by XRD measurements using a synchrotron source, which allows one to measure even weak intensities as those from thin

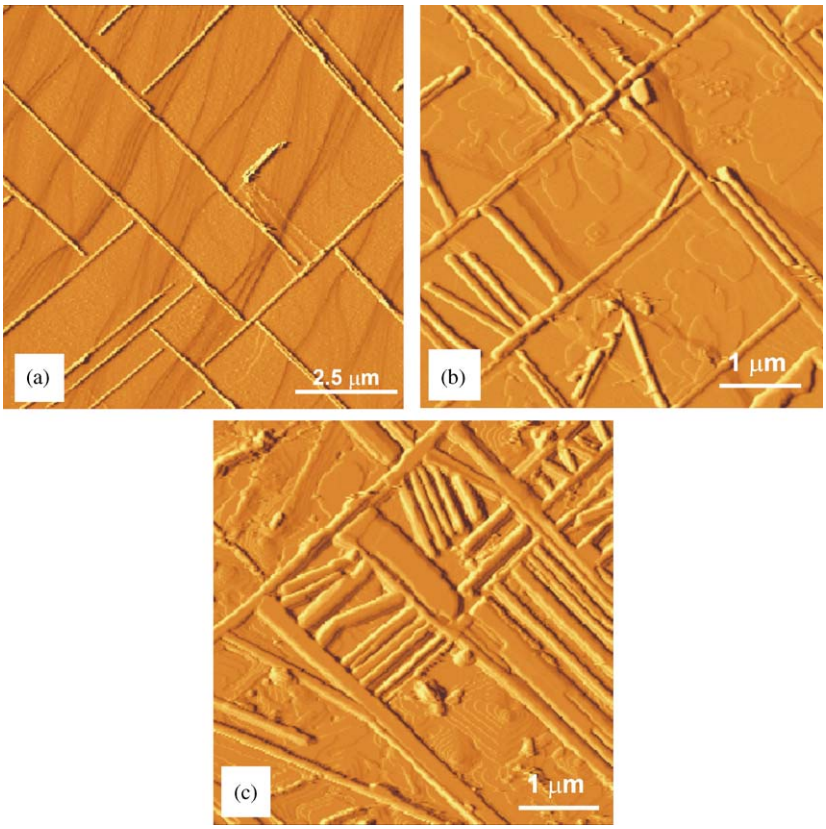

Fig. 2. AFM images of the PSP films grown within (a) 45 s, (b) 10 min, (c) 40 min.

organic layers. In order to get the scans where the peak positions of the films are not dependent on the equipment and the energy of the synchrotron beam, we have used a so-called L-scans technique [21]. In principle, L50-scan is a $\Theta/2\Theta$-scan, where you measure the intensity not over 2Θ but over multiples of the lattice constant $L_{\mathrm{KCl}} = 6.2917\,\text{Å}$ of the substrate. The $L(hkl)$ value can be then calculated as

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

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

Fig. 5 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. 2a and 2c. The scans reveal at least four different growth orientations parallel to the surface of the substrate: $(1\,1\,\bar{1})$, $(1\,1\,\bar{2})$ and $(2\,0\,\bar{3})$ reflections are due to lying molecules, whereas the (0 0 6) reflection is due to standing molecules [12,21]. Thereby, in full agreement with results of AFM investigations, the (0 0 6) reflection appears only for thicker films grown within 40 min. Referring to that we can clearly ascribe the last orientation to the islands, with the long axes of the molecules approximately perpendicular to the surface of the substrate ('end-on'). Correspondingly, the needles comprise three other epitaxial orientations, where the long molecular axes are aligned approximately parallel to KCl(0 0 1) surface ('edge on').

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

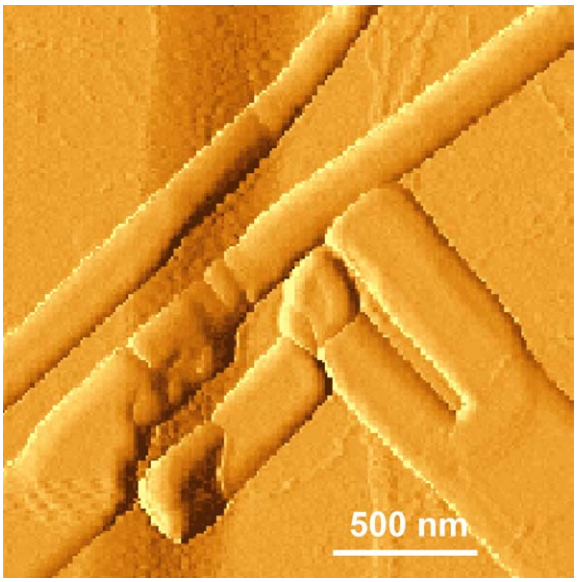

Fig. 3. AFM image of a T-shaped contact between needles. PSP film was grown within 5 min at 80 °C.

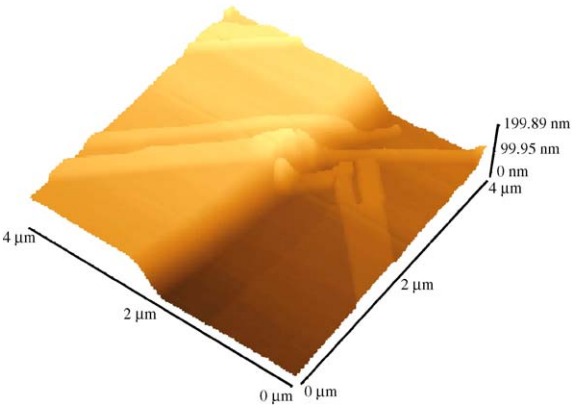

Fig. 4. 3D-AFM image of a PSP needle overgrowing a surface step. The height of the step in the picture is 95 nm. The film was deposited for 5 min.

4. Conclusion

We have investigated the growth of PSP on KCl(0 0 1) by HWE. Two different morphologies were found within the films: needles and terrace-structured islands. The needles are the initial growth stage of the films, generating a rectangular network, with typical lengths of several micrometers at a growth time of 45 s. The islands, coexisting 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. Thereby, the needles (like on mica) are built up of molecules aligned with their long molecular axes approximately parallel to the surface and the islands show 'standing' orientation of molecular axes.

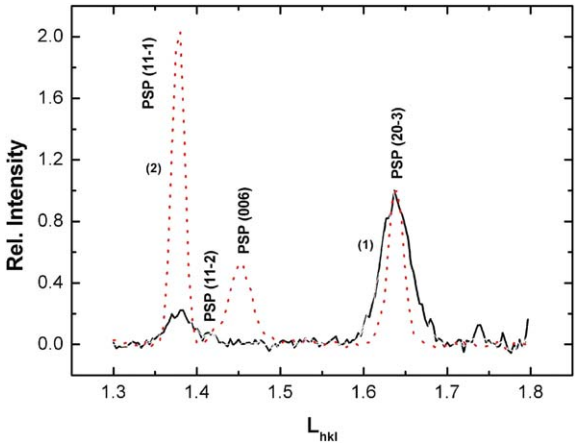

Fig. 5. *L*-scans for PSP on KCl(0 0 1) corresponding to standard $\Theta/2\Theta$-scans. PSP films were grown for 45 s (1) and 40 min (2).

Acknowledgements

Research was supported by the Austrian Foundation for Advancement of Scientific Research (FWF Projects P-15155, P-15626, P-15627). Part of this work was performed within the Christian Doppler Society's dedicated laboratory on Plastic Solar Cells funded by the Austrian Ministry of Economic Affairs and Konarka Austria GmbH. We also thank the Cornell High Energy Synchrotron Source (CHESS, Ithaca, USA) for providing beam-line time (Project EM541). CHESS is a national user facility supported by NSF and NIH/NIGMS under award DMR 9713424.

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