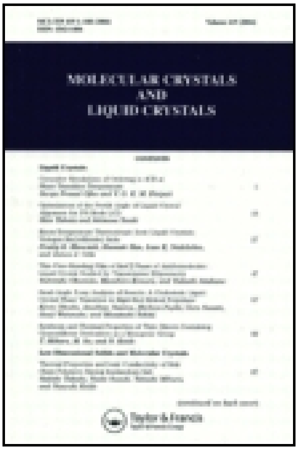

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Highly aligned organic semiconductor thin films grown by hot wall epitaxy

A. Andreev [a], H. Sitter [a], R. Resel [b], D. -M. Smilgies [c], H. Hoppe [d], G. Matt [d], N. S. Sariciftci [d], D. Meissner [d], D. Lysacek [e] & L. Valek [e]

[a] Institute for Semiconductor and Solid State Physics, University Linz, Linz, A-4040, Austria

[b] Institute of Solid State Physics, Graz University of Technology, Austria

[c] CHESS G-line, Cornell University, Ithaca, NY, 14853, USA

[d] Linz Institute for Organic Solar Cells (LIOS), PhysicalChemistry, University Linz, Austria

[e] Institute of Physical Engineering, Brno University of Technology, Brno, Czech Republic

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HIGHLY ALIGNED ORGANIC SEMICONDUCTOR THIN FILMS GROWN BY HOT WALL EPITAXY

A. Andreev and H. Sitter*
Institute for Semiconductor and Solid State Physics,
University Linz, A-4040 Linz, Austria

R. Resel
Institute of Solid State Physics, Graz University of Technology,
Austria

D.-M. Smilgies
CHESS G-line, Cornell University, Ithaca NY 14853, USA

H. Hoppe, G. Matt, N. S. Sariciftci and D. Meissner
Linz Institute for Organic Solar Cells (LIOS),
Physical Chemistry, University Linz, Austria

D. Lysacek and L. Valek
Brno University of Technology, Institute of Physical
Engineering, Brno, Czech Republic

In this work we use atomic force microscopy to study the early growth stages of para-sexiphenyl (PSP) films grown on mica by Hot Wall Epitaxy. It is shown that self-organization of PSP molecules occurs during the growth controlled mainly by the substrate temperature and deposition time. In addition X-ray diffraction measurements were performed using synchrotron radiation. These measurements confirmed very high crystalline quality of the grown films.

Keywords: organic epitaxy; crystalline thin films; atomic force microscopy; x-Ray diffraction

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*Corresponding author. E-mail: andrei.andreev@jku.at

1. INTRODUCTION

π-conjugated small molecules like ***oligo-thiophenes***, ***oligo-phenylenes*** or ***phthalocyanines*** have already been successfully used as active layers in field effect transistors, light emitting diodes and in solar cells [1–8]. Especially during the last year important progress was achieved in the field of new devices made from such molecular materials. This includes ambipolar thin film transistors, organic solid state laser and organic solar cells [9]. These devices were made from single crystals of high purity and extended size. Further practical development of these new applications can be expected using a thin film technology. High quality crystalline thin films with defined orientation of the molecules are hence necessary to be successful in realization of these future applications.

Thin films of ***para-sexiphenyl*** (PSP) molecules, which are interesting for the application in blue organic light-emitting diodes (OLED) with polarized light emission [10], have been grown previously on oxidized and non-oxidized GaAs, KCl, mica, glass and ITO substrates using conventional physical vapor deposition [3,6,10,11] and organic molecular beam epitaxy (OMBE) [12,13]. 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 a self-organization of PSP occurs during Hot Wall Epitaxy (HWE) on single crystalline mica substrates, resulting in large scale ordered needle-like structures of high crystallinity [14], which show dichroic ratios in emission up to 14 [15]. However, the growth regularities of such high anisotropic films were not clear jet, although this is important for achieving highly ordered PSP films on other substrates. In this work an AFM investigation of the early growth stage of PSP on mica is presented, in order to find the process controlling parameters. In addition X-ray diffraction (XRD) was used to determine the crystalline quality of the grown films.

2. EXPERIMENT

PSP, obtained from Tokyo Chemical Industries, was purified by threefold sublimation under dynamical vacuum. HWE was used as evaporation technique, which turned out to be very appropriate for Van der Waals epitaxy [16]. The used substrates were freshly cleaved (001)-oriented mica. The vacuum during growth was about 6×10^{-6} mbar and the PSP source temperature was fixed at 240°C. The substrate temperature was 90°C or 150°C, growth time was in a range from 5 sec to 60 min. Further growth details can be also found in Ref. [14,15]. The film morphology was imaged by AFM using NanoScope IIIa Microscope operated in tapping mode on air.

A Philips X'Pert system with an ATC3 texture cradle was utilized for XRD-pole figure measurements performed in Schultz reflection geometry using Cr-K_α radiation and a secondary graphite monochromator [14]. Further XRD investigations were performed at the F3 station at the Cornell High Energy Synchrotron Source (CHESS). Monochromatic radiation with a wavelength of 1.23985 Å was used in combination with an 4-circle goniometer. The use of an intense and well-collimated beam allows to measure weak intensities from organic materials and is definitely an important step towards accurate structure determination of thin organic films. The software packages Powder Cell 2.3 [17] and Stereogramm [18] were used for XRD data analysis.

3. RESULTS AND DISCUSSION

The PSP film morphology with increasing growth time in the range from 5 to 90 sec is shown in the AFM images of Figure 1. The growth temperature was 150°C. As depicted in Figure 1a,b only small uniformly distributed 3D-islands with a compact shape can be detected for the samples grown within 5–10 seconds. The surface morphology changes drastically if growth time was increased from 10 to 25 sec: island shape transition occurs resulting in typical needle-like structures with elongated 3D-islands. Figure 1c–d show that the islands become thereby progressively longer, quickly reaching a fixed asymptotic width while their height remains much smaller than their length and width, as already described in Ref. [19]. Interestingly, that the same behavior was also found for the samples grown by 90°C, however in this case islands shape transition occurs later – between 25 and 45 seconds of growth time.

Some of these extraordinary features could be qualitatively explained (see also [12,19]) in terms of strain-induced heteroepitaxial island growth, well known in inorganic heteroepitaxy. For example, Tersoff and Tromp [20] have theoretically predicted 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 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 main results (see also [19]) agree well with these theoretical predictions.

Previously [14], we used a laboratory X-ray source and diffraction pole figure technique in order to characterize the crystallographic structure of thick PSP films grown on mica. Figure 2 shows four pole figures of crystalline PSP film. The detailed analysis of this data performed in [14] based

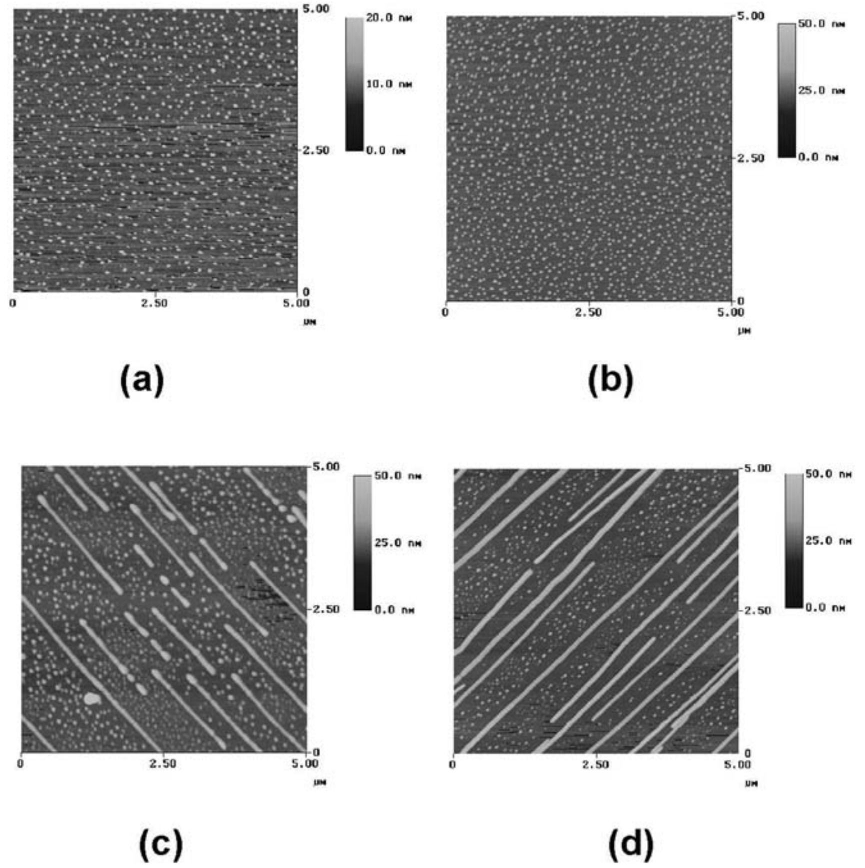
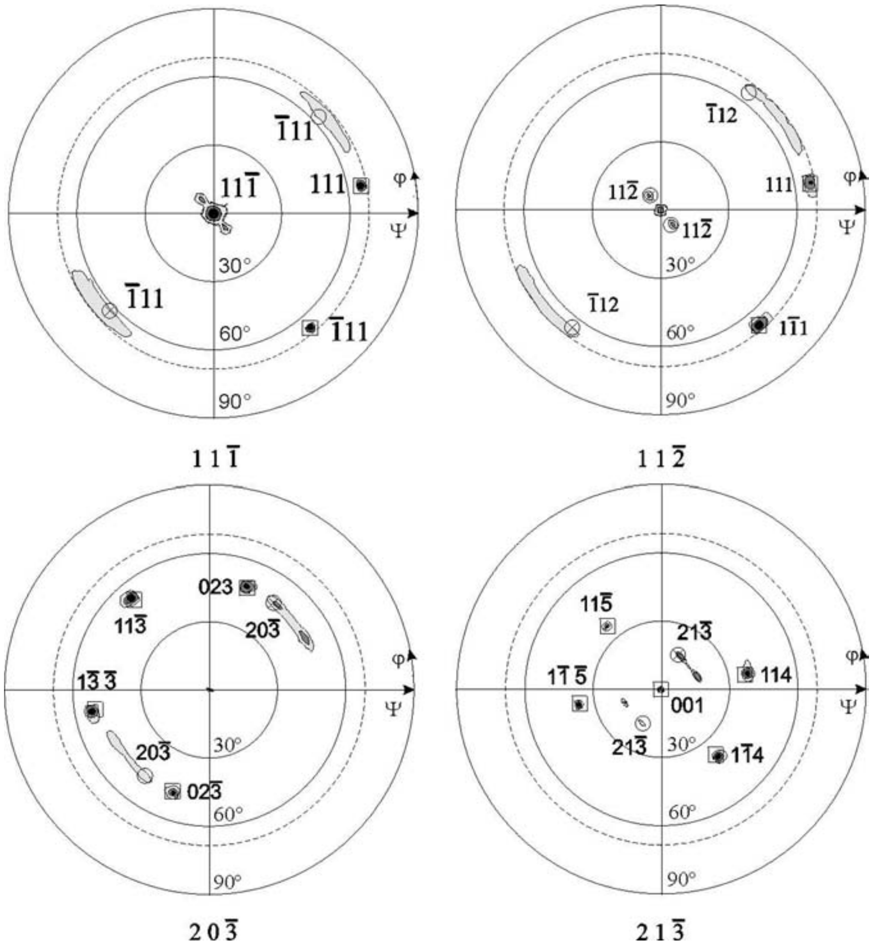


FIGURE 1 AFM images of the PSP films grown at a time of a) 5 sec; b) 10 sec; c) 25 sec; d) 90 sec. The growth temperature was 150°C.

on the bulk structure of PSP [21] revealed three similar crystallographic orientations of PSP crystallites: the (11-1), the (-1—11) and the (11-2) crystallographic planes parallel to the substrate surface. This investigations proved the epitaxial character of the PSP films. However, the enhanced pole densities within the pole figures were considerably smeared out, especially at higher ψ angles (see Fig. 2), which was assumed as the results of wide beam-geometry (widely open slits of the instrument) needed to obtain measurable intensities of the film reflections [14]. As a consequence, it was difficult to investigate the degree of epitaxial order carefully, since the observed Full Width at Half Maxima (FWHM) values were mainly limited by the resolution of the diffractometer [14]. Moreover, due to the



$1\,1\,\bar{1}$ $1\,1\,\bar{2}$

$2\,0\,\bar{3}$ $2\,1\,\bar{3}$

FIGURE 2 Pole figure measurements of PSP on mica (001) taken from the four strongest reflections of PSP [14], which are indicated below each figure. The dashed line indicates the measurement limit of $\Psi = 75°$. The orientation of one type (together with the antiparallel type) of epitaxially grown crystallites of PSP are marked by circles (crossed circles). The identified mica reflections are indicated by squares.

weakness of the reflections it was impossible to measure very thin films like those presented in Figure 1.

In order to check the degree of order of the films we performed XRD investigations on a synchrotron source, which yields partially similar information as pole figures. Figure 3 shows a typical φ-scan for the

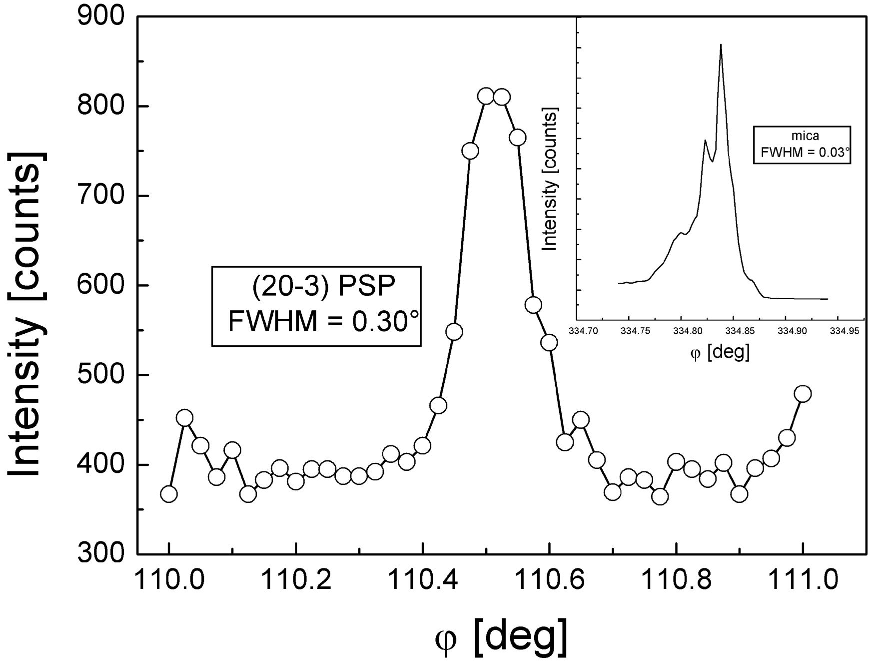


FIGURE 3 φ-scan for the 20-3 reflection of a PSP film measured at $\psi = 55.5°$ and $2\Theta = 18.54°$. The insert shows a corresponding φ-scan of the mica substrate; 113 reflection was investigated at $\psi = 52.6°$ and $2\Theta = 19.94°$.

characteristic 20–3 reflection at $\psi = 55.5°$ and $2\Theta = 18.54°$ (see corresponding pole in Fig. 2) of the PSP film grown within 90 sec. Note, that the morphology of this film is depicted in Figure 1d. The instrumental broadening was determined on the mica 113 reflection of the sample's substrate, a φ-scan at $\psi = 52.6°$ and $2\Theta = 19.94°$ is depicted in the inset of Figure 3. From that result it can be concluded that the contribution of the instrumental broadening to the FWHM of the 20-3 reflection of PSP is negligible small. The observed FWHM is only 0.3°, which is much less than FWHM obtained from pole figure measurements. Considering this result the elongated shapes of enhanced pole densities obtained in Ref. [14] (see also Fig. 2) can be really referred to the wide beam-geometry. On the other hands, this data confirms a good in-plane alignment of PSP crystallites within the film.

Figure 4 shows a typical Rocking curve measured at $2\Theta = 15.67°$ for the characteristic 11-1 reflection of the same PSP film. For comparison the Rocking curve of the mica(004) reflection at $2\Theta = 14.26°$ was measured (see inset of Fig. 4). The rocking curves of mica show an irregular shape,

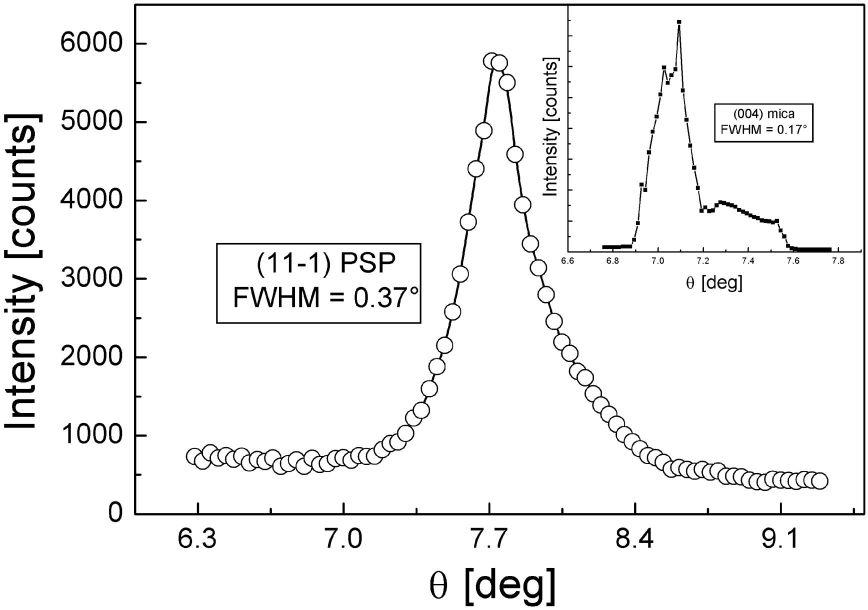


FIGURE 4 Rocking curve for the 11-1 reflection of the PSP film at $2\Theta = 15.67°$. Insert shows corresponding Rocking curve for the 004 reflection of the mica substrate.

which appears in single crystals of layered crystal structures like graphite, mica, a.o. The Rocking curve of PSP (11-1) has a remarkable narrow FWHM of only 0.37°, which differs not much from the corresponding FWHM of the mica substrate. It confirms a very good out-of-plane alignment of PSP crystallites and thus (together with the data of Fig. 3) high degree of order in the film.

In order to collect more statistic about crystalline quality of thin PSP films and to better understand the mechanism of the defect formation during the growth we performed also rocking curve measurements for 11-1 reflection of PSP for different layers grown at various growth times and substrate temperatures. Additional interest to such investigations arises from the fact that there exist only very few papers in which rocking curves were reported for organic thin films [22–26]. As presented in Figure 5 our study of FWHM reveal no clear dependence on the growth time or substrate temperature. The FWHM values are quite gritted but all of them remain below 0.5°. That is definitely due to the different quality of the mica substrates used, which could be caused by the cleavage procedure (compare also the inserts in the Figs. 3 and 4). It is worthwhile to mention, that

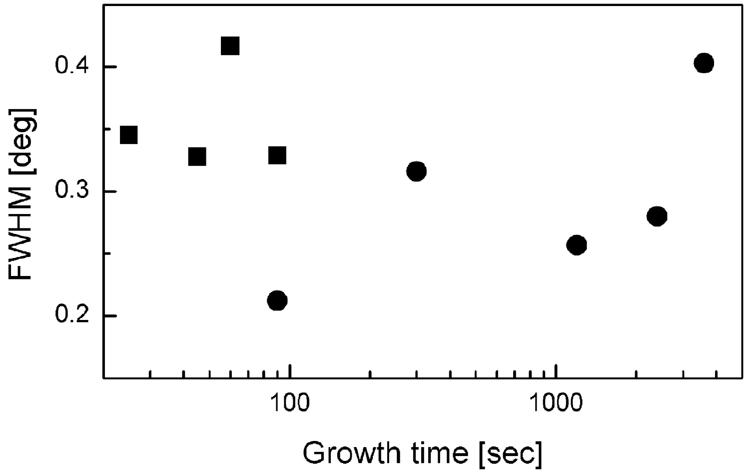


FIGURE 5 FWHM values for PSP films grown within various times at substrate temperatures of 90°C (●) and 150°C (■).

the best FWHM of 0.06° was obtained for the 11-1 reflection of a PSP film grown at 90°C for 300 sec on a mica substrate with a FWHM the 004 reflection of 0.02°.

4. CONCLUSIONS

The HWE growth of PSP thin films on crystalline mica substrates was investigated. AFM studies of the earlier stage of the growth have clearly shown that self-organization of PSP molecules occurs during HWE resulting in needle-likes structures. XRD investigations using synchrotron radiation confirmed very high degree of epitaxial order of the grown films.

SUMMARY

It is known that para-sexiphenyl (PSP) molecules form highly ordered crystalline needle-like structures, if they are deposited on mica substrate by Hot Wall Epitaxy (HWE). In this work we use atomic force microscopy to study the early growth stages of these structures in detail in order to find the growth process controlling parameters. It is shown that self-organization of PSP molecules occurs during the growth controlled mainly by the substrate temperature and deposition time.

On the other hand we used X-ray diffraction technique in order to determine the crystalline quality of the grown films. These measuremets confirmed very high crystalline quality of the PSP films. In particular, the best film investigated showed rocking curve width of 0.06°, which is an outstanding value for small molecule thin films.

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