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Oriented organic semiconductor thin films

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Abstract

In this part of our investigations, we mainly use atomic force microscopy to study the growth of *para-sexiphenyl* (PSP) films on mica. It is shown that self-organization of PSP molecules occurs during the deposition controlled by the substrate temperature and deposition time. In addition, X-ray diffraction (XRD) measurements were performed using synchrotron radiation. They confirmed the very high crystalline quality of the grown films.

Keywords: Organic epitaxy; Crystalline thin films; Atomic force microscopy; X-ray diffraction

1. Introduction

The 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. Their difficult and expensive preparation limits the applicability for practical devices. A more practical approach to these new applications can be expected using thin film technology. However, here a high quality of the crystalline thin films is needed with a defined orientation of the molecules in order to be successful in future applications, which in general is not obtained by thin film preparation methods.

Thin films made of *para-sexiphenyl* (PSP) molecules are very interesting for the application in blue organic light-emitting diodes (OLED) with polarized light emission [10]. Such films 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 determine the 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 of up to 14 [15]. However, the growth regularities of such highly anisotropic films were not clear jet. In this paper, AFM investigation of the growth of PSP on mica are presented, performed in order to find the process controlling parameters. In addition, X-ray diffraction (XRD) was used to determine the crystallographic characteristics of the films.

2. Experimental

Para-sexiphenyl obtained from Tokyo Chemical Industries was purified by threefold sublimation under dynamic vacuum. Hot wall epitaxy was used as evaporation technique, which turned out to be very appropriate for Van der Waals epitaxy [16]. The used substrates were freshly cleaved (0 0 1)-oriented mica. The base pressure during growth was

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about 6×10^{-6} mbar and the PSP source temperature was fixed at 240 °C. The substrate temperature was 90 or 150 °C, the growth time varied between 5 s and 60 min. The average deposition rate was ∼1 nm min^{-1}. Further growth details can also be found in [14,15]. The film morphology was imaged by AFM using a Nanoscope IIIa microscope operated in tapping mode in air. XRD investigations were performed at the F3 station at the Cornell High Energy Synchrotron Source (CHESS) in Ithaka. Monochromatic radiation with a wavelength of 1.23985 Å was used in combination with a four-circle goniometer. The use of an intense and well-collimated beam allows to measure the weak intensities obtained from organic materials and is 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 morphologies of films prepared with increasing growth times in the range from 5 to 90 s is shown in the AFM images of Fig. 1. The growth temperature here was 150 °C. As depicted in Fig. 1(a) and (b) only small uniformly distributed 3D-islands with a compact shape can be detected for the samples grown within 5–10 s. The surface morphology changes drastically if the growth time was increased from 10 to 25 s; an island shape transition occurs resulting in typical needle-like structures with elongated 3D-islands. Fig. 1(c) and (d) show that the islands thereby become progressively longer, quickly reaching a fixed asymptotic width, while their height remains much smaller than their length and width, as already described in [19]. Interestingly, the same self-organized behavior was also found for the samples grown at 90 °C, however, in this case

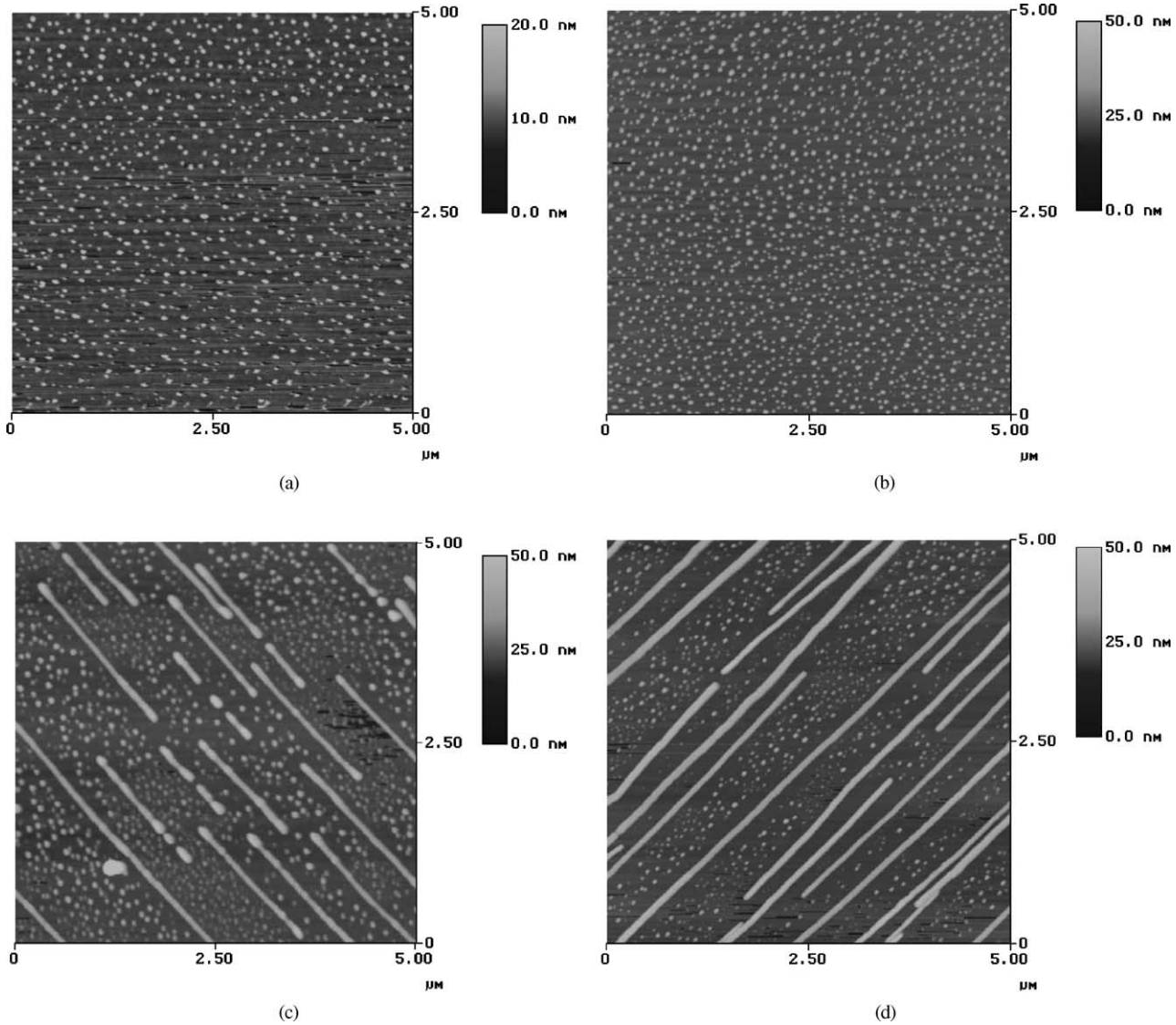

Fig. 1. AFM images of the PSP films grown within (a) 5 s; (b) 10 s; (c) 25 s; (d) 90 s. The growth temperature was 150 °C.

the islands shape transition occurs later—between 25 and 45 s of growth time.

As is evident from Fig. 1(d), all needles are parallel to each other (see also [15]) having the same preferential orientation relative to the substrate. XRD and transmission electron diffraction investigations [14,20] revealed that the needle axis are mainly turned by 24° relative to (1 0 0) zone axis of the mica substrate within an accuracy of ±5°. Such alignment of the needles seems to be based on a specific interaction between the deposited PSP molecules and the different layers of mica as was discussed in [14,20].

Some of these extraordinary features can be explained qualitatively (see also [12,19]) in terms of strain-induced heteroepitaxial island growth, well known in inorganic heteroepitaxy. For example, Tersoff and Tromp [21] 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 (see also [19]) agree well with these theoretical predictions.

Previously [14], we used a laboratory X-ray source and XRD technique in order to characterize the crystallographic structure of thick PSP films grown on mica. This investigations proved the epitaxial character of the PSP films. However, due to the weakness of the reflections it was difficult to perform more detailed investigations, especially for very thin films like those presented in Fig. 1.

In this work, we now performed XRD measurements using a synchrotron source, which allows to measure even weak intensities as those from thin organic layers. Such investigations in combination with transmission electron diffraction measurements [22] reveal generally that even very thin PSP films show the same crystallographic structure as thicker films studied in [14]. Figs. 2 and 3 show typical $\Theta/2\Theta$-scans for the PSP films grown on mica at various growth times and substrate temperatures. Note that the AFM morphology of some of these films is given in Fig. 1. In line with our previous work [14], all measurements reveal only strong PSP (1 1 −1) reflections. It is worthwhile to mention, that we were able to detect the peaks even for very thin PSP films as those shown in Fig. 2(b). It confirms a good crystalline quality of such films. Furthermore, one can see that the peak detection limit for the layers grown at 150 °C was even lower, which should be due to a better crystalline

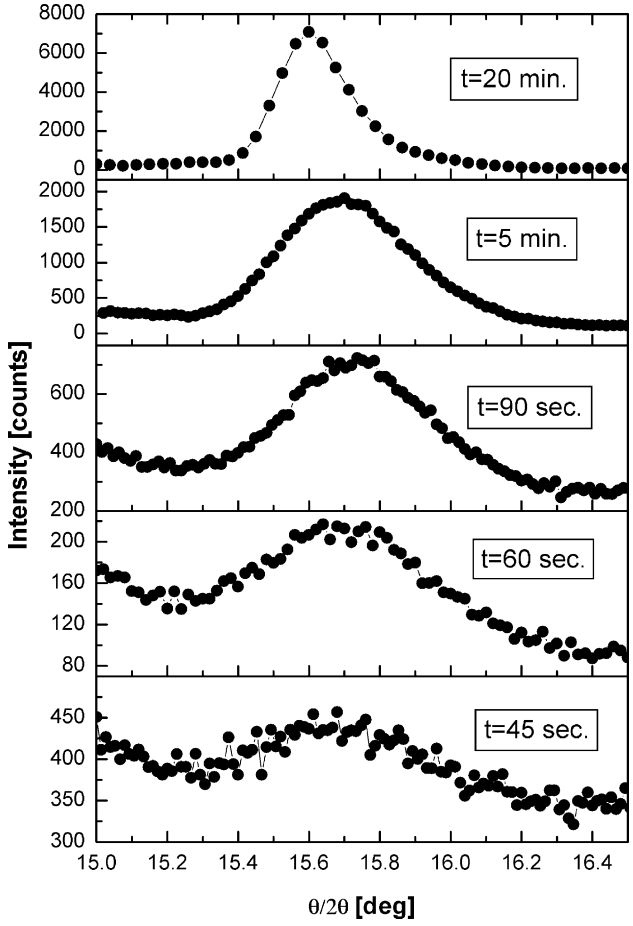

Fig. 2. $\Theta/2\Theta$-scans of the (1 1 −1) reflection of PSP for different growth times. The growth temperature was 90 °C.

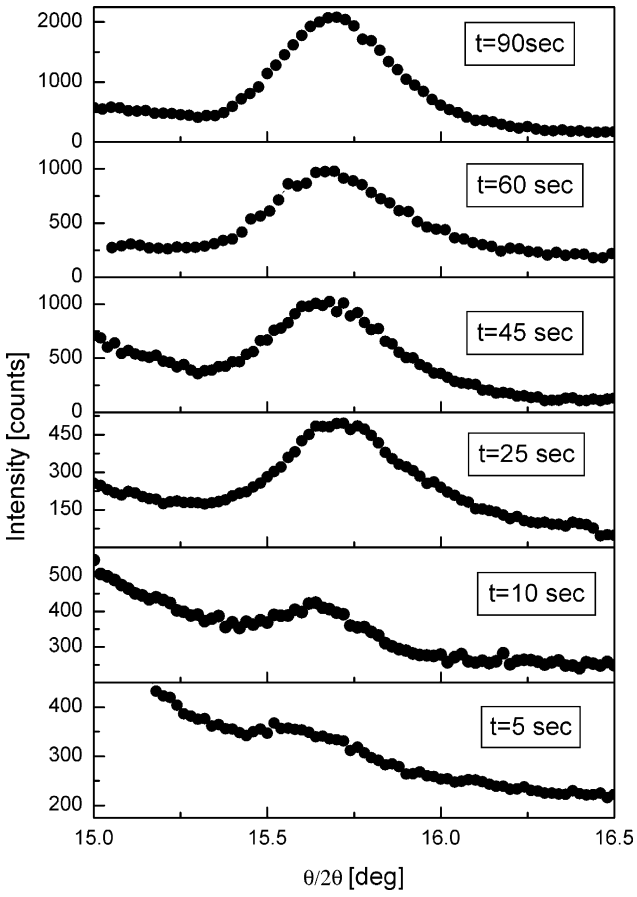

Fig. 3. $\Theta/2\Theta$-scans of the (1 1 −1) reflection of PSP for different growth times. The growth temperature was 150 °C.

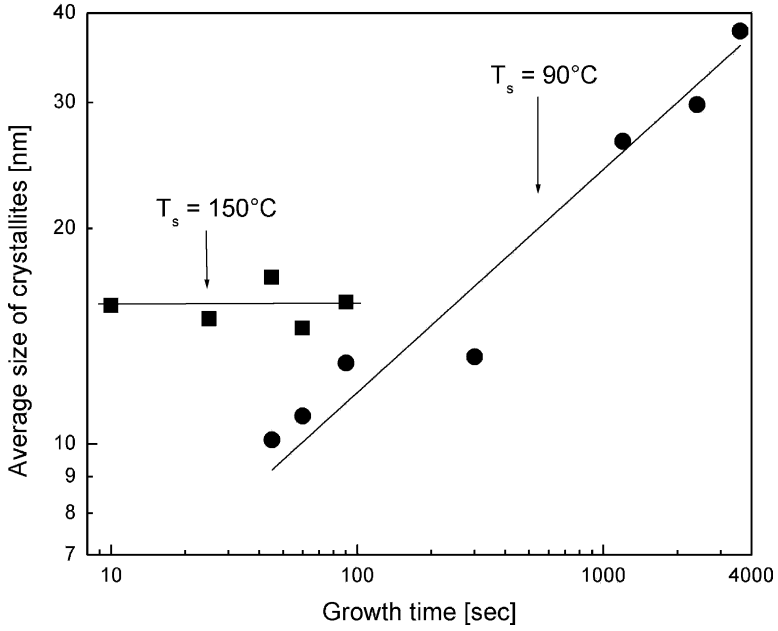

Fig. 4. The average crystallites sizes as calculated using the Scherrer formula in dependence on growth time and substrate temperature.

quality or/and higher thickness of them, the later one being in accordance with [19].

Using the well known Scherrer formula [23] and the data (widths of the peaks) presented in Figs. 2 and 3, we were able to calculate the average size of the PSP crystallites within the PSP films. Fig. 4 shows the results in dependence on growth time and substrate temperature. One can see that at least for time up to 200 s, the dependence of the size on the growth time is different for the films grown at 150 and 90 °C. Namely, for the films grown at 90 °C, the size of the crystallites increased with increasing the growth time, while for the 150 °C, it remained more or less constant during the deposition. Similar trend have been found previously for the islands height at a substrate temperature of 90 °C as measured by AFM [19]. Furthermore, the crystallites are clearly bigger, if the film was grown at elevated temperature of 150 °C, which is also in accordance with previous AFM investigations [19].

The so called rocking curves (Θ-scans) provide a direct measure for the degree of order of the grown films. Additional interest in these investigations arises from the fact that there are only very few papers published, in which rocking curves were reported for organic thin films [24–28]. Fig. 5 shows a typical rocking curve measured at $2\Theta = 15.67°$ for the characteristic (1 1 −1) reflection of the PSP film grown within 90 s. Note, that the morphology of this film is also given in Fig. 1(d). For comparison, the rocking curve of the mica (0 0 4) reflection at $2\Theta = 14.26°$ was measured (see inset of Fig. 5). The rocking curves of mica show an irregular shape, which appears in single crystals of layered crystal structures like graphite, mica, a.o. The rocking curve of PSP (1 1 −1) has a remarkable narrow FWHM of only 0.37°, which differs not much from the corresponding FWHM of

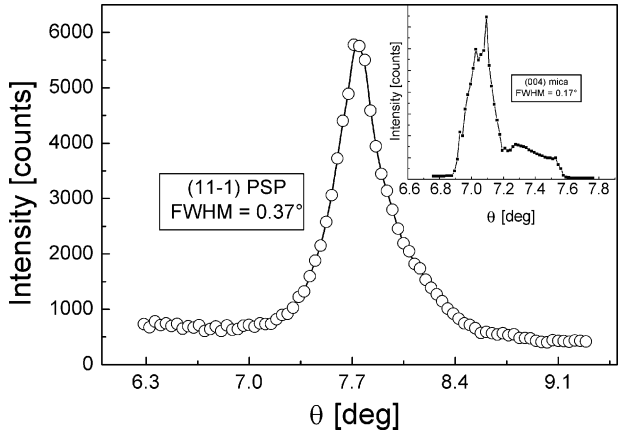

Fig. 5. Rocking curve for the (1 1 −1) reflection of the PSP film at $2\Theta = 15.67°$. The insert shows a corresponding rocking curve for the (0 0 4) reflection of the mica substrate.

the mica substrate itself. It confirms a very good out-of-plane alignment of PSP crystallites and thus (together with the data of Figs. 2 and 3) a high degree of order in the film.

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 needle-like structures, as theoretically described by Tersoff and Tromp [21]. XRD investigations confirmed the high degree of epitaxial order of the grown films.

Acknowledgements

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