Oriented Organic Semiconductor Thin Films

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In this part of our investigations, we use atomic force microscopy and X-ray diffraction to study the growth of para-sexiphenyl (PSP) films on mica. It is shown that self-organization of PSP molecules occurs during the growth controlled by the substrate temperature and deposition time. X-ray diffraction studies confirmed very high crystalline quality of the grown organic films.

Introduction

The ability to control the molecular order in organic thin films consisting of long anisotropic oligomers like *oligo-thiophenes* or *oligo-phenylenes* is essential to study the relation between their structure, surface morphology and their optical and electrical properties. On the other hand, ordered thin films of organic semiconductor *para-sexiphenyl* (PSP) are interesting for the application in organic light-emitting diodes (OLED) with polarized blue light emission [1]. Recently, we reported that a self-organization of PSP molecules occurs during Hot Wall Epitaxy (HWE) on mica resulting in well ordered crystalline needle-like structures with a length to width ratio up to 500 [2], [3]. However, the growth regularities of such highly anisotropic films were not clear yet. In this work, we have used atomic force microscopy (AFM) and X-ray diffraction (XRD) to investigate the morphology, growth kinetic and crystalline quality of these films in the early growth stages, in order to find the process controlling parameters.

Experimental

PSP obtained from Tokyo Chemical Industries was purified by threefold sublimation under dynamic vacuum. HWE was used as evaporation technique [2], [3]. The used substrates were freshly cleaved (001)-oriented mica. The base pressure during growth was about 6×10^{-6} mbar and the PSP source temperature was fixed at 240 ºC. The substrate temperature was 90 ºC or 150 ºC, the growth time was varied between 5 sec and 60 min. The film morphology was imaged by AFM using a Dimension 3100 system (Digital Instruments) operated in tapping mode on air. 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 a 4-circle goniometer.

Results

The PSP film morphology with increasing growth time in the range from 5 to 90 sec is shown in Fig.1. The growth temperature was 150 °C. As depicted in Figs.1 (a) and (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. Figs.1 (c) and (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. A similar behavior was found for the samples grown by 90 °C; however, in this case the island shape transition occurs later – between 25 and 45 seconds of growth time.

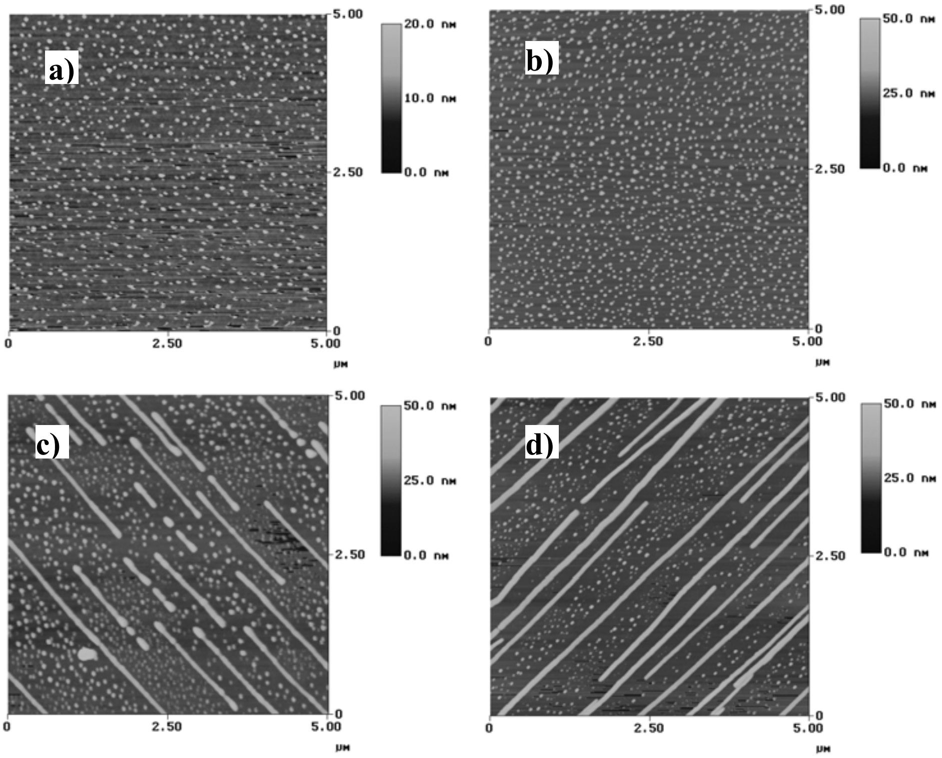

Fig. 1: AFM images of the films grown at 150°C within (a) 5; (b) 10; (c) 25; (d) 90 sec.

Some of these extraordinary features can be explained qualitatively in terms of strain-induced heteroepitaxial island growth, well known in inorganic heteroepitaxy. For example, Tersoff and Tromp [4] 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 results agree well with these theoretical predictions.

We performed also XRD measurements in $\Theta/2\Theta$ mode for PSP films of different thickness in order to get information about the variation of interplanar spacing in the growth direction d(11-1) with increasing layer thickness, i.e. about presence of lattice deformation (strain). As shown in Fig.2, the d(11-1) value increases rapidly with increasing needle height approaching the bulk value at a thickness of ≈25 – 30 nm. Such behavior implies that thin PSP layers are strained and this strain is relaxed within the first ≈25 – 30 nm (~60 monolayers) of the film. These observations suggest that weak Van der Waals interactions between the PSP film and the mica substrate are nevertheless strong enough to produce a lattice deformation, which is likely to be the driving force [4], [5] for the needle-like morphology shown in Fig. 1.

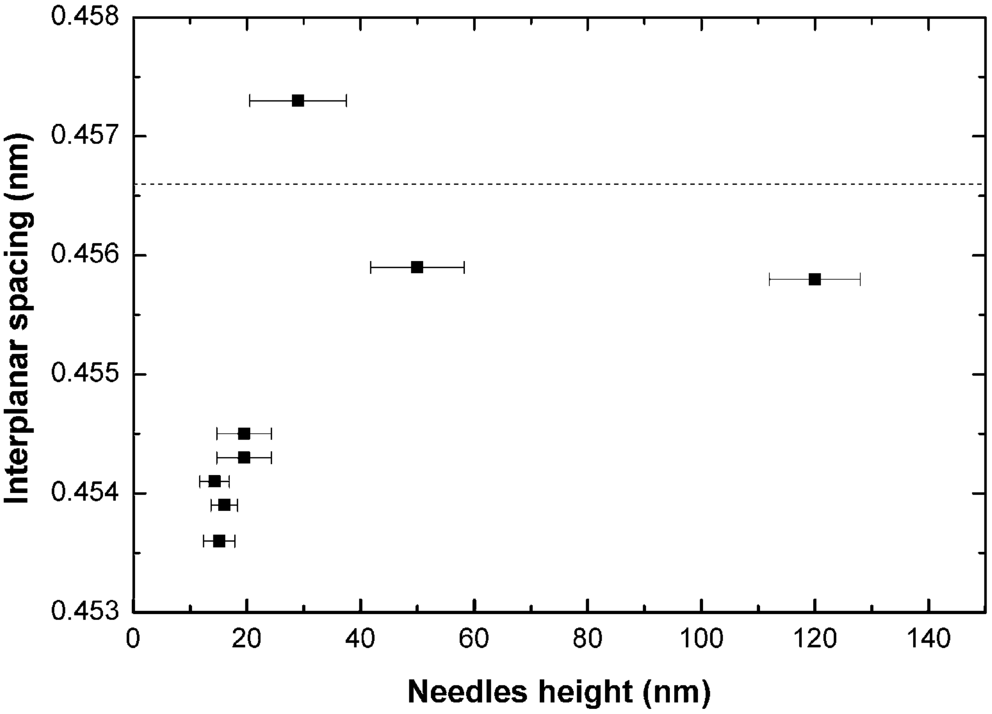

Fig. 2: Interplanar spacing d(11-1) as a function of the average needles height for PSP layers grown at 90°C.

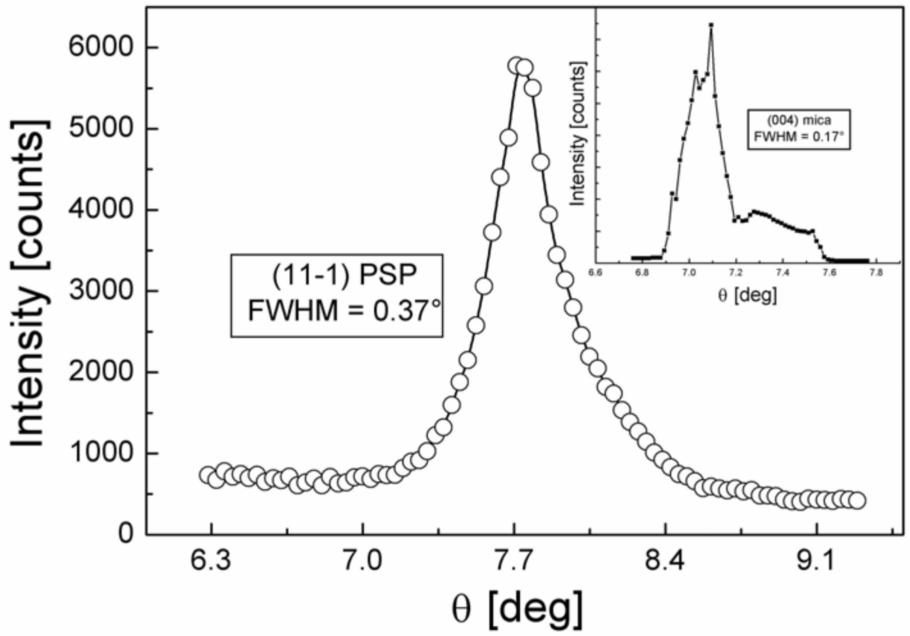

Fig. 3: Rocking curve for the 11-1 reflection of the PSP film. Insert shows corresponding curve for the 004 reflection of the mica substrate.

The so-called Rocking curves (i.e. Θ–scans) provide us 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 [5]. Figure 3 shows a typical Rocking curve measured at 2Θ = 15.67° for the characteristic 11-1 reflection of the PSP film grown at 150 °C within 90 sec (see also Fig. 1(d)). The Rocking curve is remarkably narrow for organic films with a FWHM of only 0.37°. For comparison, the Rocking curve of the mica substrate (004) reflection at 2Θ = 14.26° was measured (see inset in Fig.3). The rocking curve of mica shows an irregular shape, which appears often in single crystals of layered compounds like graphite, mica, a.o. The FWHM value of the mica substrate differs not much from the corresponding FWHM of the PSP film itself. These data confirm a very good out-of-plane alignment of PSP crystallites and thus a high degree of order in the film.

Conclusion

The HWE growth of oriented thin films of PSP on 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 highly anisotropic needle-like structures. XRD investigations using synchrotron radiation confirmed a very high degree of epitaxial order of the films and demonstrated that thin PSP layers are strained and this strain is relaxed within the first ≈25 – 30 nm of the film.

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