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Epitaxially grown sexiphenyl nanocrystals on the organic KAP(0 1 0) surface

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ABSTRACT

Nanocrystals of the organic molecule sexiphenyl are grown on the (0 1 0) cleavage plane of potassium hydrogen phthalate (KAP). The single crystalline organic surface is composed exclusively by phenyl rings and displays two distinct directions of aromatic rows forming surface corrugations. Sexiphenyl crystals grow epitaxially ordered with the (2 0 $\bar{3}$) plane parallel to KAP(0 1 0) with the long molecular axes of the molecule aligned along one specific surface corrugation; empirical force field calculations confirm the experimentally observed epitaxial alignment of the sexiphenyl crystals. The sexiphenyl crystals grow as elongated islands, which can be shown to be of single crystalline nature.

1. Introduction

Fundamental research on mechanisms of aggregation of organic molecular materials is an important step for the understanding of film growth mechanisms and, in succession, for controlling the growth [1–3]. The effort in this field is basically motivated by the potential of organic semiconductors in diverse electronic devices (light-emitting devices, photovoltaic cells and field-effect transistors). The strict dependence of device performances on molecular orientation is due to the anisotropy of the molecules, the molecular crystals and the correlated electronic and optical properties [4–6]. Therefore, the ability to control molecular orientation and crystallographic order of the molecular materials is highly beneficial for improving device performances. Moreover, in a device, the crystal properties such as crystal structure, grain size and strain show distinct influence. In particular sexiphenyl, which is a rod-like molecule and a blue light-emitting organic semiconductor with an outstanding high quantum yield, shows blue light emission perpendicular to the long molecular axis (LMA) [7,8]. Moreover, the sexiphenyl molecular crystal, a layered crystal with the so-called herringbone arrangement of molecules within each single layer (herringbone layer), is reported to be a wave guiding crystal in the plane of the herringbone layers [9]. The waveguide effect abruptly ends at grain boundaries [10]. Therefore, ordered, single crystalline structures are of particular interest for future applications.

Recently, the field of interest of organic molecular films has expanded beyond the growth on metallic, semi-conducting and insulating surfaces to organic heteroepitaxy, often realized by a multilayer growth [11–14]. In the present study, we follow this way, using the highly ordered cleavage plane of potassium hydrogen phthalate—KAP(0 1 0)—as organic template for the growth study. This surface is molecularly flat and shows phenyl rings pointing out of the crystal [15]. Furthermore, it displays two distinct directions of surface corrugations running along ⟨1 0 1⟩ and [0 0 1]. The surface characteristics, the oriented phenyl rings as well as the surface corrugations, are likely to induce an epitaxial growth of sexiphenyl—what was finally observed.

2. Experimental

The KAP single crystals (purchased from Ekspla, Vilnius and Lithuania) were mechanically cleaved in air immediately before

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introduction into the growth chamber for organic molecular beam epitaxy [16]. High purity sexiphenyl (p6P, $C_{36}H_{26}$) purchased from Tokyo Chemical Industries was deposited at a base pressure of 10^{-7} Torr, a growth rate of 0.3 nm min^{-1}, and a substrate temperature of 300 K. Films with nominal thicknesses between 10 and 20 nm were prepared, as monitored by a quartz microbalance [17].

The surface morphology of the films was investigated by atomic force microscopy (AFM) using a Digital Instrument Nanoscope IIIa MMAFM equipped with E- and J-type scanners. The out-of-plane orientation as well as the in-plane alignment of the sexiphenyl crystallites was determined by X-ray diffraction (XRD) techniques using a PHILIPS X'PERT system equipped with an ATC3 cradle operated with CrKα radiation and a secondary monochromator. The measurements were based on the orthorhombic crystal structure of KAP with lattice constants of $a = 9.61$ Å, $b = 13.33$ Å and $c = 6.48$ Å [18], and on the monoclinic structure of sexiphenyl with $a = 8.09$ Å, $b = 5.57$ Å, $c = 26.24$ Å and $\beta = 98.17$ Å [19]. The software packages POWDER CELL, MERCURY and STEREOPOLE were used for data analysis [20,21].

Atom–atom potential calculations were performed to study the correlation between the orientation of p6P crystals on the KAP(0 1 0) plane in terms of potential energy. A modified version of the AutoDock3 molecular docking package [22] was used in combination with the UNI empirical force field without point charges on atoms [23]. A simulation box with 351^3 grid points and a grid spacing of 0.217 Å was used in order to sample the interaction potential with a fine grid. Preliminary simulations with 251^3 grid points were satisfactory, but definitely less accurate on determining the potential energy minima. The KAP(0 1 0) substrate surface was modeled with a slab composed by $11 \times 2 \times 17$ unit cells for *a*-, *b*- and *c*-axis, respectively, giving rise to a total of 1728 formula units of $C_8H_5O_4K$ and 31104 atoms. The sexiphenyl crystal was modeled by two herringbone layers of sexiphenyl molecules representing a slice of the $(2\,0\,\bar{3})$ plane. Two different sets of simulations runs were performed; the first one was based on a p6P slab consisting of three molecular layers parallel to $(2\,0\,\bar{3})$ with 3/4/3 and 4/3/4 molecules for the two herringbone layers (i.e. 7 molecules contact the plane of the substrate) (996 docking runs), the second one comprised a stacking of 5/4/3 and 4/3/4 molecules (i.e. 9 molecules contact the plane of the substrate, 1092 docking runs) to check the relevance of the lateral size of the crystallite. For the latter, only the 982 docked structures with the 5+4 contact p6P molecules were used for final statistics.

For transmission electron microscopy (TEM), the films were covered with a uniform carbon film and detached from the KAP substrate. Bright field images, diffraction patterns and high-resolution images were recorded by a PHILIPS CM12 electron microscope operating at energy of 120 keV.

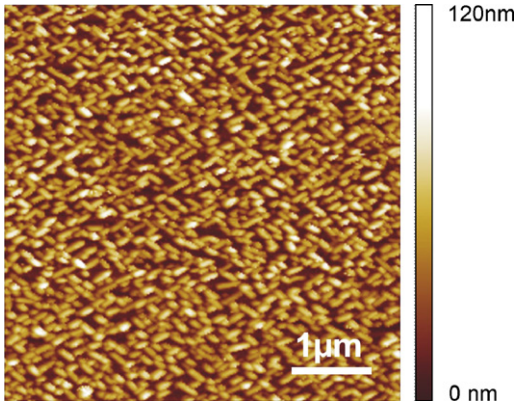

Fig. 1. AFM of a 10 nm-thick sexiphenyl film on KAP(0 1 0): elongated islands are observed with two distinct preferred growth directions inclined by an angle of 70° to each other. Some areas appear dark and are not covered by needles.

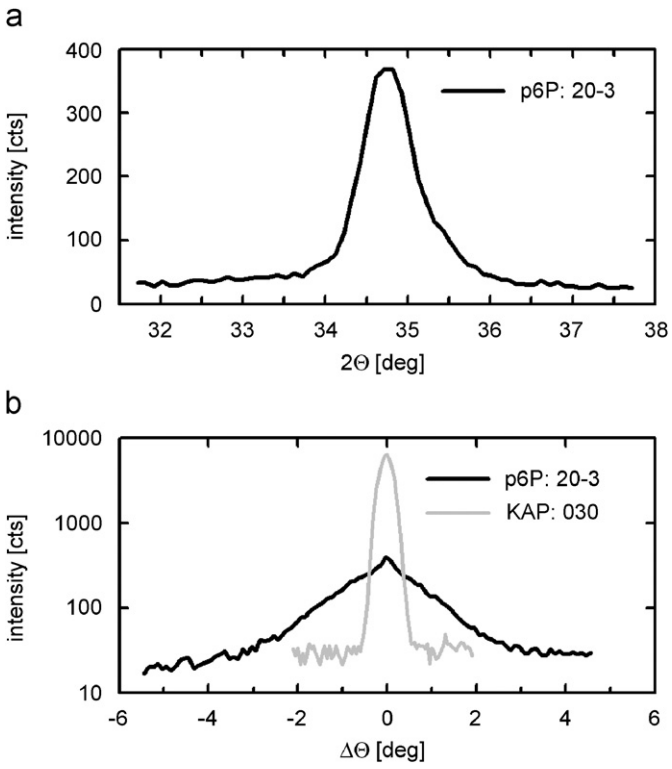

Fig. 2. XRD of sexiphenyl crystals grown on KAP(0 1 0): the specular scan shows the $20\bar{3}$ diffraction peak of sexiphenyl (a) and rocking curves across the 030 specular diffraction peak of the substrate and of the $20\bar{3}$ orientation of the organic layer (b).

3. Results and discussion

An AFM image is shown in Fig. 1, where small elongated islands of sexiphenyl are observed. The islands have a tabular shape with an average height of 40 nm, a width of 80 nm and a characteristic length of 300 nm. The surface is not completely covered by these islands, also some dark areas <100 nm appear. The elongated islands are aligned along the two preferred azimuthal directions which are inclined by 70° ($\pm 10°$) relative to each other.

The crystallographic properties of the islands were determined by XRD specular scans, the results are shown in Fig. 2a. The presented peak is identified as the $20\bar{3}$ diffraction of p6P and indicates that the crystals grow with the $(2\,0\,\bar{3})$ plane parallel to the surface. There are several examples of epitaxially grown p6P films where this $(2\,0\,\bar{3})$ plane is found parallel to the substrate surface; generally this plane of p6P is formed parallel to the substrate surface when either the interaction of the p6P molecules with the substrate is rather weak like for KCl(1 0 0) or surface corrugations induce the formation of this specific plane of p6P [24,25]. The film mosaicity is probed by a rocking curve of this diffraction peak (Fig. 2b). As a reference, the rocking curve of the KAP(0 3 0) peak is shown in the same graph as it reflects the experimental broadening. The FWHM of the p6P peak is 1.3°, while in case of the KAP a peak width of 0.3° is observed. Therefore, a mosaicity of approximately 1° can be concluded, which is a good value for organic–organic heteroepitaxy [26].

The epitaxial alignment of the p6P crystals was determined by recording a set of pole figures. One pole figure is representatively