Growth of Unidirectionally Oriented Pentacene Nanofibers by a Roller Method

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Oriented crystal fibers of pentacene were produced by a simple casting process from trichlorobenzene solution at elevated temperature. The solution was placed in the air gap between a glass roller and a glass substrate. The width of the air gap was determined by a Teflon spacer wound around both ends of the roller. The roller was moved over the substrate with a constant speed and crystal fibers with approx. 100 nm height, micrometer width and a length of up to 100 µm were formed in the rolling direction. The fibers were characterized by optical microscopy and scanning electron microscopy. [DOI: 10.1380/ejssnt.2007.103]

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Organic field effect transistors (OFETs) are necessary building blocks for ‘plastic electronic’ devices. A tremendous amount of research in the last decade has led to advances in materials, processing techniques and thus devices. One of the most promising materials for OFETs is pentacene, a polycyclic aromatic compound with a mobility of more than 50 cm²/Vs [1]. Since pentacene is virtually insoluble in common organic solvents at room temperature, it is usually vacuum evaporated to form thin films, a method which limits its applicability. The crystalline morphology of the films depends very much on the surface energy of the substrate, substrate temperature, evaporation speed, and other parameters. Furthermore, patterning of the organic semiconductor needs a shadow mask. Thus the overall size of the patterned area and the pattern dimensions (pattern width, pattern spacing, etc) are only within certain limits.

In order to allow the advantages of solution processing (cost effective, large area, continuous roll-to-roll process, mask-less patterning) substituted pentacenes have been synthesized and OFETs have been reported [2]. But since the crystal morphology depends on the chemical structure and thus on the shape of the molecules in a poorly predictable way, this approach is prone to trial and error.

On the other hand, it is known that pentacene can be recrystallized from 1,2,4-trichlorobenzene [3] and recently it was reported that OFETs of unsubstituted pentacene can be produced by solution casting at around 200°C [4].

Here we report on the patterning of pentacene by using a roller apparatus that allows the formation of unidirectionally grown microfibers with submicrometer thickness and a length of up to 100 µm.

The roller apparatus has been described in detail before [5]. It consists of a glass rod with Teflon spacers, that is placed on the substrate (glass, mica or silicon) on a temperature-regulated hotplate. A hot solution of pentacene (Aldrich Inc.) in 1,2,4-trichlorobenzene (TCI, Japan) is placed in the air gap between roller and substrate. Capillary force sucks the solution under the roller, which is moved over the substrate at a speed of a few ten mm/min. Optical and polarizing micrographs were taken by a CCD camera (Spot RT, Diagnostics Inc) equipped microscope (Olympus BX-50). Scanning electron micrographs were obtained by a Hitachi 3500 electron microscope.

We have already reported on the use of such a roller apparatus for preparation of unidirectional fibers of charge transfer complexes [6]. The fiber morphology can be easily controlled by concentration, roller speed and temperature.

Here, at a substrate temperature of 200°C crystal morphology is somewhat heterogeneous and made of thin fibers with a width of approx. 1 µm and a length of several ten µm, and crystal fibers with small lateral protrusions (leaf-like crystals) that have a width of several µm. Figure 1 shows the optical and polarizing micrograph of some of the leaf-like crystals. Polarizing microscopy indicates that the crystals are single crystalline, since their birefringence is homogeneous. It also seems the crystal orientation of individual fibers is not random, because there are groups of crystals with similar birefringence color. The dotted line in the polarizing micrograph shows the borderline between two domains. At this peculiar analyzer position, the upper domain is birefringent while the lower domain remains dark. This distinct grouping also is a strong indication that the crystals are not composed of randomly oriented nanocrystals.

Lowering the casting temperature to 175°C leads to very long and well-oriented fibers along the rolling direction, as can be seen in Fig. 2. Further lowering the temperature to 160°C give samples with heterogeneous crystal morphology and orientation. Other parameters that could influence crystal morphology are concentration, solvent and roller speed, as reported for the crystal formation of Charge transfer complexes [6]. Detailed studies using pentacene are in progress and will be reported in the future.

The unidirectional growth of the fibers is a direct consequence of the roller action. At elevated temperature the trichlorobenzene will slowly evaporate. Since the solution is located in the gap between substrate and roller, the only place where the solvent may evaporate is near the three-phase-line (contact line of the liquid with the substrate). Evaporation of solvent leads to a concentration increase.
FIG. 1: Optical microscope image of pentacene fibers formed at 200°C. The upper part is a transmission micrograph, the lower part a polarized image between crossed polarizers. The dotted line separates two domains with different crystal orientation. The scale bar is 20 µm.

FIG. 2: Optical microscope image of pentacene fibers formed at 175°C. In order to visualize the very thin fibers, the picture had to be electronically enhanced by adjusting brightness and contrast. The arrows indicate the position and orientation of the fibers. The scale bar is 20 µm.

FIG. 3: Scanning electron micrographs of a fiber sample prepared at 200°C. The scale bar is 5 µm.

of the solute and to crystal seed formation. The solution height is only a few ten µm close to the three-phase-line and thus crystals will adhere to the substrate. Moving the roller along the substrate automatically also drags the three-phase-line with it across the substrate. Thus crystal growth is limited to the rolling direction. Scanning electron microscopy confirms that isolated crystals with a uniform thickness are formed. Figure 3 shows a set of unidirectional fibers that have a width of less than one µm and a length of several times the width. The height of the fibers is in the range of several ten to hundred nm.

Finally, we could not observe this type of homogeneous growth that leads to such a high degree of fiber orientation with other film formation processes, such as spin coating, dip coating or drop casting. Minakata, et al. [4] have reported on the oriented growth of crystals by dropcasting, but their atomic force images show domains and domain boundaries on the micrometer scale. Our method produces isolated crystal fibers that are homogeneous and defect-free on the micrometer and submicrometer scale, thus greatly reducing defects, such as grain boundaries, that could negatively influence the electric properties. In conclusion, the roller casting method has a very high po-
potential for easy patterning of various organic materials. Here, we showed that even a poorly soluble annulated aromatic as pentacene can successfully patterned by this method.

The performance of the pentacene fibers as organic field effect transistors, and especially the measurement of charge mobility is currently under way.

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