Organic Field Effect Transistors from Oriented Pentacene Crystal Fibers

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1. Introduction

Organic electronics receives increasing interest in recent years. Since the discovery of organic semiconductors in 1965 [1] there has been a steady increase in publications covering the topic. The field of 'plastic electronics' is rapidly expanding and devices are reported to show a performance that is sufficient for commercial applications. Organic field effect transistors are an essential part for future organic devices and much work has been done on the fabrication of polymeric as well as low molar mass hole and electron conductors. Dry processes such as vacuum evaporation or molecular beam epitaxy, as well as wet methods, such as solution casting have been explored. Generally, sublimation of low molar mass materials leads to polycrystalline films, in which grain boundaries limit the electric properties [2]. Surface modification of the SiOx in the channel and optimization of the evaporation conditions could improve the electric characteristics to a certain extend [3]. On the other hand, a wet process could be used to overcome the problem of grain boundaries, since organic compounds, in principle, can form single crystals when recrystallized from solution. Recently it has been reported that pentacene can be spin cast from hot trichlorobenzene solution [4] and we have described the formation of parallel aligned pentacene microfibers by using a hot trichlorobenzene solution and a roller apparatus [5]. This self-patterning is one example for a mask-less process to produce micropatterns very well suited for the mass production of transistor arrays. Here, we describe the fabrication of organic field effect transistors (OFET) on narrow microelectrodes by using this process.

2. Experimental details

Pentacene (Aldrich Inc.) and 1,2,4-trichlorobenzene (TCI Inc.) were used as purchased. Field effect transistors were prepared by patterning Au source and drain electrodes with a thickness of 40 nm (on top of a 1 nm Cr pattern) by a lift-off technique on heavily-doped n$^+$ Si substrates. The SiOx dielectric layer had a thickness of 300 nm. The channel width of the transistor was 25 μm in all cases, with a length of either 10 or 25 μm. These substrates were cleaned by immersion into acidic hydrogen peroxide solution, followed by extensive rinsing with water and isopropanol immediately before coating the organic layer.

We used a roller apparatus to produce fibers of crystalline organic compounds. A solution f each compound is placed in an air gap between a glass roller and the substrate. Moving the roller over the substrate leads to crystallization at the receding solution edge. Further receding then leads to a one-dimensional growth of the crystal along the rolling direction. A variety of crystalline materials, among them electron donors, electron acceptors, and CT complexes

have been patterned in such a way. Fiber dimensions are typically around 50-100 nm height, 100-1000 nm width and 0.1-2 mm length [1].
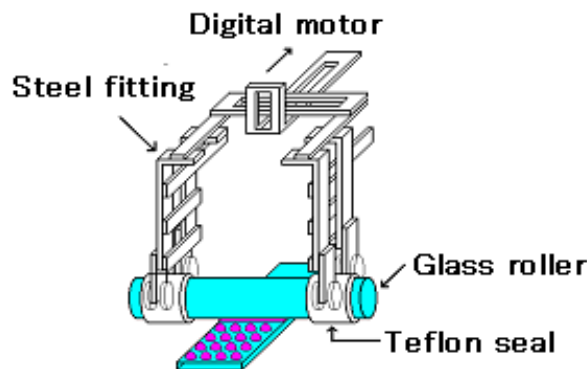

Fig. 1   Schematic of the roller apparatus and experimental setup.

3. Results and Discussion

Oriented pentacene fibers were prepared by a method already reported [5]. A hot solution of pentacene in trichlorobenzene is placed in a heated roller apparatus, and the roller is pulled over the substrate with a constant speed. Crystallization at the receding solution edge leads to the formation of crystal seeds that grow into parallel fibers while the solution recedes [6]. By changing the roller speed and substrate temperature, we were able to produce different pentacene morphologies. Slower roller speeds, at any given temperature, lead to laterally extended crystal fibers, since the growth of the crystals depends on the diffusion of molecules from solution to the growing crystal edge. Faster speeds limit the diffusion of the dissolved pentacene to the growing crystal edge and thus the lateral growth of the crystals is reduced. We found that 30 mm/min is a sufficient speed to produce well-aligned fibers with a width of around 1 μm. Higher speeds also lead to more homogeneous crystal thicknesses. A speed around 10 mm/min gave crystal plates. Higher temperature increases diffusion as well as the local pentacene concentration due to the enhanced solvent evaporation at the solution edge. Hence the crystals grow faster and thus have a more laterally extended shape and become plate-like. The best temperature for fiber growths was between 130 and 150°C. Figure 2 shows the electron micrographs and the carrier mobilities of several samples. The pictures were taken at different viewing angles, but all samples have the same channel width of 25 μm. The roller direction is from right to left in all samples. The height of the depositied pentacene is comparable with the electrode

thickness, which is 40 nm. Sample A shows that the micronsize fibers densely occupy the channel, but due to the dendritic morphology only a small fraction of the pentacene actually connects source and drain electrodes. From the picture we estimate that the combined widths of the active portion of pentacene in the transistor is 30% of the channel width. The observed mobility was 0.0011 cm^2/Vs, but correcting for the coverage density of the pentacene, we can calculate a mobility of 0.0035 cm^2/Vs. a similar sample is shown in Figure 2B. Here, the drain and source electrodes are connected via three fibers, which were significantly wider that in sample A and show less dendritic branches. Their measured mobility was already an order of magnitude higher and gave a corrected mobility of 0.044 cm^2/ Vs. Plate-like pentacne crystals can be prepared, too. As can be seen in Figure 2C, the full width of the channel is covered by pentacene. The difference in pentacene thickness, thicker at the right electrode and substantially thinner at the left electrode, may come from a pinning and stick-slip motion of the solution that is caused by the electrode edges [7]. This may also be the reason for the visible defects on top of source and drain electrodes. Even though the channel also shows a few of those defects, we were able to achieve a mobility of 0.19 cm^2/Vs. This is a reasonable value for a completely covered gap, and a value of 0.47 cm^2/Vs has been reported recently for very thin pentacene OFETs in the so-called planar bottom contact configuration [8].
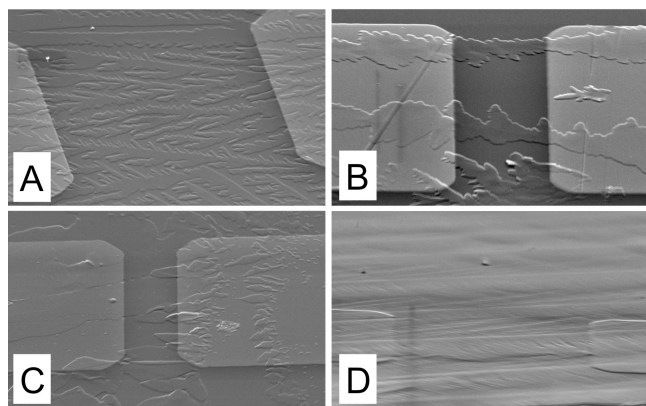

Fig. 2   Scanning electron micrographs of pentacene OFETs prepared by the roller method. For detailed information about samples A to D, see the text.

The last of our samples, which can be seen in Figure 2D shows a quite homogeneous coverage of the channel with only a slight surface corrugation of the pentacene film parallel to the channel direction. This sample shows a measured mobility of 0.64 cm^2/Vs. This large value may be due to the fact that the organic semiconductor crystal covers also areas besides electrode gap through which carriers may flow. A simple estimation using an online electrostatic field simulator showed that the pentacene-covered area outside the channel may contribute two- to three-fold to the total carrier mobility in case of an isotropic material. Thus the mobility in the channel can be estimated to be around 0.2 cm^2/Vs, which is comparable to sample C.

4. Conclusion

A hot pentacene solution was used to produce bottom contact field effect transistors by a roller method. Depending on the solution casting conditions, large plate-like crystals or unidirectionally aligned microscale crystal fibers can be produced. Plate-like crystals show hole mobility in the gap of 0.2 cm^2/Vs, whereas fibers have mobilities in the range of 10^{-3} to 4 x 10^{-2} cm^2/Vs. Even though mobilities of more than 1 cm^2/Vs can be routinely achieved with vacuum deposited films of pentacene OFETs in the top contact configuration, it has to be taken into account that in the present case, we use the less effective bottom contact configuration and a wet process. Nevertheless, our work shows that solution casting is a promising approach to produce transistor arrays of pentacene by using the self-patterning of fibers.

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