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Single-crystal tetrathiafulvalene microwire arrays formed by drop-casting method in the saturated solvent atmosphere

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ABSTRACT

We developed a drop-casting method to grow the well-aligned single-crystal tetrathiafulvalene (TTF) microwire arrays with success ratio as high as 86%. The key improvement over the earlier study is that the substrate is placed in an apparatus which is filled with the saturated solvent vapor at room temperature. The saturated solvent atmosphere ensures stable environment and adequate time to form the arrays with high success ratio, and to dramatically improve the crystalline quality. Combined with the optimized concentration, the highly ordered single-crystal TTF microwire arrays are obtained. Based on these microwire arrays, the assembly of devices can be easily realized in one step. These results show the potential of this facile method to form the high-quality arrays, and the assemblies of nanoscale circuits for fundamental studies and future applications.

1. Introduction

Organic single-crystal microwire arrays have attracted much attention in the last decade because they combine the advantages of single-crystal microwires and the highly-ordered arrays. On one hand, the single-crystal microwires are free of grain boundaries or molecular disorder [1–3], which provides an ideal model to investigate the nature of the materials and to elucidate fundamental factors dictating performance [4,5]. The microstructured single crystals are known to have good performance [1,2]. On the other hand, the microwire arrays are desirable for the large-scale and high efficiency microdevices fabrication. The highly-ordered and well-aligned microwires might exhibit superior properties compared to their disordered counterparts [6]. Electrons can transport directly from one end to the other along the aligned microwires, while they might travel circularly then be wasted through crosslinked networks resulting from randomly dispersive microwires. The microwire arrays have shown the potential in field-effect transistors (FETs) [7,8], light-emitting diodes (LEDs) [9], logic computations [10] and other fields [11,12].

The growth of single-crystal microwire arrays is promising and desired for the further study. The representative progress is mainly performed with solution-based method, including dip coating [13], zone casting [14] and drop casting [15]. The drop-casting method is most extensively used due to its facile process and no requirement of specific equipments. However, in drop-casting method the evaporation rate of the common volatile solvent is significantly affected by the environmental atmosphere, leading to the poor controllability of the experimental results. And generally in the atmospheric environment, the common volatile solvent in the droplet evaporates too fast for the molecules to assemble into single crystals. Thus the microwire arrays are always formed at random with poor crystalline quality in uncontrollable locations. In addition, the good solubility of the organic semicondutors in the common volatile solvent is pre-requisite based on the solution method. In this study, using tetrathiafulvalene (TTF) as the material and dichloromethane as the solvent, a drop-casting method in the saturated solvent atmosphere has been developed to grow the well-aligned single-crystal microwire arrays with high success ratio.

TTF and its derivatives have been intensively investigated as semiconducting layers in OFETs because of their high performance and good processability [16,17]. TTF is an important organosulfur compound with the planar molecular conformation, exhibiting low dimensional nanostructures and high mobility owing to the good overlapping of π–π orbits and S•••S interactions [18,19]. And it owns good electron donor ability with highest occupied molecular orbital (HOMO) levels (−4.73 eV) close to the work function of usual metallic electrodes, leading to little energy

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barrier for charge injection from metal electrodes into the active layer [20]. These facts contribute to the high performance of the OFETs based on the TTF nanostructures. On the other hand, TTF is generally soluble in common organic solvents, which is favorable for large-scale production of nanoscale devices using the solution method. Although lots of reports have been made on single crystal of TTF and its derivatives [21,22], only few have reported on the TTF single-crystal microwire arrays until now [13], which hinders the development of TTF in the integrated electronics. Therefore the assembly and scaling of the TTF microwires into arrays are requisite for general purpose productions.

In our experiment, we developed a drop-casting method to grow the arrays of single-crystal TTF microwires with success ratio as high as 86%. The saturated solvent atmosphere is employed to slow down the evaporation rate of the solvent in the droplet, resulting in the relatively stable environment and adequate time for the growth of high-quality TTF microwire arrays. With the optimized concentration of the TTF/dichloromethane solution, we yield well-aligned single-crystal TTF microwire arrays. With these microwire arrays the devices can be easily fabricated in one step based on the pre-prepared pattern of electrodes. These results demonstrate that this method may be used to realize the fabrication of the high-density and high-performance devices and circuits in nanoelectronics.

2. Experimental Section

2.1. Growth of wire arrays

TTF was purchased from Alfa Inc., and purified by vacuum sublimation. The organic compound was dissolved in dichloromethane at the concentration of 0.005–0.05 M (moL/L). A droplet of TTF/dichloromethane solution was cast onto the substrate and allowed to evaporate in an apparatus which is filled with dichloromethane vapor at room temperature. Glass, quartz, silicon (Si), and silicon/silicon dioxide (Si/SiO_2) were used as substrates. All substrates were cleaned by sonication in acetone and dichloromethane for 10 min. Then they were dried in an oven at 100 °C. After that, the substrates were dipped in the chromic acid lotion for 20 min, followed by cleaning with flowing deionized

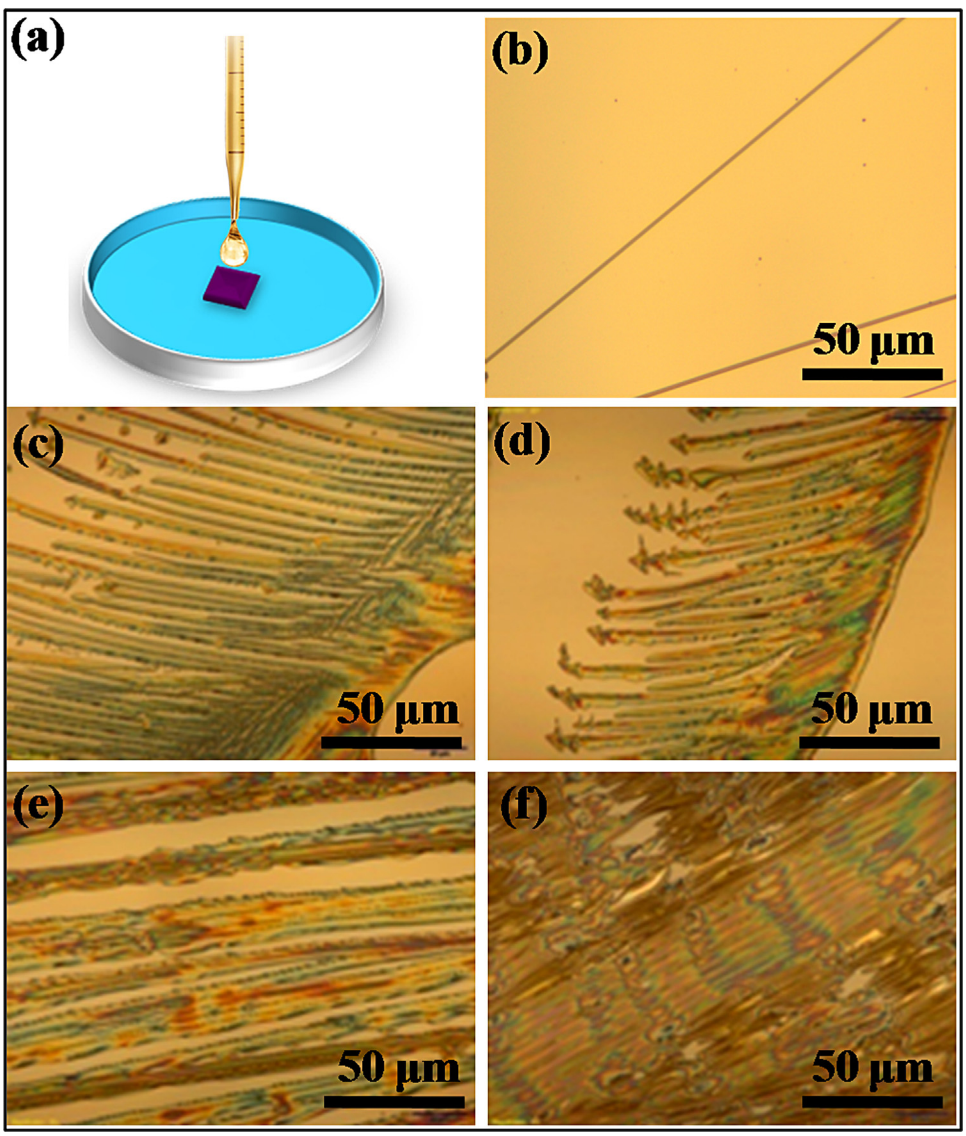

Fig. 1. (a) Schematic diagram of the experimental apparatus and procedure of the traditional drop-casting method. (b–f) The optical microscopy images of TTF individual single-crystal microwires (b), and polycrystalline microwire arrays grown on clean Si/SiO_2 substrate using different solution concentration of (c) 0.005, (d) 0.01, (e) 0.02, (f) 0.05 M by the traditional drop-casting method.