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研究課題名（和文）Self-organizing_terminal-exposed_oligomers_for_high-performance_OTFTs_based_on_fully-printing_technique

研究課題名（英文）Self-organizing_terminal-exposed_oligomers_for_high-performance_OTFTs_based_on_fully-printing_technique

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研究成果の概要（和文）：1. 解像度1umでデバイスを印刷する技術を実現。本研究では、平行真空紫外光による表面改質を用いた独自の印刷技術を開発した。この印刷に よって、均質な特性を有するデバイスや、複雑な形状を持つ電子回路を、大面積、フレキシブル、透明な基材の上に形成することが初めて可能に なった。
2. 完全印刷プロセスによって有機トランジスタを大面積に形成。本研究において、基板を傾けることで発生する重力の影響を用いて、マイクロ液滴アレイの乾燥工程を一様に制御し、高品質な半導体膜を大面積でパターニングすることに成功した。この手法を用いて、完全印刷トランジスタ を大面積に形成し、素子間の分離を完全に行うことに成功した。

研究成果の概要（英文）：1. Realization of 1-Micro-Resolution Printing of Electronic Circuits and Devices. In this research, we developed the spontaneous patterning based on the parallel vacuum ultraviolet (PVUV) technique, which enabled the homogeneous integration of complex, high-resolution electronic circuits even on large-scale, flexible, transparent substrates.
2. Large-area, solution-processed discrete organic thin-film transistors. In this research, we developed a homogeneous dewetting on large-area micro-droplet arrays, which was caused by the gravity-induced deformation of droplets on a tilted substrate. This method allowed the deposition of discrete organic semiconducting thin films for fully-printed organic thin-film transistors (OTFTs).

研究分野：Organic Electronics

キーワード：organic transistor　crystalline film　printing technique

１．研究開始当初の背景

The ever-increasing demand for next-generation flexible, large-area and low-cost electronic devices requires intensive construction techniques for coating active layer, insulating layer and electrodes. In order to integrate mass of each electronic element into a typical circuit, we may resort to printing techniques. Recently, in our group, OTFT fabricated by fully-printing technique using C8-BTBT on polymer films showing high mobility up to 7.9 $cm^2 V^{-1} s^{-1}$ opens an applicable way for achieving large-area integrated circuits at room temperature (shown in Figure 1), the performance of which can be comparable with the oxide semiconductor of *a*-IGZO (Hosono et al. *Nature*, 2004).

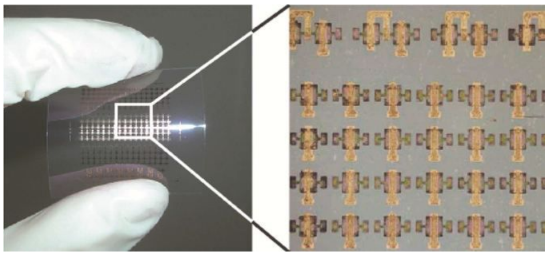

Figure 1 OTFT arrays fabricated by printing technique (Minari et al., *Adv. Funct. Mater.*, 2014)

The applicant used to prepare self-organizing semiconducting molecular columns with highly ordered and densely packed lattice and succeeded in obtaining high (two order of magnitude high than others) and stable ambipolar mobility over a wide temperature range from 25 to 170 °C for long period of two months (Liu et al. *Chem. Mater*., 2014). This result mainly originated from the narrower two-dimensional π-π interaction distance, thereby leading to the possibility of charge carrier transporting without being deeply trapped.

This research proposes to apply such closer packed structure based on new self-assembling terminal-exposed oligomers in OTFT through printing techniques. This kind of molecular system can acclimatize itself to the printing environment through its own self-organization functionality, thereby ensuring high-quality large-area thin organic semiconducting layers for stable high-performance OTFTs in mass scale.

２．研究の目的

This proposal aims to fabricate high-performance organic thin film transistors (OTFTs) using self-organizing organic semiconductors through fully-printing techniques. The applicant plans to establish novel molecular self-organizing semiconductor based on ‘terminal-exposed’ oligomers. The oligomers crystalize into closely-packed lattice structures due to the self-organizing ability, resulting in the high charge carrier mobility up to 10 $cm^2 V^{-1} s^{-1}$ with high thermal stability up to 200 °C. Fundamental understanding of molecular orientation and transport mechanism will be investigated to further improve the OTFT performance. Fully-printed flexible devices will be made using the self-organizing oligomers.

３．研究の方法

The applicant will develop the self-organizing oligomers and achieve high-mobility OTFTs by printing techniques, principally based on modifying molecular structures and devices’ conformation as well as adjusting printing procedures. For FY 2015, all designed oligomers will be synthesized and characterized, and further used to fabricate OTFTs; preliminarily, the fundamental understanding of charge carrier transport will be clearly clarified. From FY 2016 on, construction of devices will be improved toward high-performance, miniaturization and integration through optimizing printing process, interface contact and patterning structures. During this research, a novel semiconducting molecular system will be established and also high-performance OFETs with average mobility up to 10 $cm^2 V^{-1} s^{-1}$ will become more easy-process and applicable. This work will be carried out in Minari group (Fully-printed electronics laboratory) in NIMS.

４．研究成果

(1) Realization of 1-Micro-Resolution Printing of Electronic Circuits and Devices

High-resolution patterning of functional materials into microstructures received increasing interests in optical, electronic, biological and sensory applications. Typically, the fluidic self-assembly on dewetting surfaces enabled the spontaneous fabrication of various long-range ordered nanoparticle rings and stripes as well as multilayered structures, thus offering the advantage of avoiding complicated and expensive lithographical substractive processes. Therefore, spontaneous patterning of electronic circuits is presently considered as the most promising, nonlithographic, mold-free approach especially for large-area plastic devices.

In this research, we propose the spontaneous patterning based on the parallel vacuum ultraviolet (PVUV) technique, which enabled the homogeneous integration of complex, high-resolution electronic circuits even on large-scale, flexible, transparent substrates. Irradiation of PVUV effectively changes the surface wettability of a polymer

substrate into hydrophilic, and the wettability contrast acts as the guide for a metal nanoparticle ink. Thus we can obtain high-resolution circuits on a polymer substrate using a simple coating process. We also developed materials and processes which allow the formation of circuits at room temperature, thus we can form high-resolution circuits on a heat-sensitive polymer substrate without using the high-temperature annealing processes. We developed the present technique to fabricate short-channel organic thin-film transistors (OTFTs) in large-area arrays on a plastic substrate. The spontaneous patterning also allowed selective deposition of charge injection layers which reduced the contact resistance (R_c) to 1.5 kΩ cm. As a result, the spontaneously solution-processed OTFTs exhibited high field-effect mobility (μ_{FET}) values of 0.3 and 1.5 cm^2 V^{-1} s^{-1} with the channel lengths (*L*s) of 1 and 5 μm, respectively, which is comparable to that of vacuum-deposited devices.
(Liu. X., et al. *Advanced Materials* 2016, DOI: 10.1002/adma.201506151. Highlighted in *EE Times Japan*, *Nanotech Japan*, *Yahoo News* and **日本化学工業日本**)

This spontaneous patterning strategy for scaling down the electronics, in combination with the homogeneous integration method, should be promising for fully solution-processed, lithography-free, large-area, high-resolution flexible devices.

(2) Large-area, solution-processed discrete organic thin-film transistors

Inducing a unidirectional dewetting has been identified as one of the most effective approaches to deposit highly aligned crystallized thin films for solution-processed electronics in low cost, high efficiency. Therefore, many efforts have contributed to exploiting the direction-controlled dewetting via adjusting the moving directions of upper or bottom substrates, or by modifying substrate surfaces using a special treatment.

Here, we report a homogeneous dewetting technique on large-area microdroplet arrays (MDAs) (300 MDs, 4cm × 4cm), which was caused by gravity-assisted deformation of droplets on a tilted substrate, and enables the formation of aligned crystalline thin films for device application. It was found that increasing the tilted angle enables the deformation of droplets, thus leading to the homogeneous receding of upper contact lines from top to bottom on the MDAs. Moreover, this method allows the deposition of discrete organic semiconducting thin films for fully-printed organic thin-film transistors (OTFTs). In particular, when using a tilted angle of 90 degree, the obtained films exhibited the optimal surface morphology, which could be understood through a theoretical interpretation. Furthermore, the dewetting behavior of water enables the selective deposition of transition-metal oxides for modifying semiconductor/electrode interfaces to lower the contact resistance in OTFTs. The contact resistance was significantly decreased from 14.9 kΩ cm to 3.8 kΩ cm in the fully-printed OTFTs, which results in the increase in the field-effect mobility (μ_{FET}) from 9.2 cm^2 V^{-1} s^{-1} (before treatment) to 13.1 cm^2 V^{-1} s^{-1} (after treatment).

The presented method of using the homogeneously unidirectional dewetting to selectively fabricate aligned crystalline thin films and doping layers would not need any template and is totally compatible with conventional photolithography that has been widely used in the industry of TFT technology.

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〔図書〕（計 0 件）

〔産業財産権〕

○出願状況（計 0 件）

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〔その他〕
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http://www.nims.go.jp/group/minari/en/

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