On-Substrate Synthesis of Organic Metal Films, Electrodes, and Circuits

T. Hasegawa, M. Hiraoka, Y. Takahashi, T. Yamada, and Y. Tokura
Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8562, Japan

Abstract

One of key issues toward "plastic electronics" is to design and implement printable functional materials to manufacture a wide variety of electronic devices quickly and easily on flexible substrates by conventional printing processes. This report presents an approach of synthesizing barely-soluble molecular conductor films directly on substrates. It is shown that metallic organic charge-transfer complex films can be fabricated by an inkjet printing (IJP) technique in which the soluble donor and acceptor components are printed individually and combine on the substrate to form metallic films. The method enables us to produce high quality thin films of tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) with an electrical conductivity of about 10 S/cm. Use of the TTF-TCNQ films as source/drain electrodes affords pentacene thin-film transistors and inverters showing sharp on/off switching at low voltages.

1. Introduction

Binary molecular materials, or organic CT complexes, provide versatile electronic functionalities as a result of ground-state electron transfer between component donor and acceptor molecules.[1] Quite high room-temperature electrical conductivities, reaching around 10^3–10^4 S/cm, can be achieved with a variety of CT compounds, e.g. TTF-TCNQ. These materials are often called "*synthetic metals*", and their particular electronic properties have been major subjects of study in materials physics for more than 30 years.[2] However, the application of these functional organic materials into the "*plastic electronics*" is highly restricted, chiefly because of poor processability as a result of their high crystallinity and low solubility. In contrast, the study of printable conducting materials has been hitherto focused on soluble materials, including conducting polymers,[3,4] inorganic nanometal clusters,[5] or metal precursors.[6] Nonetheless it has been argued that the solvent affinity of these soluble materials causes problems in subsequent fabrication processes: the resultant films are vulnerable to further printing processes [7] or require post-processing annealing.[4-6]

Here we present a "*double-shot inkjet printing*" (DS-IJP) technique where we take advantage of a unique characteristic of the CT compounds that individual component donor and acceptor molecules generally show much higher solubility than do their complexes. Table 1 illustrates the solubility of some donors and acceptors and their CT complexes in dimethylsulfoxide (DMSO). This shows clearly that there is a considerable decrease in solubility as a result of complex formation in conventional CT complexes. We show that microscale intermixing on substrates of dense droplets of inks containing donors and acceptors results in the instantaneous formation of CT complexes that form high-quality synthetic metal films without post-processing annealing.

2. On-Substrate Synthesis of Molecular Conductor films: Double-Shot Inkjet Printing Method

We used a piezoelectric drop-on-demand IJP apparatus with double IJP heads (Microjet, Picojet 2000CW), shown schematically in Figure 1. The donor and acceptor inks were

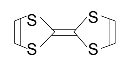
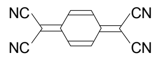
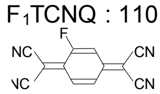
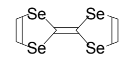
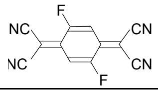
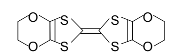
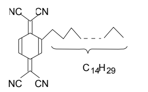
Donor (g/L)	Acceptor (g/L)	CT-Complex (g/L)
TTF : 770 	TCNQ : 16 	TTF-TCNQ : 0.8
	F$_1$TCNQ : 110 	TTF-F$_1$TCNQ : 2
TSF : 640 		TTF-F$_2$TCNQ : 0.5
	F$_2$TCNQ : 20 	TSF-F$_1$TCNQ: 0.7
		TSF-F$_2$TCNQ: 0.7
BO : 41 	C_{14}TCNQ: 1.6 	BO$_9$(C_{14}TCNQ)$_4$: 3.6

Figure 1. Solubility of some electron donors, electron acceptors, and their charge-transfer complexes in dimethylsulfoxide (DMSO).

formed by dissolving donors [TTF or tetraselenafulvalene (TSF)] or acceptors [TCNQ, 2-monofluoro-TCNQ (F$_1$TCNQ), or 2,5-difluoro-TCNQ (F$_2$TCNQ)] in DMSO, respectively. The solution was filtered through a mesh filter with a pore size of 0.5 μm before injection into the IJP heads. In the process, **1** a first drop of the donor ink is overprinted by **2** a second drop of the acceptor ink at an identical position within 2 s to **3** form a mixed droplet on the substrate before **4** the solvent is fully evaporated. From the head, a droplet with volume of about 100 pL is ejected from an opening of ϕ50 μm and travels at a velocity v of 2–3 m/s. The size of the droplets on the surface is about 110–130 μm. In the fabrication of all the films we set the substrate temperature at 35 °C. It takes about 10 s for the CT complex to form, during which time a gradual colour change from green to dark brown occurs. It then takes an additional 10 s before the films become more transparent as the DMSO solvent evaporates. We estimated the film thickness by using a stylus profiler. The film conductivity was estimated for rectangular patterned films by two probe method using the measured thickness values (see Figure 1).

We found that adding a small amount of acetylcellulose (AC, average molecular weight 40,000) to the donor and acceptor inks was effective in giving uniform patterned films more reproducibly. We used the inks containing 30 % AC relative to the weight of donor or acceptor materials for all the films and devices. The conductivity is not reduced by the presence of the amount of AC additives. As an example of donor (or acceptor) ink formation, 20 mg of TTF (or TCNQ) and 6 mg of AC were dissolved in 2 mL of DMSO using an ultrasonic bath for about 1 h, to give a 50 mM solution of TTF (or TCNQ), with 30 weight percent of AC additive relative to the weight of TTF (or TCNQ). Addition of the amount of AC increases the viscosity of DMSO solution from 2.1 to 3.7 mPa s. We believe that the

