Organic Electronics 58 (2018) 231–237

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Printing technology based on isotropic liquid phase of naphthalene diimide derivatives for n-type organic transistors

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ARTICLE INFO

Keywords:
Organic thin-film transistor
n-type
Naphthalene diimide
Wet process
Melting point

ABSTRACT

Solution processes are well suited for large-scale production of thin films of organic active layers in transistors. However, environmentally hazardous chlorine-based solvents are required for conventional solution processes. Here we introduced a new wet-process approach, without the use of toxic solvents, for creating isotropic phases of several naphthalene tetracarboxylic acid diimide derivatives substituted at the N and N′ positions with long alkyl chains of varying lengths (NTCDI-C*n*). Thin films of NTCDI-C*n* were prepared by this process, the dependence of the device performance on the thickness of the thin films and the length of the NTCDI-C*n* alkyl chains was investigated, and the process was optimized. The devices of NTCDI-C*n* exhibited a relatively high electron mobility (~0.1 cm^2/V), and a maximum electron mobility of 0.38 cm^2/V was obtained from the 50-nm-thick NTCDI-C13 TFT.

1. Introduction

Organic thin film transistors (OTFTs) have attracted considerable attention owing to their potential applications in the fabrication of next generation electronic devices such as flexible displays, radio frequency identifier (RFID) tags, and sensor networks. The performance of OTFTs has been improved greatly over the past few decades [1–3]. In general, two main fabrication methods (namely, thermal evaporation and solution processing) have been used to produce thin films of organic semiconductors (OSCs) as active layers for OTFTs. It has been reported that these material systems, generated through either fabrication method, can outperform amorphous silicon-based transistors [4–6]. However, demand for low cost and easy processing has led to the manufacture of OTFTs by solution processing. These devices tend to be inferior to their thermally evaporated counterparts, in terms of performance. In addition, solution processing requires environmentally hazardous chlorine-based organic solvents such as chloroform and dichlorobenzene, which are used to dissolve and deposit organic semiconductors. The development of a process to solve these problems is necessary for commercialization. For example, Sakai et al. have recently reported printing processes [7–10] and Matsushima et al., on the other hand, have reported a process with no vacuum-and-solvent [11].

Another approach involves a liquid formula-suspension, in which OSC small particles are dispersed in a liquid medium that can be regarded as an alternative to OSC solutions used for wet processes [12,13]. OSC suspensions do not require OSCs to be soluble in the dispersion media, and environmentally friendly organic solvents, including water, can be used. We have previously reported a preparation of a perylene tetracarboxylic diimide (PTCDI) small particle colloidal suspension as an alternative to OSC solutions. However, the performance of OTFTs prepared from suspensions by spin coating tends to be inferior to that of devices prepared from solutions by spin coating. This is because suspensions form thin films with many grain boundaries, which can adversely affect transport of the charge carriers [12]. On the other hand, when it comes to other classes of electric and electronic materials except for OSCs, there are, in fact, excellent reports about formation of conductive and/or semiconductive thin-films or layers based on particles such as metals and metal oxides [14–16].

We demonstrate a new wet process for preparing thin-films of OSCs based on OSC suspensions, which is named a transfer-printing process. In this process, thin films consisting of OSC small particles, prepared from a suspension, are annealed at a temperature higher than their melting point, between the substrate and a plastic film with a solvent repellent finish. During annealing, the OSC solid melts and flows before crystallizing on cooling. The number of OSC small particles should decrease, resulting in fewer grain boundaries in the OSC thin-films. Thus, this treatment can improve the performance of OTFTs.

The key point for this process is the melting points of the OSCs. In

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https://doi.org/10.1016/j.orgel.2018.04.004
Received 17 January 2018; Received in revised form 14 March 2018; Accepted 2 April 2018
Available online 10 April 2018
1566-1199/

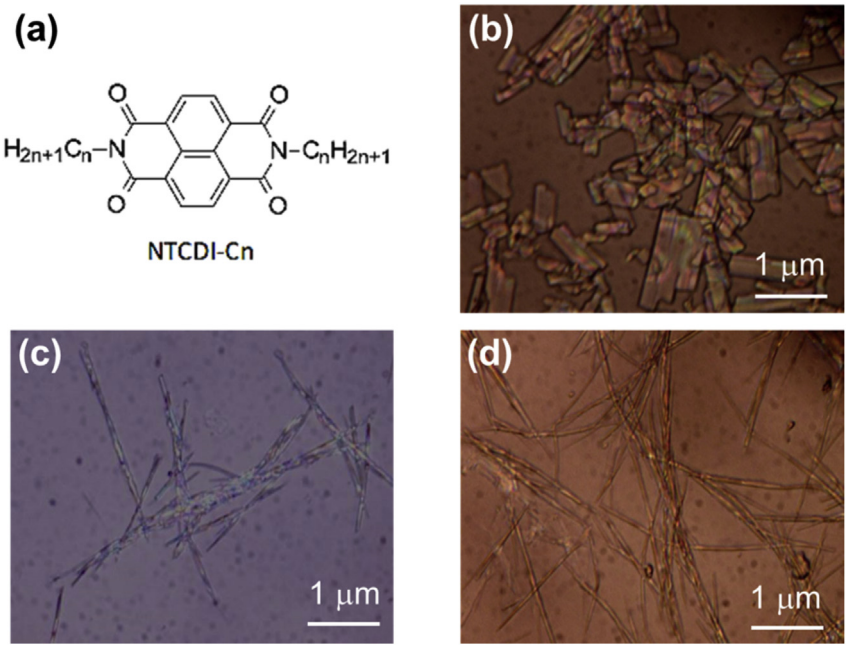

Fig. 1. (a) Chemical structure of the organic semiconductors NTCDI-C*n* and microscope images of the crystals in NTCDI-C*n* suspensions prepared on a glass plate; NTCDI-C8 (b), -C13 (c), and -C15 (d).

Table 1
Phase transition behavior of each NTCDI-C*n* measured by using differential scanning calorimetry (DSC). K and LC represent crystalline and liquid crystalline states, respectively.

NTCDI	Transition Temperature (°C)		
	K-K	K-LC	LC-IL
C8	–	171.1	185.1
C13	109.2	143.6	162.3
C15	114.2	139.6	156.2

this study, we used naphthalene tetracarboxylic diimides with long alkyl chains at the *N,N′* positions (NTCDI-C*n*, see Fig. 1), which show a relatively high field-effect electron mobility ($> 0.1\ cm^2\ V^{-1}\ s^{-1}$) according to our previous studies [17,18]. NTCDI-C*n* becomes an isotropic liquid (IL) at relatively low temperatures of approximately 150–180 °C, as shown in Table 1. Although NTCDI-C*n* is inferior to PTCDI-C*n* in terms of electron affinity and extension of the π-electron system [19], NTCDI-C*n* is more favorable in terms of processing owing to the formation of their IL phases at fairly low temperatures. We will clearly show that NTCDI-C*n* TFTs prepared by a transfer-printing process exhibit comparable performance to those of devices prepared by thermal evaporation and spin-coating of NTCDI-C*n* thin-films. In addition, we report the thickness dependence of thin films of NTCDI-C13 on the performance of OTFTs and the effects of the length of the alkyl chains of NTCDI-C*n*.

2. Methods

2.1. Organic semiconductor suspension

NTCDI-C*n* derivatives were synthesized from naphthalene-1,4,5,8-tetracarboxylic acid dianhydride and the corresponding alkylamine according to literature procedures [20]. NTCDI-C*n* suspensions were prepared through the so-called re-precipitation method as follows. First, a 0.1 wt% chloroform solution of NTCDI-C*n* was prepared and then was injected into 2-propanol (IPA) under vigorous stirring. The injection rate was 100 μL/min controlled by a micro syringe pump. NTCDI-C*n* suspensions were finally prepared after concentration to 0.1 wt% and removal of the remaining chloroform from the suspension under vacuum, as shown in Fig. 1(a). Fig. 1(b), (c) and (d) show granules of NTCDI-C8, 13, 15 in their suspensions after drying on a slide glass. The granules were needle-like crystals, approximately 3 μm in length and 100 nm in width.

2.2. Transfer-printing process

Fig. 2 shows the process flow diagram. A 75-μm-thick polyimide (PI) film, obtained from UBE INDUSTRIES, LTD. (UPILEX®-75 S), was treated with a solvent repellent reagent following a previously reported process. A 0.5-wt% 1-butanol solution of *N*-phenyl-3-aminopropyltrimethoxysilane was spin-coated on a PI film at 2000 rpm for 45 s and then annealed at 90 °C for 5 min on a hot plate. CYTOP solution (purchased from AGC) as a solvent repellent reagent was spin-coated at 5000 rpm for 60 s onto the film and annealed at 180 °C for 20 min in an oven. The water contact angle on the surface was 114.4°. Hereafter, the treated PI films are denoted as transfer-printing films. A 10–150 μL portion of the suspension was softly dropped onto the film, and then the droplet was carefully dried on a cold metal block to remove IPA. The film was turned upside down and placed on a Si wafer with a 200-nm-thick SiO_2 layer, and then an arbitrary load was applied to the film to hold the film on the wafer. The setup was annealed above the melting point of each NTCDI-C*n* for 1–2 h in a vacuum oven, and then cooled down slowly. The annealing temperature was measured with a thermocouple attached to the surface of another Si wafer placed right alongside the transfer-printing set. The averaged maximum temperature in the annealing processes for NTCDI-C13 was 173 ± 1.8 °C. In the case where the maximum annealing temperature was below the melting point, the solid did not melt and flow under the transfer-printing film. An OSC film was left on the Si wafer after peeling off the transfer-printing film [Fig. 3(a)].

2.3. Characterization of the transfer-printed film

The resulting transfer-printed films were characterized with a Bruker scanning probe microscope (Dimension ICON PTX) and Rigaku rotaflex X-ray diffractometer with Cu-Kα radiation (154 pm). The