Organic Electronics 14 (2013) 1656–1662

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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

High-speed organic single-crystal transistors gated with short-channel air gaps: Efficient hole and electron injection in organic semiconductor crystals

Mayumi Uno [a,b,*], Takafumi Uemura [b], Yusuke Kanaoka [a], Zhihua Chen [c], Antonio Facchetti [c], Jun Takeya [b]

[a] Technology Research Institute of Osaka, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan
[b] ISIR, Osaka University 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
[c] Polyera Corporation, 8045 Lamon Avenue, Skokie, IL 60077, USA

ARTICLE INFO

Article history:
Received 24 January 2013
Received in revised form 28 February 2013
Accepted 3 March 2013
Available online 13 April 2013

Keywords:
Organic transistor
Organic semiconductor
Single crystal
High speed

ABSTRACT

Short-channel, high-mobility organic filed-effect transistors (OFETs) are developed based on single crystals gated with short-channel air gaps. The high hole mobility of 10 cm^2/Vs for rubrene, and high electron mobility of 4 cm^2/Vs for PDIF-CN_2 crystals are demonstrated even with a short channel length of 6 μm. Such performance is due to low contact resistance in these devices estimated to be as low as ~0.5 kΩ cm at gate voltage of −4 V for rubrene. With the benefit of the short channel length of 4.5 μm in a new device architecture with less parasitic capacitance, the cutoff frequency of the rubrene air–gap device was estimated to be as high as 25 MHz for drain voltage of −15 V, which is the fastest reported for p-type OFETs, operating in ambient conditions.

1. Introduction

Due to the recent development of high-mobility organic semiconductors and new processing techniques, organic field-effect transistors (OFETs) may enable driver circuits for such as flexible displays, flexible radio frequency identification (RF-ID) tags, and light-weight and wearable electronics [1–3]. However, present high-mobility (>10 cm^2/Vs) OFETs, based on either single-crystal or single-crystal-like semiconductors, were demonstrated only for long-channel lengths ($L \sim 100$ μm) devices [4–7], preventing high-speed on–off switching. Since the maximum circuit operating frequency is proportional to the transconductance g_m and inversely proportional to L^2, it is essential to realize OFETs having *both* a high-mobility semiconductor and a short channel length. Thus for short-channel devices, it is crucial to reduce the parasitic contact resistance (typically from a few kΩ cm to MΩ cm) [8–10] to values comparable to, or lower than, the channel resistance.

Studies addressing the contact resistance have been carried out for OFETs based on polycrystalline films both in top-contact (TC) and bottom-contact (BC) configurations [8–16], and it was found that lower contact resistance is typical for TC-FETs [8]. However, significant drawbacks for TC-FETs are that the current has to travel through a resistive path under the source and drain electrodes before reaching the channel region [9] and semiconductor decomposition under the contacts can occur during thermal/sputtering electrode deposition [16]. Moreover, sub-10 μm channels are difficult to fabricate, unless using costly and sophisticated orthogonal photolithography based on fluorinated photoresists [17]. In contrast, conventional photolithographic processes can be used for bottom-contact device fabrication. However, a major concern for BC-FETs having a polycrystalline semiconductor film relates to the molecular disorder occurring in the vicinity of the metal electrodes [8,11]. The scale of the disordered area typically extends several micrometers, resulting in lower-mobility

* Corresponding author at: Technology Research Institute of Osaka, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan. Tel.: +81 725 51 2661.
E-mail address: uno@tri-osaka.jp (M. Uno).

1566-1199/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2013.03.009

regions dominating the device performance. To overcome this problem, electrode surface modifications (e.g. Au) by thiol-based self-assembled monolayers [12,13] or UV/ozone treatment [14] are effective to reduce the contact resistance, however, these devices suffer of irreproducibility and poor long-term reliability due to chemical instability of most Au-thiolate SAMs [12], and these methods are not universal since it is useful for specific combinations of electrodes and a given semiconductor.

Single-crystal OFETs (SC-OFETs) have enabled the highest hole and electron mobility both for vapor-grown crystals [4,5,18] and for recently developed solution-crystallized organic semiconductors [6,7] with long-channel-lengths devices. Such SC-OFETs will play a key role in organic circuits because of not only their exceptional charge carrier mobility, but also negligible hysteresis and small subthreshold swing. These features originate from the inherently small number of charge-trapping states due to their substantial molecular order. In this report, we fabricated SC-OFETs with 'micro' air–gap architectures to minimize the effect of the interfacial molecular disorder on the contact resistance, thus combining the high mobility of single crystals and an ideal metal-to-semiconductor contacts. Free-space gap structures were first introduced by Menard et al. [4], to examine the fundamental charge transport property in organic semiconductor crystals. For that purpose, long channel lengths (L = ~1.3 mm) were adopted to minimize the effect of the contact resistance. On the other hand, in this study, we purposely down-scaled the transistor dimension to understand the contact resistance and to examine intrinsic high-frequency carrier dynamics in organic semiconductors. The result is that we achieved rubrene SC-OFETs having the highest cut-off frequency (~25 MHz) in air to date, which was attributed to both the absence of molecular disorder in the vicinity of the source electrode enhancing carrier injection and to the minimized parasitic gate-source/drain electrodes capacitance.

2. Short-channel, single-crystal OFETs gated with air gaps on Si substrates

2.1. Fabrication of short-channel air–gap structures

Fig. 1a shows a cross-section of the 'micro' air–gap SC-OFET fabricated on a Si substrate having L from 6 μm to 50 μm. These air–gap structures were fabricated by partially dry-etching a Si substrate followed by surface oxidation. Si substrates were vertically etched with mixture gases of SF_6 and CHF_3 in portions of 1:1 with the gas pressure of 33 Pa and etching power of 20 W per 707 cm^2 area, using reactive ion etching machine RIE-10N (SAMCO INC.). The height of the structures was set to be 0.6 μm. After thermal oxidization of silicon to the thickness of 200 nm, gold films were vacuum-deposited to the thickness of 13 nm from strictly normal directions to the substrates, forming gate, drain, and source electrodes at one time. Thin platelets of either rubrene (for p-type) or fluorocarbon-substituted dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDIF-CN_2) [18–20] (for n-type) single crystals were grown by physical-vapor-transport, and placed on the source and drain electrodes via a natural electrostatic force [5]. As the result, an air gate insulator forms in the gap space between the organic single crystal and the gate electrode. Rubrene materials were purchased from Aldrich Co. and PDIF-CN_2 were synthesized at Polyera Co. The sublimation was repeated at least twice to purify the crystals for the both materials. Rubrene crystals were laminated in ambient conditions and PDIF-CN_2 in anaerobic conditions.

Fig. 1b shows a top-view optical micrograph of the rubrene air–gap SC-OFETs with L = 6, 9, and 20 μm, based on an identical crystal. The gap height of 0.6 μm is also common to the three devices. In Fig. 1c, atomic-force-microscope (AFM) shows that the surface of our single crystals is extremely smooth, where molecularly flat and defect-free regions extend from the contacts to the entire channel

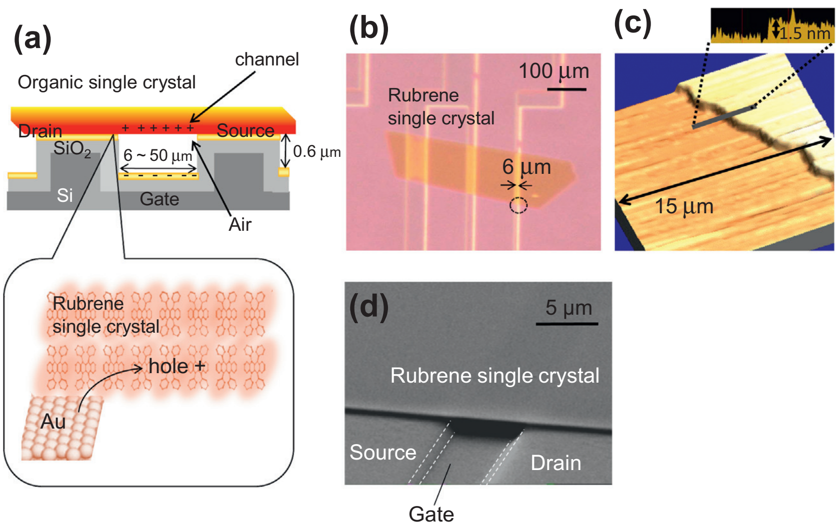

Fig. 1. (a) A cross-sectional illustration of the air–gap SC-OFETs. The lower panel is a conceptual figure to describe carrier injection from a gold electrode to a rubrene single crystal with an ideal molecular alignment. (b) Optical microscopic image of rubrene air–gap devices with different channel lengths. (c) AFM image of the surface of a rubrene single crystal, showing a molecularly-flat surface. (d) SEM image of an air–gap structure at the position shown in the dotted circle in Fig. 1b. The white dotted lines are for eye guide.