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Ambipolar charge transport of diketopyrrolepyrrole-silole-based copolymers and effect of side chain engineering: Compact model parameter extraction strategy for high-voltage logic applications

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ABSTRACT

The copolymers P24DPP-silole and P29DPP-silole, each composed of diketopyrrolopyrrole (DPP) and silole derivatives, were synthesized using a Stille coupling reaction, and their electrical performances in organic field-effect transistors (OFETs) and circuits were investigated. While both the as-spun OFETs exhibited quite low field-effect hole mobility values, the OFETs subjected to thermal annealing at 150 °C exhibited typical ambipolar transport characteristics with average hole and electron mobility values of 1×10^{-1} $cm^2/(V\,s)$ and 2×10^{-3} $cm^2/(V\,s)$. Because the compact model was necessary to perform circuit design with the synthesized OFETs, a strategy for extracting compact model parameters was proposed for high-voltage logic circuit applications by using the industry standard compact Berkeley short-channel IGFET model (BSIM).

1. Introduction

The design and realization of new π-conjugated polymeric semiconductors for organic field-effect transistors (OFETs) has for the past decade been a topic of great research interest [1,2]. OFETs based on polymeric semiconductors have attracted considerable attention due to their potential utility in low-cost, solution-processable, and flexible/wearable electronic devices that could be used as potential alternatives to conventional silicon-based electronic devices [3,4]. To date, many types of OFETs based on polymeric semiconductors have been developed and described. Based on the main charge carriers, polymeric semiconductors can be classified as p-type, n-type, and ambipolar semiconductors, which are able to transport holes, electrons, and both holes and electrons, respectively [5]. The type of organic semiconductor used in an OFET device is primarily determined by the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the organic semiconductor molecule with respect to the work function of the contact electrode material [6].

Research efforts toward developing high-performance OFETs have focused on novel strategies for designing p-type materials [7,8]. Nevertheless, an increasing amount of attention has recently been dedicated to investigating n-type materials as well [9,10]. Although various unipolar semiconductors with high mobilities have been reported, the development of ambipolar semiconductors (p-type and n-type) suitable for use in components in complementary logic circuits has been limited. Recent studies on ambipolar semiconductors have actively investigated the use of chemical modifications to tune both the HOMO and LUMO energy levels for the purpose of achieving efficient injection of holes and electrons [11–13]. Many research groups have devoted significant attention to ambipolar semiconductors in OFETs for enhancing their electrical performance, stability and reliability

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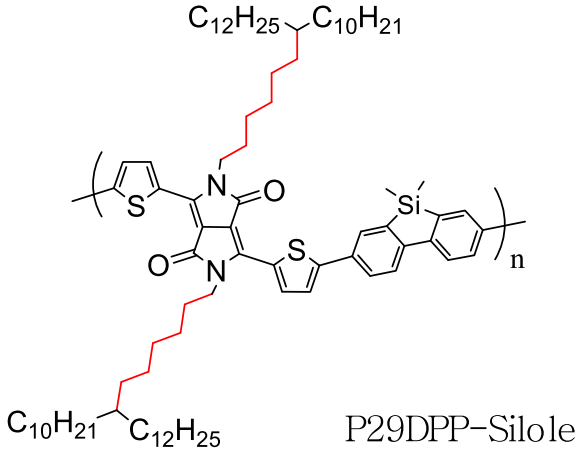

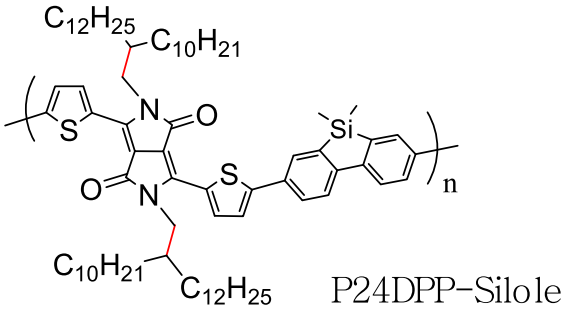

Fig. 1. Chemical structures of P29DPP-silole and P24DPP-silole polymers.

[14–17].

In the present study, we report the electrical characterization and compact model extraction results for a numerical circuit simulation of poly[2,5-bis(2-decyltetradecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione-2,7-(9,9-dimethyldibenzosilole)] and poly[2,5-bis(7-decylnonadecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione)-2,7-(9,9-dimethyldibenzosilole)), abbreviated as P24DPP-silole and P29DPP-silole, which are composed of diketopyrrolopyrrole moiety(DPP) and silole derivatives (Fig. 1). The combination of DPP and fused aromatic rings in copolymer synthesis have been previously shown to have proper π-π interchain stacking using [18]. Our group recently reported that DPP-based copolymers could exhibit fairly high hole field-effect mobility (μ_{FET}) values [8,19,20].

In a previous study, we found that substituting sulfur atoms in the thiophene rings of the DPP copolymers with selenium atoms and changing the branching position of the alkyl side chain influenced the order of the molecular packing and the field-effect mobility [20]. Siloles have also attracted attention as semiconducting blocks for polymeric semiconductors since they may exhibit high electron mobility levels. The silole group in the polymer backbone causes the σ*-orbital of the silicon-carbon bond to interact effectively with the π*-orbital of the butadiene fragment, leading to a stable (or lower) LUMO for the polymers [21]. To investigate the properties of OFETs composed of P24DPP-silole and P29DPP-silole, specifically to study the morphological and microstructural properties of their films, we performed atomic force microscopy (AFM) and X-ray diffraction (XRD) experiments. In addition, to observe the high-voltage logic circuit operation, electrical behaviors of OFETs were modeled by using BSIM4 which is a widely used standard compact model in the industry [22].

2. Experiments

2.1. Materials

P24DPP-silole and P29DPP-silole were prepared by using the previously reported method [23]. The number average molecular weights and polydispersity indexes (PDIs) of the polymers were measured by carrying out gel permeation chromatography (GPC) with a polystyrene standard calibration. The number average molecular weight and PDI were determined to be, respectively, 22 kg/mol and 2.84 for 24-DPP-silole, and 19.8 kg/mol and 3.11 for 29-DPP-silole.

2.2. Morphological characterization

XRD experiments were performed using X-rays with an energy level of 11.57 keV at the 5A beamline at the Pohang Accelerator Laboratory (PAL), Pohang, Korea. The measurement angle was gradually increased from 1° to 18° in 0.05° steps in the out-of-plane direction and from 1° to 15° in 0.05° steps in an in-plane direction. AFM experiments were conducted using a Multimode Illa (Veeco Inc.) operating in tapping mode with a silicon cantilever. The thin-film samples used in the XRD and AFM studies were fabricated by spin-coating at 2000 rpm with the 0.2% chloroform solution on an octadecyltrichlorosilane (ODTS)-modified silicon wafer to mimic the device fabrication process, followed by drying under vacuum at room temperature. After film deposition, the samples were annealed at 150 °C to observe the effect of thermal annealing. The thicknesses of semiconducting films were measured by ellipsometer (J.A. Woollam Co. Inc.)

2.3. Device fabrication and measurements

To fabricate OFETs based on P29DPP-silole and P24DPP-silole, we used heavily N-doped silicon with a 300-nm-thick thermally grown SiO_2 as a dielectric layer. The capacitance of the dielectric layer was 10.5 nFcm^{-2}. OFET properties of the P24DPP-silole and P29DPP-silole were characterized in a bottom gate/top contact architecture with gold source/drain electrodes (with the channel region having a length of 100 μm, and width of 1500 μm). Before modifying the silicon oxide surface with ODTS, the surface of silicon oxide was cleaned with a piranha solution [H_2O_2 (40 mL)/concentrated H_2SO_4 (60 mL)] for 20 min at 280 °C, rinsed with distilled water several times, and treated with ozone for 15 min. P29DPP-silole and P24DPP-silole copolymers constructed onto each chemically modified SiO_2 surface were spin-coated at 2000 rpm from 0.2 wt% chloroform. The OFET devices were annealed at 150 °C for 10 min under a nitrogen atmosphere. OFET device measurements were taken in an N_2-purged glove box (H_2O, O_2 < 0.1 ppm) using both Keithley 2400 and 236 source/measure units. The μ_{FET} values were extracted in the saturation regime from the slope of the source-drain current.

2.4. Computational simulations

In order to apply synthesized OFET to integrated circuits, it is essential to provide a design environment using EDA (Electronic Design Automation) tool. To do this, a compact model capable of describing