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Flexible organic phototransistors based on a combination of printing methods

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ABSTRACT

Highly photosensitive organic phototransistors (OPTs) are successfully demonstrated on a flexible substrate using all-solution process as well as a combination of printing methods which consist of roll-to-plate reverse offset printing (ROP), inkjet printing and bar coating. Excellent electrical switching characteristics are obtained from heterogeneous interfacial properties of the reverse-offset-printed silver nanoparticle electrode and the inkjet-printed *p*-channel polymeric semiconductor. In particular, the OPTs exhibit remarkably photosensitivity with a photo-to-dark current ratio exceeding 5 orders. This optoelectronic properties of the combinational printed OPTs are theoretically and experimentally studied, and found the comparable tendency. In addition, excellent mechanical stability is observed with up to 0.5% of strain applied to the OPTs. Hence, by manufactured with a combination of various graphic art printing methods such as roll-to-plate ROP, inkjet printing, and bar coating, these devices are very promising candidates for large-area and low-cost printed and flexible optoelectronics applications.

1. Introduction

Recently, organic photo detectors based on π-conjugated molecules have remarkably been attracted as devices for optical communications, digital imaging, and sensing [1]. The optoelectronic properties (i.e., charge generation, transport, and recombination) of organic semiconductors can be relatively easily tunable by controlling their molecular structures; these semiconductors generally exhibit excellent photocurrent generation efficiency [2,3]. The spectral sensitivity of the organic active materials can also be modified to either be panchromatic or selectively tuned to a specific wavelength from ultraviolet to near infrared (NIR) regions [3]. Moreover, the low-temperature and solution processability of the functional organic materials as well as soft mechanical properties allow for their use in a variety of innovative light-signal detection systems such as large-area imagers and scanners, NIR or X-ray detection in bio-medical applications, short-range plastic optical-fiber-based transceivers, position-sensitive detectors, and integrated sensoristics for Lab-on-a-chip [4].

Organic phototransistors (OPTs) are a type of photo detector device in which the incident light signal can modulate the charge-carrier density in the active channel of organic field-effect transistors (OFETs), thereby changing

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the channel conductance. Compared to conventional photodiodes, the OPTs are able to detect the light signal more sensitively without serious problems such as noise increment, and they are easily interpretable into electronic circuitry because of their complementary metal oxide semiconductor (CMOS) like configuration. To this end, a number of π-conjugated organic molecules, including vacuum-deposited or solution-processed small molecular semiconductors and polymers, are widely applied [4–6].

Graphic art printing (GAP) methods, such as screen [7], bar coating [8], inkjet [9], flexographic [10], gravure [11], offset [12], and spray [13], are more simply able to form a patterned layer compared with conventional photolithography and lift-off processes. Organic optoelectronic devices, including OPTs manufactured by GAPs, have attracted significant interest because of their potential to set a new paradigm in the fabrication process of low-cost, large-area, and flexible devices: displays [14], photovoltaics [15], flash memories [16], and radio frequency identification tags [17]. Previous research has focused on conventionally processed optical devices, so there has been a lack of studies on flexible optoelectronics based on the printing techniques. A few of the light-responsive OPTs have been used to partially solution-processed and/or inkjet-printed organic photo-active semiconductor on rigid substrate [18,19].

We reported previously heterogeneous interfacial properties between the reverse-offset-printed silver (Ag) source/drain (S/D) and spin-coated *p*-channel organic semiconductor on glass substrate [20]. Herein, we report optoelectronic properties of highly photosensitive flexible OPTs based on a combination of printing methods. Sequential printing processes of reverse offset printing (ROP) for Ag S/D electrodes, inkjet printing for an active semiconductor layer, bar coating for polymer gate dielectrics, and inkjet-printed conductive polymer for gate electrodes facilitate the fabrication of cost-effective large-area, flexible, organic image sensors and scanners. We examine both theoretically and experimentally the optoelectronic properties of the flexible OPTs manufactured by a combination of printing methods. The mechanical bending properties are also characterized for the flexible devices.

2. Experimental

The Ag S/D electrodes were fabricated by roll-to-plate reverse offset printing (ROP). Ag nanoparticle pastes (Ag content: 39 wt%, viscosity: 1.5 cPs at 0.4 rpm, surface tension: 25.8 mN m^{-1}; ANP Co.) were dispensed under the control of a syringe pump onto the surface of the polydimethylsiloxane (PDMS) blanket roll. The PDMS-covered blanket was rolled over the cliché which is printing plate with intaglio patterns, and then the extra ink was eliminated from the blanket and transferred onto the top of the cliché surface. The remaining Ag paste, which was in the desired pattern on the blanket, was transferred onto plastic or glass substrates. For a cliché with intaglio patterns, a 6-in. Si wafer was patterned by photolithography and a deep reactive ion-etching process. To remove the various additives and residual solvents in the printed Ag paste, the substrates were thermally cured at various temperatures on a hotplate for 20 min in air. The substrates were then cleaned with deionized water, acetone, and isopropyl alcohol for 10 min each, sequentially. The polymer semiconductor poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-(E)-1,2-di(2,2′-bithiophen-5-yl)ethene] (PDPP-DBTE) was synthesized [21], and dissolved in dichlorobenzene to obtain a 6 mg/ml solution. The inkjet-printed PDPP-DBTE films were formed using a 50 μm orifice diameter piezoelectric-type single nozzle (Microfab, Inc.) in air, after which they were thermally annealed at various temperatures for 30 min in an Ar-purged glove box. As a gate dielectric layer, poly(methyl methacrylate) (PMMA) (Sigma Aldrich, MW = 120 k, dielectric constant ε_r = 3.5) was dissolved in n-butyl acetate (nBA) (120 mg ml^{-1}), and the solution was bar-coated (thickness = ~1.2 μm). The film was then baked at 100 °C for 30 min in the same glove box to remove residual solvent. The top-gate/bottom-contact (TG/BC) structure of the OPTs was completed with the formation of the gate electrode using the inkjet printer (UJ200MF, Unijet, Korea) of a conducting polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Clevios PH1000, H.C. Starck). The PEDOT:PSS was thermally annealed on a hotplate at 80 °C for 2 h in the Ar-purged glove box.

3. Results and discussion

The OPTs were fabricated monolithically on a flexible substrate via a combination of various printing processes, as shown in Fig. 1a. At first, S/D electrodes (using Ag nanoparticle paste) were printed by a roll-to-plate reverse offset printing technique, which can easily produce complicated and fine S/D electrode patterns on a scale of approximately 20 μm in line and space. The complicated and fine comb-pattern electrode with short channel length of 20 μm was designated for high integration as well as the high switching property. As the channel length was decreased, mobility was decreased revealing serious contact resistance of short channel OFETs. Polymeric semiconductor, PDPP-DBTE, as a photo-active channel layer was then formed by a drop-on-demand inkjet printing process onto the Ag S/D electrodes [channel width/length (W/L) = 1000 μm/20 μm]. Fig. 1b and c shows the chemical structure of the PDPP-DBTE polymer semiconductor and its inkjet-printed features, respectively [21]. A polymer gate dielectric layer, PMMA, is then deposited by bar coating onto the active layer [8]. As a top-gate electrode, PEDOT:PSS conducting polymer was finally formed by the inkjet printing method, as shown in Fig. 1d. The digital camera image of flexible OPTs (6 × 6 phototransistor array), which was formed on a transparent and colorless polyimide (PI) plastic substrate, is shown in Fig. 1e.

The typical transfer (drain current I_D vs. gate voltage V_G) and output (I_D vs. drain voltage V_D) characteristics of the flexible PDPP-DBTE OFETs fabricated by a combination of printing methods are shown in Fig. 1f and g, respectively. According to the gradual channel approximation and its common equation for FETs in the saturation regime (at