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Organic devices based on pentacene and perylene by the neutral cluster beam deposition method

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In this study, on the basis of *p*-type pentacene and *n*-type *N,N′*-dioctyl-perylene-3,4,9,10-tetracarboxylic acid diimide (PTCDI-C8) organic field-effect transistors (OFETs) and two-input complementary NAND logic gates in the top-contact device configuration were produced and characterized. The organic active layers were deposited on hydroxyl-free polymethylmethacrylate (PMMA)-modified indium tin oxide (ITO) glass gate substrates by the neutral cluster beam deposition (NCBD) method. The morphological and structural properties of the organic semiconducting active layers on the PMMA substrates were examined using atomic force microscopy, X-ray diffraction and contact-angle goniometry. Based on the growth of high-quality, well-packed crystalline films on the PMMA dielectric-modified ITO gate substrates, the *p*- and *n*-type transistors exhibited hole and electron mobilities of 0.247 and $7.23 \times 10^{-2}\,\mathrm{cm^2/Vs}$, respectively, in the air without encapsulation. The trap density and activation energy were also derived from the transport characteristics for the temperature dependence of the mobilities in the temperature range $20-300\,\mathrm{K}$ for the first time. Because of the well balanced *p*- and *n*-type OFETs in the devices, the complementary metal-oxide semiconductor (CMOS) NAND logic circuits exhibited a high voltage gain and a large noise margin with slight hysteresis.

1. Introduction

Organic thin-film semiconductor devices using π-conjugated molecules have been extensively studied owing to their many promising advantages such as low cost, easy fabrication, processing, and mechanical flexibility, as well as new aspects for fundamental studies. The preparation of crystalline organic thin films is one of the essential aspects in manufacturing high-performance organic-based optoelectronic devices. The traditional vapor deposition techniques such as physical vapor deposition and atomic layer deposition have been utilized to produce high-quality organic active layers. Unlike such conventional approaches, however, the less popular neutral cluster beam deposition (NCBD) method used in this study turned out to be simple and promising for producing diverse organic-based thin film devices [1–3]. Cluster beams have been used widely in gas-phase dynamics to understand the effects of intermolecular interactions at the molecular level [4–6]. Neutral cluster beams consisting of weakly bound molecules are produced by evaporated organic molecules undergoing adiabatic expansion in a high vacuum. The collision of unique cluster beams with high translational kinetic energy and directionality with a room temperature substrate induces facile decomposition of the clusters into individual molecules, and the subsequent energetic migration of the molecules leads to the formation of smooth and uniform thin films. In particular, the distinctive advantages of low-substrate-temperature deposition cannot be achieved by traditional vapor deposition techniques.

Organic field-effect transistors (OFETs) have gained significant interest as they are competitive, flexible, economical alternatives to the traditional hydrogenated amorphous silicon transistors [7–11]. For developing more complex organic-based integrated circuits (ICs), simplifying circuit designs and fabrication processing are very important. Complementary metal-oxide semiconductor (CMOS) technology based on integrating both *p*- and *n*-type OFETs on the same substrate is quite attractive, because complementary circuits not only simplify the IC designs but also have desirable characteristics such as high noise immunity and low power dissipation [12]. This is well illustrated by logic gates such as inverters, NAND gates, SRAM cells, and ring oscillators [13–15].

Logic gates are considered as the most basic circuit elements in the CMOS technology and act as key building blocks of logic architectures for manufacturing more complicated organic-based

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ICs [16–18]. Based on the two unipolar OFETs with good balance, high performance in air, ideal power-efficient organic CMOS circuits can be realized. From a practical standpoint, in contrast to a variety of *p*-type devices, most *n*-type OFETs exhibited a lack of air stability and/or low mobility when exposed to the air or moisture [19,20]. To overcome such problems, common SiO_2 gate dielectric layers were modified by hydroxyl-free polymer dielectrics such as polymethylmethacrylate (PMMA) and octadecyltrichlorosilane (OTS) as the gate dielectrics [21–24]. The polymeric materials have attracted extensive attention as preferable gate dielectric materials, because of their ease of processing, flexibility, and hydrophilicity. In particular, the characteristic structures of hydroxyl-free PMMA decrease strong electron traps at the organic semiconductor/dielectric interfacial layer, resulting in better electrical characteristics and operational stability of *n*-type OFETs [25–27].

In this study, we describe OFETs and two-input complementary NAND logic gates deposited on hydroxyl-free PMMA dielectric-modified indium tin oxide (ITO) gate by the NCBD method. Fig. 1 outlines the schematic of the complementary NAND gate in the top-contact configuration with the molecular structures of *p*-type pentacene, *n*-type *N,N′*-dioctyl-perylene-3,4,9,10-tetracarboxylic acid diimide (PTCDI-C8). Herein, the NAND logic gate with the top-contact device configuration is composed of two *p*-channel OFETs in parallel and two *n*-channel OFETs in series. We first focused on the dielectric, morphological, and structural properties of the organic semiconducting active layers deposited on the PMMA substrates. Afterwards, the trap density and activation energy were also derived from the transport characteristics for understanding the temperature dependence of the mobilities in the range of $20-300$ K for the first time. Various device parameters were extracted from the current–voltage (*I*–*V*) characteristics of the OFETs and the voltage transfer characteristics (VTCs) of the CMOS NAND gates. The realization of complementary logic circuits is discussed based on a good balance between the components of *p*- and *n*-type OFETs on the PMMA substrates.

2. Experimental

As the gate electrodes for the transistors and input electrodes for the NAND gates as shown in Fig. 1, the ITO gates were patterned by chemical etching. The electrodes were cleaned to improve the device performance using a series of sequential ultrasonic treatments. Atop the substrates as gate dielectrics, 8 wt% PMMA (Sigma-Aldrich, average molecular weight: 996,000) dissolved in toluene was spin-coated with an average thickness of 5500 Å and then cured for 3 h under vacuum at 400 K.

The pentacene and PTCDI-C8 (Sigma-Aldrich) active layers were deposited onto the dielectric layers using a homemade NCBD system [1], as previously described in detail. Briefly, the apparatus is composed of two graphite crucibles for pentacene and PTCDI-C8, a drift region, and the substrate. Each as-received organic sample was placed inside an enclosed evaporation crucible with a 1.0-mm diameter and 1.0 mm-long nozzle and sublimated by separate resistive heating in the range 500–520 K and 540–570 K for pentacene and PTCDI-C8, respectively. Each organic vapor then underwent adiabatic supersonic expansion into the high-vacuum drift region at a working pressure of $\sim 6.0 \times 10^{-6}$ Torr. Cluster beams were produced at the throat of the nozzle and directly deposited onto the PMMA dielectrics. The *p*-type pentacene was first deposited using a properly shaped shadow mask, and then the *n*-type PTCDI-C8 was deposited through another shadow mask. The optimized thickness and deposition rate of pentacene and PTCDI-C8 were determined to be 600 Å at 0.5–1.5 Å/s and 650 Å at 0.5–2.0 Å/s, respectively. Finally, Au electrodes were deposited on the active layer by the thermal evaporation using properly shaped shadow masks at a rate of 6–8 Å/s.

The morphology, crystallinity, and contact angle of the organic layers grown on the PMMA substrates were examined by atomic force microscopy (AFM: PSI Co.), X-ray diffraction (XRD: Rigaku Co.), and contact-angle goniometry (Kyowa Interface Science Co.), respectively. All the electrical characteristics of the devices in this study were investigated in the air, unlike most of the previous

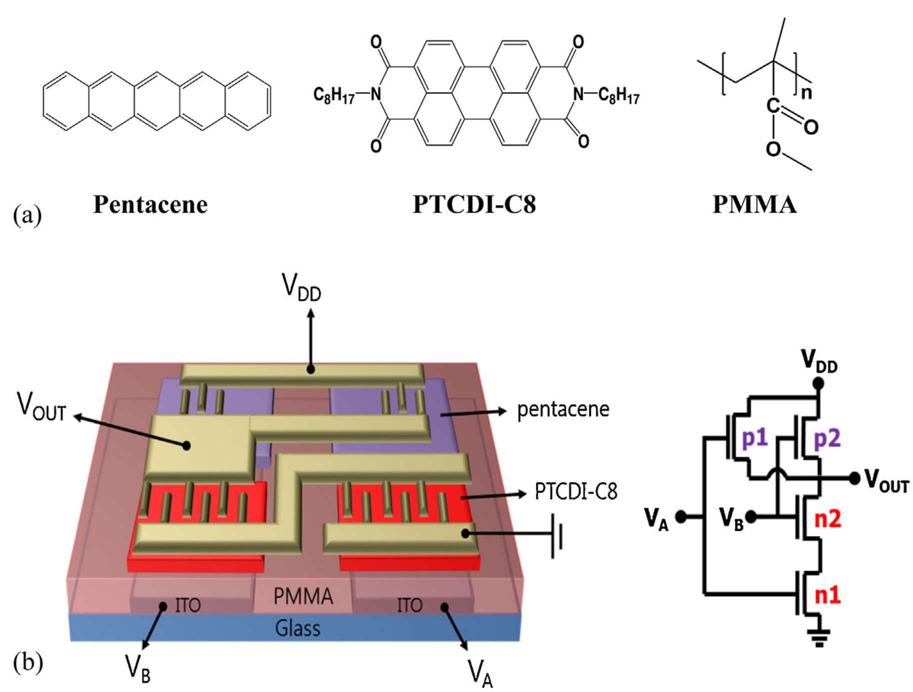

Fig. 1. (a) Molecular structures of pentacene, PTCDI-C8, and PMMA. (b) Schematic and circuit diagram of the complementary NAND gate.