



Letter

High performance n-type organic–inorganic nanohybrid semiconductors for flexible electronic devices

Yerok Park^a, Kyu S. Han^a, Byoung H. Lee^a, Sangho Cho^a, Kwang H. Lee^b, Seongil Im^b, Myung M. Sung^{a,*}

^a Department of Chemistry, Hanyang University, Seoul 133-791, Republic of Korea

^b Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Republic of Korea

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ABSTRACT

We report a high-performance and air-stable flexible and invisible semiconductor which can be substitute for the n-type organic semiconductors. N-type organic–inorganic nanohybrid superlattices were developed for active semiconducting channel layers of thin film transistors at low temperature of 150 °C by using molecular layer deposition with atomic layer deposition. In these nanohybrid superlattices, self-assembled organic layers (SAOLs) offer structural flexibility, whereas ZnO inorganic layers provide the potential for semiconducting properties, and thermal and mechanical stability. The prepared SAOLs–ZnO nanohybrid thin films exhibited good thermal and mechanical stability, good flexibility, transparent in the visible range, and excellent field effect mobility ($>7\text{cm}^2/\text{Vs}$) under low voltage operation (from -1 to 3V). The nanohybrid semiconductor is also compatible with pentacene in p–n junction diodes.

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1. Introduction

Flexible thin film transistors (TFTs) have been extensively studied over the past few decades because they have potential applications in low-cost displays, wearable devices, paper displays, and flexible electronics [1–6]. In particular, flexible semiconducting materials are considered essential elements for development of flexible TFTs. Organic semiconductors such as small organic molecules, conjugated oligomers, and conducting polymers are promising materials in electrical performance comparable to amorphous silicon (ca. $1\text{cm}^2/\text{Vs}$) [7–10]. Most high-performance organic semiconductors are more likely to transport holes as charge carriers rather than electrons, leading to p-type semiconductors. In contrast, development of n-type organic semiconductors falls far behind p-type materials [11–15]. Compared to the field effect mobility ($15\text{cm}^2/\text{Vs}$) of p-type organic semiconductors

such as single crystal rubrene, the highest reported electron mobility of n-type organic semiconductors is $1.83\text{cm}^2/\text{Vs}$, which was obtained by employing thiazole derivatives [16,17]. This inferior electrical performance is caused by the inherent instability of organic anions (i.e. carbanions) which are known to react with oxygen and water in ambient conditions. Those factors also cause degradation of electrical performance in organic semiconductor devices [18–22]. Tuning electron affinity or modifying hydrophobic functionalities of n-type organic semiconductors can prevent the carbanions from reacting with oxygen and water under the normal operating conditions of devices. Despite the efforts of many research groups for over a decade, however, it is still difficult to enhance the field effect mobility of n-type organic semiconductor FETs to levels as high as p-type ones [23–27].

Organic–inorganic nanohybrid thin films provide both the stable and elegant optical, electrical, and magnetic properties of inorganic components and the structural flexibility of organic components [28–30]. Organic–inorganic hybrid superlattices are particularly attractive as flexible

* Corresponding author. Tel.: +82 2 2220 2555; fax: +82 2 2299 0762.
E-mail address: smm@hanyang.ac.kr (M.M. Sung).

semiconducting materials because they allow the combination of the excellent electrical and flexible properties of inorganic and organic components, respectively. Recently, we developed a new vapor phase deposition method of high quality self-assembled organic layers (SAOLs), called molecular layer deposition (MLD), in order to realize precisely controlled organic–inorganic nanohybrid superlattices [31–33]. MLD is a gas phase process analogous to atomic layer deposition (ALD), which is a potentially powerful method for preparing high quality multicomponent superlattices under vacuum conditions. Using the MLD method, high quality organic thin films can be quickly formed with monolayer precision under ALD conditions (temperature, pressure, etc.) [34–37]. The MLD method can be combined with ALD to take advantages of the possibility of obtaining organic–inorganic nanohybrid thin films [38–40].

Herein, we report a high-performance and air-stable flexible semiconductor which can be substituted for n-type organic semiconductors. We combined crystalline inorganic nanolayers with organic layers, leading to organic–inorganic nanohybrid semiconductors. The inorganic layer constitutes an extended framework bonded by powerful covalent or ionic interactions to furnish high carrier mobility and good thermal and mechanical stability. The organic layer adds mechanical flexibility to the inorganic framework. MLD combined with ALD (MLD–ALD) was applied to fabricate a new n-type organic (SAOLs)–inorganic (ZnO) nanohybrid semiconductor on flexible plastic substrates with accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, multilayer processing capability, sharp interfaces, and excellent film qualities at low temperature. The prepared SAOLs–ZnO nanohybrid thin films exhibited good thermal and mechanical stability, good flexibility, and excellent field effect mobility ($>7 \text{ cm}^2/\text{V}\cdot\text{s}$) under low voltage operation (from -1 to 3 V). Furthermore, we also demonstrate the performance of p–n junction diodes prepared with the SAOLs–ZnO nanohybrid superlattices and pentacene.

2. Experimental section

2.1. Preparation of Si substrates

The flexible substrates employed in this study were cut from Glastic[®] polyethersulfone films (i-components Inc.). The polyethersulfone (PES) substrates were cleaned with methanol and de-ionized water, and blow-dried with nitrogen to remove contaminants. The Si substrates were cut from n-type (1 0 0) wafers (LG Siltron) with resistivity in the range of $1\text{--}5 \Omega \text{ cm}$. The Si substrates were initially treated with a chemical cleaning process that involved degreasing, HNO_3 boiling, NH_4OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen to remove contaminants and to grow a thin protective oxide layer on the surface [41]. The ITO-coated glass substrates were cleaned with acetone, methanol, de-ionized water, and blow-dried with nitrogen to remove contaminants.

2.2. Molecular layer deposition with atomic layer deposition (MLD–ALD)

The ZnO thin films were deposited onto the substrates at $150 \text{ }^\circ\text{C}$ using diethylzinc (Zn 52.0 wt.%, Aldrich) and H_2O as ALD precursors. Ar served as a carrier and purging gas at a rate of 50 sccm. The diethylzinc (DEZ) and water were evaporated at $20 \text{ }^\circ\text{C}$. The cycle consisted of a 0.5 s exposure to DEZ, a 5 s Ar purge, a 1 s exposure to water, and a 5 s Ar purge. The vapor pressure of the Ar in the reactor was maintained at 300 mTorr. Alkene-terminated self-assembled organic layers (SAOLs) were formed by exposing the substrates to $[\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{SiCl}_3]$ (Aldrich; 96%) with H_2O vapor at $150 \text{ }^\circ\text{C}$ in the ALD chamber. 7-Octenyltrichlorosilane (7-OTS) and water were evaporated at 100 and $20 \text{ }^\circ\text{C}$, respectively. Exposure times in this process were 5 s for 7-OTS with water vapor and 10 s for the Ar purge. The reactor pressure during the process was about 300 mTorr. The terminal C=C groups of the SAOLs were converted to carboxylic acid groups with ozone treatment in the ALD chamber [31]. The ozone was generated by an ozone-generator and dosed to the 7-OTS coated samples for 30 s at $150 \text{ }^\circ\text{C}$. The C=C groups of the SAOLs reacted with ozone to convert to carboxylic acid groups, which provided highly active adsorption sites for the anchoring of the next monolayer. The SAOLs–ZnO nanohybrid superlattices were grown using the cyclic MLD–ALD process.

2.3. Device fabrication

The 100 nm-thick Cr gate electrode of the TFT was formed on the PES substrates by radio frequency sputter through shadow masks (pressure: $\sim 10^{-8}$ Torr, temperature: room temperature, radio frequency power: 300 W). The 30 nm-thick SAOLs– Al_2O_3 dielectric layer was grown by MLD–ALD at $150 \text{ }^\circ\text{C}$. The SAOLs–ZnO nanohybrid thin films as active channel layers were deposited by MLD–ALD through shadow masks in intimate contact with the substrates. The channel dimension was $50 \mu\text{m}(\text{L}) \times 100 \mu\text{m}(\text{W})$. The 100 nm-thick Al source and drain electrodes were deposited by thermal evaporation through shadow masks under a pressure of $\sim 1 \times 10^{-6}$ Torr. An inverted staggered structure was employed in TFT device fabrication. The 55 nm-thick SAOLs–ZnO nanohybrid n-type semiconducting layer was deposited on the ITO-coated glass by MLD–ALD. The pentacene (Aldrich; 99%) p-type semiconducting layer was fabricated on the SAOLs–ZnO layer through a shadow mask at room temperature by thermal evaporation. The deposition rate was fixed to 1 \AA/s using an effusion cell (ALPHAPLUS Co., LTE-500S) in a vacuum chamber under a pressure of $\sim 1 \times 10^{-7}$ Torr. The thickness of the pentacene films was 50 nm as monitored by a quartz crystal oscillator and confirmed by ellipsometry. The 100 nm-thick Au dot electrodes ($300 \mu\text{m}$ in diameter) were deposited by thermal evaporation in a vacuum chamber under a pressure of $\sim 1 \times 10^{-6}$ Torr.

2.4. Sample characterization

The samples were analyzed by JEOL-2100F transmission electron microscopy. Specimens for cross-sectional TEM

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