



Journal of Information Display

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tjid20

High performance carbon nanotubes thin film transistors by selective ferric chloride doping

Noh-Hwal Park, Eun Sol Shin, Gi-Seong Ryu, Jimin Kwon, Dongseob Ji, Hyunjin Park, Yun Ho Kim & Yong-Young Noh

To cite this article: Noh-Hwal Park, Eun Sol Shin, Gi-Seong Ryu, Jimin Kwon, Dongseob Ji, Hyunjin Park, Yun Ho Kim & Yong-Young Noh (2022): High performance carbon nanotubes thin film transistors by selective ferric chloride doping, Journal of Information Display, DOI: 10.1080/15980316.2022.2141362

To link to this article: https://doi.org/10.1080/15980316.2022.2141362

© 2022 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group on behalf of the Korean Information **Display Society**

+	1

б

View supplementary material

H HH	

Published online: 07 Nov 2022.



Submit your article to this journal 🗗

Article views: 122



View related articles 🖸



View Crossmark data 🗹

Taylor & Francis

OPEN ACCESS Check for updates

High performance carbon nanotubes thin film transistors by selective ferric chloride doping

Noh-Hwal Park^a, Eun Sol Shin^b, Gi-Seong Ryu^b, Jimin Kwon^{b,c}, Dongseob Ji^b, Hyunjin Park^d, Yun Ho Kim^{d,e} and Yong-Young Noh^b

^a 3D Convergence Center, Inha University, Incheon, Republic of Korea; ^bDepartment of Chemical Engineering, Pohang University of Science and Technology, Pohang, Republic of Korea; ^cDepartment of Electrical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, South Korea; ^dAdvanced Materials Division, Korea Research Institute of Chemical Technology (KRICT), Daejeon, Republic of Korea; ^eKRICT School, University of Science and Technology (UST), Daejeon, Republic of Korea;

ABSTRACT

Single wall carbon nanotubes (SWNT) have been a significant research topic as active layers for thin film transistors (TFTs) due to their high charge carrier mobility beyond that of crystalline silicon. In this study, we report an effective approach to achieve a very high field-effect mobility and on/off ratio for solution processed semiconducting SWNT TFTs, by selective doping through contact with a thin ferric chloride (FeCl₃) dopant layer. The semiconducting layer is formed by a double spin coating of the highly purified (> 99%) high pressure carbon mono oxide (HiPCO) SWNT sorted by wrapping of poly (3-dodecylthiophene-2,5-diyl) (P3DDT). In order to achieve effective hole injection from the top Au source electrode without increasing the off-state drain current, less purified (98-99%) SWNTs produced by the plasma discharge process sorted by wrapping of poly (9,9-di-n-dodecylfluorene) (PFDD) are formed on the top of HiPCO film. Significantly improved TFT performance is achieved by the insertion of a few nanometers of a FeCl₃ dopant layer at the semiconductor-contact interface. A significant high hole field-effect of $48.35 \pm 3.11 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (bare: $6.18 \pm 0.87 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) with a reasonable on/off current ratio of 10^5 , and low off current of $\sim 80 \text{ pA}$, are obtained by controlling the concentration of FeCl₃ dopant layer resulting in a hole mobility of $177 \pm 13.2 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$, an on/off ratio of 7.4×10^3 , and off state current of $1.2 \times 10^{-9} \text{ A}$.

1. Introduction

Carbon nanotubes (CNTs) offer considerable potential as semiconducting materials replacing silicon microelectronics, which have flourished according to the scaling law proposed by G. Moore [1–7]. The inherent superior charge carrier mobility of CNTs beyond single crystalline silicon enables hyperscaling of modern digital circuits, which can remarkably increase computing power over the downscaling of circuits. The rapid progress in CNT based high speed thin-film transistors (TFTs) has recently led to the demonstration of high speed analog and digital circuits, and even modern microprocessors [8–11]. However, this has mainly been performed using high cost, high vacuum based deposition techniques of the CNT film, such as chemical vapor deposition, while the solution processed CNT networked films suffer from a relatively low charge carrier mobility and less device uniformity [12]. Considering the above mentioned limitations, solution processed high-performance and large area uniform CNT network based TFTs should be developed [13].

To achieve high performance printed CNT TFTs, the morphology of the semiconducting CNT (semi-CNT) networked film, contact, and semiconductor-dielectric interface should be optimized [14,15]. Basically, random networked semi-CNT films are obtained by the coating of CNT dispersed solution through various solution based deposition methods. The ideal morphology of a semi-CNT networked film to facilitate charge transport is highly dense and aligned CNT networks to the channel direction because the charge transport is primarily through extended π -orbitals on the CNT growth

CONTACT Yong-Young Noh 🖾 yynoh@postech.ac.kr

ISSN (print): 1598-0316; ISSN (online): 2158-1606

Supplemental data for this article can be accessed here. https://doi.org/10.1080/15980316.2022.2141362

© 2022 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group on behalf of the Korean Information Display Society This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ARTICLE HISTORY

Received 30 August 2022 Accepted 17 October 2022

KEYWORDS

Semiconductor carbon nanotube; conjugated polymer; thin film transistors; doping direction [16]. In an aligned CNT networked film, the charge carriers can transport mainly from the source to the drain electrode through a single wall CNT (SWNT) chain effectively, hopping between a few adjunct semi-CNTs [17]. In particular, if the length of a CNT is longer than the channel length of TFTs and a single CNT can directly connect the source and drain, a ballistic charge transport can ideally occur, resulting in extremely high carrier mobility of over 1000 cm²/Vs [18,19]. Many attempts have been made to align CNTs with TFT channel, including Langmuir-Blodgett methods and applying the high electrical field assisted alignment method [20]. However, those methods worked effectively only in a small area with low reproducibility, and it is very difficult to achieve a highly aligned and morphologically uniform CNT film at the wafer scale. Thus, a more realistic alternative is currently implemented by CNT TFTs through randomly networked CNT films that exhibit high performance uniformity with a reasonable field-effect mobility.

In this study, we report a simple and effective method to obtain high performance semi-CNT TFTs by using selective ferric chloride (FeCl₃) doping at the contact. The novel feature of this work is obtaining a high drain current density at the channel of CNT TFTs by injecting large amounts of charge carrier from the top Au source electrode through the insertion of a (1) less purified semiconducting CNT layer and (2) thin FeCl₃ doping layer at the semiconductor-contact interface. The bottom gate/top contacts CNT TFTs with randomly networked semi-CNT films composed of highly purified (>99%) poly (3-dodecylthiophene-2,5-diyl) (P3DDT) wrapped high pressure carbon mono oxide (HiPCO) single well SWNT (P3DDT-HiPCO) at the bottom. Less purified (98-99%) poly (9,9-di-n-dodecylfluorene) (PFDD) wrapped plasma discharge (PD) SWNT (PFDD-PD) at the top exhibited a significantly improved hole fieldeffect of $48.35 \pm 3.11 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, with a reasonably high on/off current ratio of 10^5 (off current of $\sim 80 \text{ pA}$) from the bare devices of 6.18 ± 0.87 cm²V⁻¹s⁻¹ by inserting a 1.5 nm thick FeCl₃ layer at the contact. The hole mobility was dramatically improved, up to $177 \pm 13.2 \text{ cm}^2$ $V^{-1}s^{-1}$, with an on/off ratio of 7.4 × 10³ and an off state current of 1.2×10^{-9} A for the devices with a 2.5 nm thick FeCl₃ dopant layer.

2. Results and discussion

To achieve high-performance printed CNT TFTs, it is essential to sort semi-CNTs with electronic grade purity from bare mixtures of metallic and semi-CNTs on a mass production scale. For this purpose, various separation methods including density gradient ultracentrifugation, DNA based wrapping separation, a series of column

chromatography, and selective wrapping of conjugated polymers have been proposed [21-24]. Among these, sorting semi-CNTs through conjugated polymer wrapping is considered the most effective method owing to several advantages. A highly stable and long shelf-life semi-CNT formulation can be produced at a relatively small energy cost and short processing time because wrapping conjugated polymers can work not only as a sorting medium, but also as a surfactant of the semi-CNT to provide enough solubility in various solvents [25]. In addition, the subsequent purification process for removing excess conjugated polymers and metallic CNT is not complicated. For this study, we obtained highly purified (>99%) semi-CNT by wrapping P3DDT on HiPCO SWNTs, and a less purified (98-99%) PFDD wrapped plasma discharge (PD) SWNTs (PFDD-PD) [26]. The polymer-CNT composite semiconductors were obtained by a selective dispersion method using P3DDT-HiPCO semi-CNT and PFDD-PD semi-CNT, as reported previously [26]. The chemical structure of P3DDT, PFDD, SWNT, and the schematic of the semiconducting-CNT ink fabrication procedure are provided in Figure S1 and Figure 1(a).

Figure 1(b) shows the UV-vis-NIR absorption spectra of P3DDT-HiPCO semi-CNT composite solutions. The absorption peaks appear in the 1000–1500 nm, and 600-800 nm bands corresponding S₁₁ and S₂₂, respectively [27-29]. S_n indicates the electronic transition energy between corresponding levels in the valance and conduction band [30]. Due to overlapping between the absorption of the P3DDT polymer (440-600 nm) and the absorption peak of metallic HiPCO CNTs in UVvis-NIR absorption spectra, the P3DDT-HiPCO semi-CNT composite film was also analyzed using the Raman spectra. Figure 1(c) displays that the radial breathing mode (RBM) of the Raman spectra is excited at 633 nm. The P3DDT-HiPCO semi-CNT composite film has a flat baseline in the metallic region $(180-235 \text{ cm}^{-1})$, which confirms a high-purity semiconducting material [31]. The purity of the P3DDT-HiPCO semi-CNT composite sample was estimated to be >99% based on the absorption spectra, Raman spectra, and an off state current of more than 10 P3DDT-HiPCO TFTs [27,29,32]. Absorption peaks of the PFDD-PD semi-CNT composite solution appeared in the 1400-1900, 700-1100, and 450-550 nm bands for S11, S22, and S33, respectively, as shown in Figure 1(e). The purity of semi-CNT was evaluated from the absorption peak ratio $(\Phi = A_{CNT}/(A_{CNT} + A_B))$, where A_{CNT} is the surrounding area of the M₁₁ and S₂₂ bands surrounded by the linear baseline in the 615–1190 nm region, and A_B is the area covered by the linear baseline over the same region) as proposed in the previous reports [29,33,34]. The



Figure 1. (a) Semiconducting-CNT ink fabrication procedure; (b) absorption spectra, (c) Raman spectra (633 nm excitation), and (d) TEM image of P3DDT-HiPCO and (e) absorption spectra, (f) Raman spectra, (633 nm excitation) and (g) TEM image PFDD-PD.

absorption peak ratio for the PFDD-PD semi-CNT composite solution was 0.396, and consequently the estimated purity of the PFDD-PD semi-CNT composite solution was 98–99% [29]. Figure 1(f) displays a typical RBM of the PFDD-PD semi-CNT composite spectra excited at 633 nm [29]. Figure 1(d) and (g) display the TEM image of the P3DDT-HiPCO semi-CNT, and PFDD-PD semi-CNT composite. The pristine SWNTs were formed as aggregated bundles [35,36], but the polymer-CNT composites were mostly isolated in toluene solution [37].

Bottom gate-top contact (BGTC) TFTs were fabricated using conjugated polymer wrapped semi-CNT composite ink as a channel on a photo-patternable polyimide (PI) film [38]. Heavily doped, thermally grown silicon wafer substrates 300 nm thick were used as the gate electrode. The structure of PI and the schematic structure of the BGTC are provided in Figure 2(a). The CNT film was formed by consecutive spin coating of P3DDT-HiPCO semi-CNT and PFDD-PD semi-CNT. Finally, the FeCl₃ dopant layer and Au electrode was deposited by thermal evaporation through a shadow mask for electrode patterning. Details of fabrication procedures are described in the experiment section. X-ray photoelectron spectroscopy (XPS) was used to confirm formation of the FeCl₃ layer on the semi-CNT composite film after deposition, as shown in Figure 2(b). XPS samples for the FeCl₃ doped semi-CNT composite were prepared using the same conditions for the transistor fabrication



Figure 2. (a) The schematic structure of the bottom-gate/top-contact structure and microscope image of the CNT thin film transistor, (b) X-ray photoelectron spectroscopy (XPS) analysis. All samples were prepared on a Au substrate, and the semi-CNT composite was coated on Au or on the FeCl₃/Au in the same condition used in the transistor fabrication; (c) AFM image of the undoped semi-CNT composite film (5 \times 5 um, z-scale: 10 nm) and (e) the FeCl₃ doped film (5 \times 5 um); (d) SEM image of the undoped semi-CNT composite film and (f) the FeCl₃ doped film (5 \times 5 um)

on Au. The main peaks of XPS spectra for the composite films appeared at 284 eV for C 1s peaks of both, semi-CNT and the conjugated polymers, and at 333, 355, and 641 eV for the Au substrate. The XPS spectra showed Fe 2p3 (715 eV) and Cl 2p (199 eV) peaks corresponding to the stable formation of the FeCl₃ dopant layer on the conjugated polymer wrapped semi-CNTs. Figure 2(c) to (f) show the AFM and SEM image of the undoped semi-CNT composite film (pristine), and the FeCl₃ deposited semi-CNT film. The spin coated binary semi-CNT films showed random networked morphology. The highly dense semi-CNT network film was achieved by two consecutive spin coatings of P3DDT-HiPCO semi-CNTs, and two consecutive spin coatings of PFDD-PD semi-CNTs, respectively. After each spin coating process, the film was annealed at 120°C for 90 sec to remove the residual solvent. The area density of CNT increased by the number of spin coatings, and saturated after four spin coatings (estimated CNT area density: 85%, Figure S2). Interestingly, FeCl₃ deposited films showed that FeCl₃ was well adsorbed on the semi-CNT surfaces. It is expected to effectively induce electron transport from the CNT surface to the FeCl₃ stably adhered to the semi-CNT surface because the efficiency of molecular doping strongly depends on the distance between the host and the dopant molecule [39,40]. We chose the FeCl₃ as a p-type dopant for semi-CNT based composites because it shows efficient p-type doping to various organic semiconductors [41–43]. In addition, FeCl₃ is well known as a catalyst for CNT growth and has been used as an anchoring source to functionalize CNT surfaces with various chemicals [44–47].

Figure 3(a) and (b) show the typical transfer characteristics of the printed semi-CNT TFTs, with P3DDT-HiPCO and PFDD-PD as the active layer. The typical semi-CNT TFTs composed of a PFDD-PD single



Figure 3. (a) Transfer curves of the undoped semi-CNT composite film transistors and (b) FeCl₃ (1.5 nm thickness) doped transistors ($W/L = 1000/100 \mu m$), (c) hole mobility and current on/off ratio of FeCl₃ doped transistors with 5 different FeCl₃ thicknesses and (d) bias stress test of the FeCl₃ doped transistors ($V_d = -5 V$, V_G swept from 15 V to -20 V, 100 cycles)

semiconducting layer, and the SiO₂ gate dielectric showed ambipolar characteristics with slightly better hole transport (Figure S3). The ambipolar characteristics change to unipolar p-type by applying the polyimide gate dielectrics as an effect of the fluorine atom on polyimide [26,48-57]. All transfer curves with the P3DDT-HiPCO and PFDD-PD double layer with polyimide gate dielectrics showed unipolar p-type characteristics. The printed semi-CNT TFTs with the P3DDT-HiPCO and PFDD-PD double layer exhibited a reasonably high hole mobility of $6.18 \pm 0.87 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, an on/off ratio of 10^6 , and an off state current of 1 x 10^{-12} A. The mobility of printed semi-CNT TFTs with double CNT layers is more than an order of magnitude higher than those of TFTs wrapped conjugated polymers (PFDD and P3DDT) as the active layer. This indicates that charge carriers mainly transport through the semi-CNT network instead of the wrapped polymers. The high fieldeffect mobility and current on/off ratio of semi-CNT TFTs is mainly due to the top PFDD-PD double layer for low contact resistance (R_c), and bottom P3DDT-HiPCO

for low off current. The R_c for hole injection decreased to $1.5 \text{ k}\Omega \cdot \text{cm}$ by insertion of a PFDD-PD CNT networked film between the P3DDT-HiPCO and Au electrode. The R_c for a P3DDT-HiPCO single CNT TFT was 20 k $\Omega \cdot \text{cm}$. The less purified (98–99%) semiconducting PFDD-PD CNT networked film contained a small amount of metallic CNTs leading to a high sheet conductivity, and better hole injection. In the bi-layered films, however, the channel is only formed in the highly purified P3DDT-HiPCO semi-CNT, and can maintain a low off current.

Considering the increased field-effect mobility by improving the charge injection properties through the PFDD-PD CNT networked film, we insert a FeCl₃ dopant layer that is a few nanometers thick between the PFDD-PD film and the Au source/drain electrode for a selective contact doping technique. Figure 3(b) shows typical transfer curves of the printed bilayered semi-CNT TFTs with the FeCl₃ dopant. The semi-CNT TFTs with a 1.5 nm thick FeCl₃ layer showed a significantly improved field-effect mobility of $48.35 \pm 3.11 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ (high

uniformity \geq 90.2%, see Figure S4 in supporting information), an on/off ratio of 1×10^5 , and off state current of 8×10^{-11} A. The doping concentration can be controlled by the thickness of the FeCl₃ layer. The basic electrical parameters of semi-CNT TFTs are summarized in Table 1. As the thickness (doping concentration) of the FeCl₃ layer increased, the field-effect mobility and off-state drain current increased (Figure S5). Figure 3(c) shows the field-effect mobility and on/off ratio of semi-CNT TFTs with five different FeCl₃ doping concentrations. The semi-CNT TFTs with a 1 nm thick FeCl₃ layer exhibited a slightly improved hole mobility of 10.8 ± 3.7 cm² V⁻¹s⁻¹, on/off ratio of 4×10^5 , and off state current of 1.7×10^{-12} A. By increasing the thickness of the FeCl₃ layer to 2 nm, a surprisingly high hole mobility of $116 \pm 15.16 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$, on/off ratio of 1×10^5 , and reasonably low off state current of 1.01×10^{-10} A. The 2.5 nm-FeCl₃ doped SWNT transistors exhibit a hole mobility of $177 \pm 13.2 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$, on/off ratio of 7.4×10^3 , and off state current of 1.2×10^{-9} A. To the best of our knowledge, this is one of the highest field effect mobilities and on/off current ratios obtained with printed semi-CNT TFTs reported thus far. Such an impressive high field-effect mobility is attributed to the efficient injection of a large amount of charge carrier from the FeCl₃/Au source electrode by a very low contact resistance ($R_c = 0.17 \,\mathrm{k\Omega \cdot cm}$). As the FeCl₃ thickness increased, the threshold voltage (V_{th}) gradually shifted to a positive value as the carrier density increased, and the TFTs operated in near depletion mode for FeCl₃ thicker than 2.5 nm (see Figure S5). Bias stress stability was checked for the bias stress test of FeCl₃ doped semi-CNT TFTs. The bias stress response of the FeCl₃ device was conducted at $V_d = -5$ V, and V_G ranged from 15 V to -20 V (see Figure 3(d)). After continuous bias stressing, the on and off currents stayed nearly the same with a slight shift in V_{on} (< 1 V).

Table	1.	Electrical	parameters of semi-CNT	TFTs.
			parameters or serie erri	

In order to confirm the availability of FeCl₃ doping on the semi-CNT composite film, the Fermi level (E_F) of the undoped P3DDT-HiPCO, PFDD-PD double layer (pristine), and the FeCl₃ doped film was measured using ultraviolet photoelectron spectroscopy (UPS) (Figure 4(a) and Figure S6). Figure 4(b) shows the related energy level of bare and FeCl3 doped semi-CNT composite. UPS samples were prepared on a Au substrate, the same as the XPS samples. In the UPS spectra, the cut-off binding energy of the FeCl₃ doped semi-CNT film was reduced by 0.23 eV compared to the undoped ones. Thus, the work function of the FeCl₃ doped film increased from 4.22 to 4.45 eV of the bare film. The doped film of E_f is 4.45 eV with respect to E_{vac} [59]. No distinct difference was found in samples with the FeCl₃ film over 1 nm thick. This is direct evidence of FeCl₃ p-doping of the P3DDT-HiPCO and PFDD-PD double layer, because E_F shifted towards the HOMO level due to the increase in the hole concentration. The improved charge injection through the tunneling across the Schottky barrier was achieved by selective FeCl₃ doping at the contact to reduce R_c in printed semi-CNT TFTs [42,60].

3. Conclusion

In conclusion, we reported a solution for processed high mobility and on/off ratio semi-CNT TFTs by improving charge injection properties. Compared to bare semi-CNT TFTs with a P3DDT-HIPCO single semiconducting layer, the field-effect mobility of semi-CNTs was significantly improved over $100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with high on/off current ratio of 10^5 by applying less purified PFDD-PD semi-CNT networked films and patterned FeCl₃ dopant layer at Au contact. We also demonstrated the record high and outstanding performance semi-CNT TFTs of $177 \pm 13.2 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$, on/off ratio of 7.4×10^3 and off state current of 1.2×10^{-9} A device with 2.5 nm thick

	Saturation		Linear			
Structure	μ^{a} (cm $^{2}\mathrm{V}^{-1}\mathrm{s}^{-1}$)	$V_{\rm th}$ (V)	$M (\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s}^{-1})$	Off state current (A)	On/off ratio	<i>R_c</i> (kΩ·cm)
P3DD-HiPCO film [26]	Max 0.2 0.173 + 0.027	-10	Max 0.08 0.045 ± 0.035	2×10^{-12}	$1.4 imes 10^6$	20
PFDD-PD [26]	Max 7.5 6.7 ± 0.8	8	Max 2.3 1.725 + 0.0575	$2.3 imes 10^{-9}$	$\textbf{2.4}\times \textbf{10}^{4}$	1.0
Undoped semi-CNT composite film	Max 7.08 6.18 ± 0.87	4	Max 0.06 0.05 ± 0.0145	1×10^{-12}	$1.2 imes 10^{6}$	1.5
FeCl ₃ doped composite film (1 nm)	Max 14.5 10.8 ± 3.7	10.8	0.12	1.7×10^{-12}	4×10^5	
FeCl ₃ doped composite film (1.5 nm)	Max 51 48.35 ± 3.11	10	$\begin{array}{c}Max0.45\\ 0.4\pm0.0575\end{array}$	8×10^{-11}	$1 imes 10^5$	0.17
FeCl ₃ doped composite film (2 nm)	Max 131 116 ± 15.16	24	1.0	7.4×10^{-11}	$1.6 imes 10^5$	
FeCl ₃ doped composite film (2.5 nm)	Max 190.2 177 + 13.2	36	1.8	$3.19 imes 10^{-10}$	6.2×10^4	

^aMobility (μ) was calculated using the standard formulation in linear and saturation regions (electrical parameters for 8 devices for each condition, $V_d = -0.1$ and -20 V, respectively). Contact resistance (R_c) was evaluated by the Y-function method [58].



Figure 4. (a) Ultraviolet photoelectron spectroscopy (UPS) analysis and (b) related energy level of bare and FeCl₃ doped semi-CNT composite. All samples were prepared on a Au substrate, and the semi-CNT composite was coated on Au or on FeCl₃/Au under the same fabrication conditions. The reference is bare semi-CNT film.

FeCl₃ dopant layer. This selective doping method offers a promising prospect for high-performance printed random networked semi-CNT TFTs and integrated circuits, without complicated, large area, and uneven CNT alignment technology.

3.1. Experiment

3.1.1. Conjugated polymer-carbon nanotube composite

P3DDT (20,000 < $Mn < 50,000 \text{ gmol}^{-1}$, Leika metal) and PFDD (Mw \approx 15,000–200,000, Lumtec). HiPCO SWNTs and PD SWNTs were purchased from Nanointegris Inc. Toluene solutions of P3DDT (2 mg/ml) and PFDD (2 mg/ml) were prepared and heated at 80°C for 2 h for complete dissolution. After cooling, 1 mg of the HiPCO and PD based SWNT powders were added to P3DDT and PFDD solutions, respectively. The solutions were combined in an ultrasonic bath (Branson 5510) for 1 h, and then centrifuged at 85,000 g for 1 h to separate semi-CNT. The supernatant fluid was further centrifuged first at 199,000 g for 1 h, and then ultra-centrifuged at 320,000 g for 12 h, to remove all the residual polymer (Vision scientific Inc VS-65 ultracentrifuge, V1308Ti fixed rotor). The produced pellets were washed 5 times to remove all the polymer and then collected. Finally, these enriched semi-CNTs were re-dispersed in toluene using an ultrasonic bath.

3.1.2. Device fabrication

The substrates were sequentially washed in an ultrasonic bath with deionized water, acetone, and isopropanol for 10 min each. Semi-CNTs were deposited on SiO_2 (60 mg

ml⁻¹ in cyclohexanone) by spin coating at 1000 rpm for 60 s. The spin-coated films were then baked at 90°C for 120s and exposed to 365 nm UV light at a dose of more than $1.5 \text{ J} \text{ cm}^{-2}$ for cross-linking and patterning the semiconducting active layer. The films were subsequently annealed on a hot plate at 90°C for 10 min and 110°C for 30 min. Semi-CNTs were then deposited by spin coating twice at 700 rpm for 60 s, and the resulting films were annealed in a glove box on a hot plate at 120°C for 30 min in N₂ filled glove box. Exposed PI was developed with cyclohexanone, acetone, and isopropyl alcohol for 10 s each, and then annealed on a hot plate at 120°C for 30 min to remove the residual solvents and moisture. The development process removed unnecessary organic-CNT composite films to pattern the semiconducting layer. The FeCl₃ was evaporated through a metal mask source and drain electrodes were deposited on the hybrid films by thermal evaporation under 5.0 \times 10⁻⁶ torr with a 1.0 Å s⁻¹ deposition rate.

3.1.3. Measurement

To quantify the purities of semi-CNT, UV–Vis spectra was measured using a Carry 5000 (Varian Inc.) spectrophotometer. Raman measurements were obtained using a LabRAM HV Evolution (HORIBA), while transmission electron microscopy (TEM) images were obtained using a JEM-2100f (JEOL). Atomic force microscope (AFM) topographic images were obtained using a XE-100 (PSIA) scanning probe microscope. A Keithley 4200 SCS instrument in a nitrogen filled glove box was used to perform electrical measurements. Capacitance–voltage (CV) measurements were performed using a Keithley 4200 connected to an Agilent 4284 LCR meter. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were measured at the Korea Basic Science Institute (KBSI).

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This study was supported by the Ministry of Science & ICT through the NRF grant funded by the Korean government [grant number 2021R1A2C3005401], Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education [grant number 2022R1A6A1A0305170511] and the Korea Basic Science Institute (National research Facilities and Equipment Center) grant funded by the Ministry of Education [grant number 2022R1A6C101B762].

Notes on contributors



Noh-Hwal Park is a research professor at the 3D Convergence Center of Inha University. He received his PhD degree in materials science and engineering from Seoul National University (SNU) in 2018. He worked at POSTECH as a postdoc. His research interests include the field of monolithic 3D integration using novel

materials such as carbon nanotubes, oxide materials, high-k materials, and heterogeneous integration.



Yong-Young Noh is Chair Professor of the Department of Chemical Engineering of Pohang University of Science and Technology (POSTECH). He received his PhD degree in 2005 from GIST and then worked at the Cavendish Laboratory in Cambridge, UK, as a postdoctoral associate. Afterwards, he worked

at ETRI as a senior researcher, as assistant professor at Hanbat National University, and as associate professor at Dongguk University. His research interest is in the field of developing printable semiconductors including organic, carbon nanotubes, perovskite, metal halide and metal oxide for field-effect transistors, photodiodes and light-emitting diodes.



Eun-Sol Shin received a B.S. degree in Bio & Nano Chemistry from Kookmin University (Republic of Korea, 2012) and an M.S. degree in Chemistry from Korea University (Republic of Korea, 2014). She received her Ph.D. degree in Engineering from Dongguk University, Republic of Korea, in August 2018 under the

supervision of Prof. Yong-Young Noh. She is currently a senior researcher at SAMSUNG ELECTRO-MECHANICS CO., LTD.



Gi-Seong Ryu is a postdoc at the Department of Chemical Engineering of Pohang University of Science and Technology (POSTECH). He received his Ph.D. degree in Electronic Engineering from Dong-A University, Republic of Korea, in August 2009 under the supervision of Prof. Chung Kun Song. He worked at Media Device

Lab as a senior researcher. He joined Noh's group in 2013 as a researcher. His research fields include thin film transistor devices, OLED devices, display applications, and gas sensor applications.



Jimin Kwon is an assistant professor at the Department of Electrical Engineering of Ulsan National Institute of Science and Technology (UNIST). He received his PhD degree from the Department of Creative IT Engineering of Pohang University of Science and Technology (POSTECH) in 2018. He worked at POSTECH and at

Stanford University as a postdoc. His research interests include design and fabrication of BEOL-compatible logic and memory devices for monolithic 3D integration using novel materials such as carbon nanotubes, 2D materials, and oxide semiconductors.



Dongseob Ji is currently a Ph.D. student in the Department of Chemical Engineering at Pohang University of Science and Technology (POSTECH) under the supervision of Prof. Yong-Young Noh. He received his B.S. and M.S. degrees in energy and materials engineering from Dongguk University, Korea, in 2016 and

2018, respectively. His research interests include carbon nanotube-based field-effect transistors and solution-processed organic thin film transistors.



Hyunjin Park is a senior researcher at the Chemical Platform Technology Division of the Korea Research Institute of Chemical Technology (KRICT). He received his PhD degree from the Department of Electrical Engineering of Pohang University of Science and Technology (POSTECH) in 2019. He worked at KRICT as a post-

doctoral researcher. His research interests include the development of polymer insulators for flexible and wearable electronic systems based on computational and experimental methods.



Yun Ho Kim has been a principal research scientist at the Advanced Materials Division of the Korea Research Institute of Chemical Technology (KRICT) since 2011. He received his PhD degree in 2010 from KAIST and then worked at the Washington University in Saint Louis, US, as a postdoc. His research interests include

the field of developing high-performance engineering polymer materials for flexible electronics, energy storage devices and functional separators.

References

- W. Gomulya, J. Gao, and M.A. Loi, Eur. Phys. J. B 86, 404 (2013).
- [2] J. Zaumseil, Semicond. Sci. Technol. 30, 074001 (2015).
- [3] G.E. Moore, "Lithography and the future of moore's law," in SPIE's 1995 Symposium on Microlithography. Int. Soc. Optics Photon., 2–17 (1995).
- [4] S. Park, M. Vosguerichian, and Z. Bao, Nanoscale 5, 1727–1752 (2013).
- [5] H. Li, C. Xu, N. Srivastava, and K. Banerjee, IEEE Trans. Electr. Dev. 56, 1799–1821 (2009).
- [6] T. Belin, and F. Epron, Mater. Sci. Eng. B 119, 105–118 (2005).
- [7] Q. Cao, and J.A. Rogers, Adv. Mater. 21, 29–53 (2009).
- [8] M.M. Shulaker, G. Hills, R.S. Park, R.T. Howe, K. Saraswat, H.-S.P. Wong, and S. Mitra, Nature 547, 74–78 (2017).
- [9] M.M. Shulaker, G. Hills, N. Patil, H. Wei, H.-Y. Chen, H.-S.P. Wong, and S. Mitra, Nature 501, 526–530 (2013).
- [10] J. Tang, Q. Cao, G. Tulevski, K.A. Jenkins, L. Nela, D.B. Farmer, and S.-J. Han, Nature Electr. 1, 191–196 (2018).
- [11] D. Zhong, Z. Zhang, L. Ding, J. Han, M. Xiao, J. Si, L. Xu, C. Qiu, and L.-M. Peng, Nature Electr. 1, 40–45 (2018).
- [12] Z. Lin, Y. Huang, and X. Duan, Nature Electr. 2, 378–388 (2019).
- [13] S.-J. Han, J. Tang, B. Kumar, A. Falk, D. Farmer, G. Tulevski, K. Jenkins, A. Afzali, S. Oida, and J. Ott, Nature Nanotechnol. 12, 861 (2017).
- [14] M.Y. Timmermans, D. Estrada, A.G. Nasibulin, J.D. Wood, A. Behnam, D.-M. Sun, Y. Ohno, J.W. Lyding, A. Hassanien, and E. Pop, Nano Res. 5, 307–319 (2012).
- [15] S.-H. Lee, Y. Xu, D. Khim, W.-T. Park, D.-Y. Kim, and Y.-Y. Noh, ACS Appl. Mater. Interf. 8, 32421–32431 (2016).
- [16] S.P. Schießl, X. de Vries, M. Rother, A. Massé, M. Brohmann, P.A. Bobbert, and J. Zaumseil, Phys. Rev. Mater. 1, 046003 (2017).
- [17] Y. Wu, X. Lin, and M. Zhang, J. Nanomater. 2013, 627215 (2013).
- [18] S.J. Kang, C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M.A. Alam, S.V. Rotkin, and J.A. Rogers, Nature Nanotechnol. 2, 230 (2007).
- [19] T. Dürkop, S. Getty, E. Cobas, and M. Fuhrer, Nano Lett.
 4, 35–39 (2004).
- [20] L. Jia, Y. Zhang, J. Li, C. You, and E. Xie, J. Appl. Phys. 104, 074318 (2008).
- [21] M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, Nature Nanotechnol. 1, 60–65 (2006).
- [22] X. Tu, S. Manohar, A. Jagota, and M. Zheng, Nature 460, 250–253 (2009).
- [23] A. Nish, J.-Y. Hwang, J. Doig, and R.J. Nicholas, Nature Nanotechnol. 2, 640 (2007).
- [24] H. Liu, D. Nishide, T. Tanaka, and H. Kataura, Nature Commun. 2, 1–8 (2011).
- [25] M. Rahman, H. Younes, N. Subramanian, and A. Al Ghaferi, J. Nanomater. 2014, 102621 (2014).
- [26] N.-H. Park, S.-H. Lee, S.-H. Jeong, D. Khim, Y.H. Kim, S. Yoo, Y.-Y. Noh, and J.-J. Kim, Semicond. Sci. Technol. 33, 035017 (2018).
- [27] S.-H. Lee, D.-Y. Kim, and Y.-Y. Noh, Appl. Phys. Lett. 111, 123103 (2017).

- [28] V. Derenskyi, W. Gomulya, J.M.S. Rios, M. Fritsch, N. Fröhlich, S. Jung, S. Allard, S.Z. Bisri, P. Gordiichuk, and A. Herrmann, Adv. Mater. 26, 5969–5975 (2014).
- [29] J. Ding, Z. Li, J. Lefebvre, F. Cheng, G. Dubey, S. Zou, P. Finnie, A. Hrdina, L. Scoles, and G.P. Lopinski, Nanoscale 6, 2328–2339 (2014).
- [30] K.D. Sattler, *Handbook of Nanophysics: Nanotubes and Nanowires* (CRC Press, Boca Raton, 2010).
- [31] H.W. Lee, Y. Yoon, S. Park, J.H. Oh, S. Hong, L.S. Liyanage, H. Wang, S. Morishita, N. Patil, and Y.J. Park, Nature Commun. 2, 1545 (2011).
- [32] M.L. Geier, J.J. McMorrow, W. Xu, J. Zhu, C.H. Kim, T.J. Marks, and M.C. Hersam, Nature Nanotechnol. 10, 944–948 (2015).
- [33] T. Lei, X. Chen, G. Pitner, H.-S.P. Wong, and Z. Bao, J. Am. Chem. Soc. 138, 802–805 (2016).
- [34] I. Pochorovski, H. Wang, J.I. Feldblyum, X. Zhang, A.L. Antaris, and Z. Bao, J. Am. Chem. Soc. 137, 4328–4331 (2015).
- [35] S.H. Jeong, K.K. Kim, S.J. Jeong, K.H. An, S.H. Lee, and Y.H. Lee, Synth. Metals 157, 570–574 (2007).
- [36] S. Lyu, B. Liu, S. Lee, C. Park, H. Kang, C. Yang, and C.J. Lee, J. Phys. Chem. B 108, 1613–1616 (2004).
- [37] M. Shtein, I. Pri-Bar, and O. Regev, Analyst 138, 1490–1496 (2013).
- [38] J.-M. Won, H.J. Suk, D. Wee, Y.H. Kim, J.-W. Ka, J. Kim, T. Ahn, M.H. Yi, and K.-S. Jang, Org. Electr. 14, 1777–1786 (2013).
- [39] G.-H. Kim, L. Shao, K. Zhang, and K.P. Pipe, Nature Mater. 12, 719–723 (2013).
- [40] W.S. Jeon, T.J. Park, S.Y. Kim, R. Pode, J. Jang, and J.H. Kwon, Org. Electr. 10, 240–246 (2009).
- [41] H. Isotalo, J. Laakso, P. Kuivalainen, H. Stubb, J.E. Österholm, and P. Yli-Lahti, Phys. Status Solidi 154, 305–313 (1989).
- [42] Y. Chen, I. Shih, and S. Xiao, J. Appl. Phys. 96, 454–458 (2004).
- [43] D. Romero, M. Schaer, L. Zuppiroli, B. Cesar, and B. Francois, Appl. Phys. Lett. 67, 1659–1661 (1995).
- [44] I. Pełech, U. Narkiewicz, D. Moszyński, and R. Pełech, J. Mater. Res. 27, 2368–2374 (2012).
- [45] O.V. Yazyev, and A. Pasquarello, Phys. Rev. Lett. 100, 156102 (2008).
- [46] H. Hou, A.K. Schaper, Z. Jun, F. Weller, and A. Greiner, Chem. Mater. 15, 580–585 (2003).
- [47] M. Khavarian, S.-P. Chai, S.H. Tan, and A.R. Mohamed, Nano 4, 359–366 (2009).
- [48] A. Javey, J. Guo, D.B. Farmer, Q. Wang, D. Wang, R.G. Gordon, M. Lundstrom, and H. Dai, Nano Lett. 4, 447–450 (2004).
- [49] Y. Huang, L. Huo, S. Zhang, X. Guo, C.C. Han, Y. Li, and J. Hou, Chem. Commun. 47, 8904–8906 (2011).
- [50] X. Shao, S. Wang, X. Li, Z. Su, Y. Chen, and Y. Xiao, Dyes Pigments 132, 378–386 (2016).
- [51] Y.-M. Lin, J. Appenzeller, and P. Avouris, Nano Lett. 4, 947–950 (2004).
- [52] V. Derycke, R. Martel, J. Appenzeller, and P. Avouris, Appl. Phys. Lett. 80, 2773–2775 (2002).
- [53] X. Xian, K. Yan, W. Zhou, L. Jiao, Z. Wu, and Z. Liu, Nanotechnology 20, 505204 (2009).
- [54] M.L. Tang, A.D. Reichardt, N. Miyaki, R.M. Stoltenberg, and Z. Bao, J. Am. Chem. Soc. 130, 6064–6065 (2008).

- [55] J. Zaumseil, C.L. Donley, J.S. Kim, R.H. Friend, and H. Sirringhaus, Adv. Mater. 18, 2708–2712 (2006).
- [56] J. Zaumseil, and H. Sirringhaus, Chem. Rev. 107, 1296–1323 (2007).
- [57] B. Sun, W. Hong, H. Aziz, and Y. Li, Polymer Chem. 6, 938–945 (2015).
- [58] G. Ghibaudo, Electr. Lett. 24, 543–545 (1988).
- [59] C.-H.M. Chuang, P.R. Brown, V. Bulović, and M.G. Bawendi, Nature Mater. 13, 796–801 (2014).
- [60] T. Minari, P. Darmawan, C. Liu, Y. Li, Y. Xu, and K. Tsukagoshi, Appl. Phys. Lett. 100, 59 (2012).