# N-Channel Zinc Oxide Nanowire:Perylene Diimide Blend Organic Thin Film Transistors

Shin-Pin Chen, Yan-Sheng Chen, and Gen-Wen Hsieh

*Abstract*— **N-channel solution-processed organic thin film transistors (TFTs) based on a blend network of *N,N'*-bis (*1H,1H*-perfluorobutyl)-1,7-dicyanoperylene-3,4:9,10-tetracarboxylic diimide (PDIF-CN2) and zinc oxide (ZnO) nanowires show remarkable electron field effect mobilities of up to 0.5 cm$^2$/V·s in ambient air, which is about five-fold higher than those based on pristine PDIF-CN2 films. When tested in both bias directions the output and transfer electrical hysteresis of those blend TFTs are negligible. In addition, their low processing temperature and flexible semiconducting layer makes them a highly promising means of realizing high performance, solution-processed n-channel organic TFTs.**

*Index Terms*— **Organic thin film transistors, zinc oxide nanowire:perylene diimide blend, solution process, n-channel.**

## I. INTRODUCTION

LARGE area, flexible electronics appeals to diverse application areas ranging from the biomedical and military, to the consumer sectors. Examples include displays, photovoltaics, detectors, sensor networks and MEMS. Despite ongoing advancements in material performance and functionality and processing technologies, organic-based thin film transistors (TFTs) are somewhat limited in terms of device mobility and lifetime, which hinder their adoption on a wider scale [1]. While a number of promising solution-processed p-channel organic TFTs have been reported [2-5], the present shortage of high performance, air-stable n-channel organic semiconductors poses another challenge for realization of complementary logic circuits. These shortcomings have prompted the pursuit of augmentative material systems in the quest for higher performance transistors.

To tackle this, an alternative means utilizing semiconducting composites as the active channel is now being gradually employed in TFT fabrication. Several works considered carbon nanotubes with different polythiophene hosts for solution-processed p-channel composite transistors have been reported with improved field effect mobility [6-8]. Our recent study considered the feasibility of p-channel composite TFTs by incorporating semiconducting silicon nanowires with polythiophene hosts has further presented enhanced transistor performance [9]. It is suggested that interactions between heterogeneous materials and ambient environment are crucial to transistor performance. However, an equivalent study of solution-processed n-channel composite TFTs with high electron mobility plus acceptable ambient stability is rare [10,11].

Here, we report on the realization of high performance n-channel zinc oxide (ZnO) nanowire:perylene diimide blend organic TFTs fabricated by a simple spin-coating procedure. The employed small-molecule organic host, *N,N'*-bis-(*1H,1H*-perfluorobutyl)-1,7-dicyano-perylene-3,4:9,10-tetracarboxylic diimide (PDIF-CN2), exhibits high electron mobility, air stability and solution processability [12-13]. The one-dimensional ZnO nanostructure owing to unique wide band gap semiconductive, piezoelectric, and biocompatible properties has attracted extensive attentions on opto/electronic, photovoltaic, and nanogenerator applications. The empirical results indicate that the presence of ZnO nanowires enhances the mobility of electrons from 0.1 cm$^2$/V·s observed in the pristine PDIF-CN2 films up to 0.5 cm$^2$/V·s in ZnO:PDIF-CN2 blends.

## II. EXPERIMENTS

Intrinsic n-type ZnO nanowires with diameter of ~50-120 nm was prepared by vapor phase deposition of ZnO powder mixed with graphite at a ratio of 1:1, at the center of a quartz reaction tube heated to 950 °C in a gas mixture of Ar and $O_2$ (50:1 sccm, total pressure: 2 Torr). ZnO nanowires were subsequently grown on a Si substrate containing a 10-Å gold layer placing at the downstream end of a horizontal tube furnace. Dispersions of ZnO nanowires were then prepared by sonication in chloroform and further mixed with PDIF-CN2 powder to form a homogeneous solution of nanowire:perylene diimide blend. The solutions of PDIF-CN2 were employed with a concentration of 5–6 mg/mL where the mass ratio of ZnO to PDIF-CN2 was ~0.25 wt%.

For the preparation of ZnO:PDIF-CN2 blend transistor, a set of bottom-gate bottom-contact TFTs was fabricated on a highly doped silicon substrate as a common gate, with thermally grown $SiO_2$ (200 nm-thick, with a capacitance per

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unit area of 17 nF/cm$^2$) as the gate dielectric layer. Source and drain contact patterns (channel length: 20 μm, channel width: 500 μm) were defined by conventional photolithography and a layer of chromium (Cr, 50 nm-thick) were thermally evaporated followed by lift-off onto a SiO$_2$ dielectric surface. The surfaces were then treated with hexamethyldisilazane. Subsequently, a thin film (~120-150 nm-thick) of ZnO:PDIF-CN2 blend solution in chloroform was spin-coated onto substrates containing patterned electrodes inside a N$_2$ glove box. Pristine organic devices were also fabricated in the same manner. Upon the formation of active layer, the devices were annealed in N$_2$ at 110 °C for 60 min to enhance the crystallinity of the PDIF-CN2 film [12]. The electrical performance of n-channel blend TFT devices alongside that of pristine organic ones were measured under ambient air at room temperature by a semiconductor device analyzer (Agilent 4155c). The saturation carrier mobility ($\mu_{sat}$) was calculated by plotting the square root of the drain current ($I_D$) versus the gate-source voltage ($V_{GS}$) and fitting the slope data following the general expression [14]: $I_D = \mu_{sat} C_{ox} W/2L \cdot (V_{GS} - V_T)^2$, where $L$ is the channel length (20 μm), $W$ is the channel width (500 μm), $C_{ox}$ is the gate dielectric capacitance (17 nF/cm$^2$), and $V_T$ is threshold voltage.

Note that for the characterization of semiconducting property of ZnO nanowire, we have also fabricated ZnO nanowire-based field effect transistors. As-grown ZnO nanowires were transferred to heavily doped Si substrates covered by thermally grown SiO$_2$ (200 nm-thick) via shear-sliding contact printing [15]. To provide good electrical contact, source and drain top-contacts were defined by photolithography, thermal evaporation (Cr, 50 nm-thick), and lift-off atop the transferred nanowires. The length and width between the source and drain contacts were 2 μm and 25 μm, respectively. For nanowire transistors, we assume that the effective channel width equals the sum of the measured width of each nanowire crossing the contacts.

## III. RESULTS AND DISCUSSIONS

A simplified schematic diagram of the proposed blend TFT is illustrated in Fig. 1a, where the active channel contains random-distributed blend networks of ZnO nanowires and conjugated PDIF-CN2 molecules. Fig. 1b shows that the as-grown wurtzite ZnO nanowires were ~50−120 nm in diameter and ~5−7 μm in length and seen to be single crystalline throughout by using high-resolution scanning electron microscopy (SEM), selected area electron diffraction (see inset), and X-ray diffraction. Fig. 1c shows the tapping-mode Atomic Force Microscopy (AFM) phase image of a ZnO:PDIF-CN2 blend film, indicating that ZnO nanowires were randomly embedded in the organic host matrix. For reference, we fabricated ZnO nanowire-based field effect transistors based on the oriented nanowires by shear-sliding contact printing [15]. As shown in Fig. 2, these ZnO nanowires exhibited n-channel filed effect behaviors with an electron mobility of ~85 cm$^2$/V·s. Moreover, the estimated optical band gap energy from UV-vis spectrum was ~3.31 eV
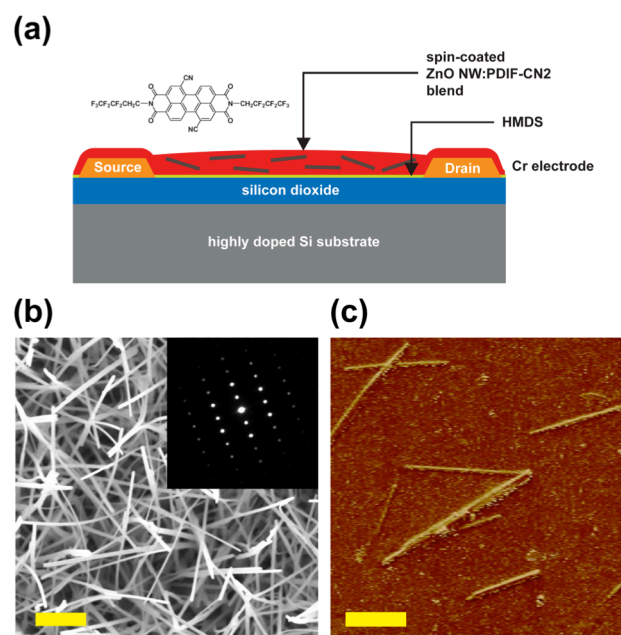


Fig. 1. (a) Schematic cross-section of the bottom-gate bottom-contact ZnO:PDIF-CN2 blend TFT structure employed in this study. (b) SEM image of as-grown ZnO nanowires (scale bar: 1.0 μm); the inset is a selected area electron diffraction pattern of single-crystalline ZnO nanowire. (c) AFM phase image of a ZnO:PDIF-CN2 blend film after annealing. (scale bar: 2.0 μm).

(data not show here).

Fig. 3 shows the output and transfer characteristics of a pristine PDIF-CN2 blend and a ZnO:PDIF-CN2 TFT, respectively. The drain current versus drain-source voltage ($I_D$-$V_{DS}$) relationships clearly resembled those of a typical n-channel field effect transistor, where the $I_D$ increased and saturated when the positive $V_{DS}$ was increased. The measurement results of the ZnO:PDIF-CN2 blend TFTs were found to consistently exhibit superior performance compared to that in the pristine state. The output currents of the ZnO:PDIF-CN2 transistor were much higher than those of pristine organic device. In the saturation regime ($V_{DS}$= 50 V,
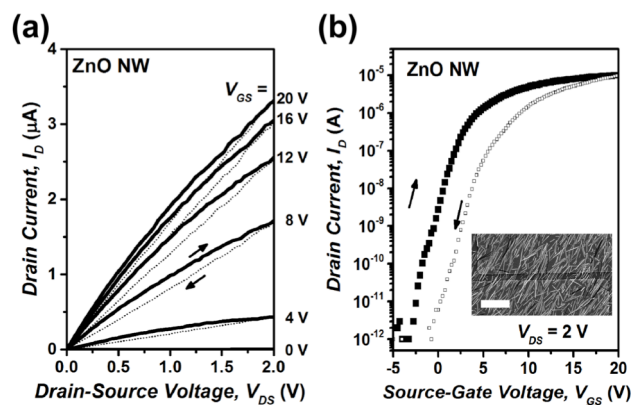


Fig. 2. Output and transfer characteristics of a multi-nanowire ZnO transistor (~23 bridging nanowires) with Cr/Au (20/50 nm) top-contact. The channel length is 2.0 μm and the estimated channel width that equals the sum of the measured width of each nanowire crossing the contacts is ~2.3 μm. The inset is a SEM image of a fabricated ZnO nanowire device (scale bar: 5.0 μm).

$V_{GS}$= 60 V), the $I_D$ of the ZnO:PDIF-CN2 TFT was up to 430 µA whereas that of the pristine one was 85 µA.

The extracted saturation field effect mobility of the pristine PDIF-CN2 with Cr source/drain contacts was in the range of 0.10 to 0.16 cm²/V·s, which were comparable to the previously reported results for PDIF-CN2 devices with gold contacts when measured in air [12]. The threshold voltage and an ON/OFF current ratio were about -10 V and $2\times10^3$, respectively. By incorporating ZnO nanowires into the organic host matrix, the performance of blend TFTs was greatly improved. The average saturation field effect mobility, threshold voltage and ON/OFF current ratio of ZnO:PDIF-CN2 blend TFTs were 0.46 cm²/V·s, -15 V, and $7\times10^2$, respectively. In the best case, the saturation field effect mobility of ZnO:PDIF-CN2 TFT was increased to 0.50 cm²/V·s, representing approximately 3-5 times enhancement over a pristine PDIF-CN2 device. Moreover, the hysteresis loop is also markedly reduced for those blend TFTs due to the addition of ZnO nanowires in the active channel, indicating that these nanowires serve as high speed alternative pathways to stay away from those charge transport obstacles (e.g. defects, impurities, grain interfaces) inside the polymer matrix. Though not optimized yet, the high electron mobility of our ZnO:PDIF-CN2 blend is comparable to the highest reported value from the spin-coated PDIF-CN2 films with poly(alpha-methylstyrene) dielectrics [16]. With respect to those high mobility PDIF-CN2 films deposited by vacuum sublimation (0.4 cm²/V·s to 0.74 cm²/V·s) [17-20] or

sophisticated, capillary force-assisted wedge-gap method (0.74 cm²/V·s to 1.3 cm²/V·s) [20,21], our spin-coated ZnO:PDIF-CN2 blend, though with inferior carrier mobility, is rather simple and low cost for large area, flexible electronic applications.

To gain a better understanding of the possible mechanism for the enhancement in mobility observed in our blend TFTs, we consider the alignment of relevant electronic energy levels between conjugated PDIF-CN2 molecule, semiconducting ZnO nanowire, and Cr source/drain contact, as shown in Fig. 4a. The lowest unoccupied molecular orbital (LUMO) energy of PDIF-CN2 is -4.5 eV relative to the vacuum level [22], the conduction band energy of ZnO nanowire is about -4.46 eV (determined using the Kelvin Probe Force Microscope with a Brucker SCM-PIT probe) and the work function of Cr contact is -4.5 eV. This suggests two possible paths that represent the efficient transport behavior of charge carriers during transistor operation. One is based on the strong π-π intermolecular interactions of conjugated PDIF-CN2 molecules and the advantageous electron injection from Cr electrode to PDIF-CN2 semiconductor. The uniformity of polycrystalline organic film, connectivity of those semiconducting crystals, as well as the energy barrier and wetting ability on source/drain electrodes are crucial [22,23]. The other path is presumably based on the heterogeneous interactions between the PDIF-CN2 molecules and ZnO nanowires. The small energy gap (~0.04 eV) between the LUMO energy of PDIF-CN2 and the conduction band energy of the ZnO nanowires suggests a very low energy barrier for local electron transfer between the two materials in the active channel. In that way, the semiconducting ZnO nanowires bridge the polycrystalline PDIF-CN2 grains, implying that electrons could be carried via band-like conduction through the path of PDIF-CN2-to-ZnO-to- PDIF-CN2 (see the AFM image in Fig. 1c). A schematic model of charge transfer for this path is illustrated in Figure 4b. Further, there could be an increased
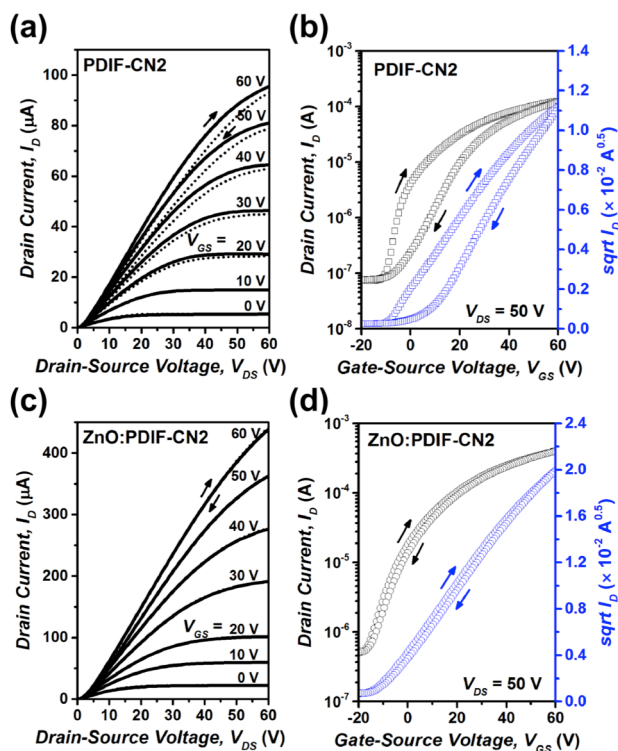
Fig. 3. Representative output and transfer characteristics of (a-b) a pristine PDIF-CN2 TFT and (c-d) a ZnO:PDIF-CN2 blend TFT. The measurement was performed at room temperature under ambient air environment, after N2 annealing at 110 °C for 60 min. The channel length and width of these devices are 20 and 500 µm, respectively.
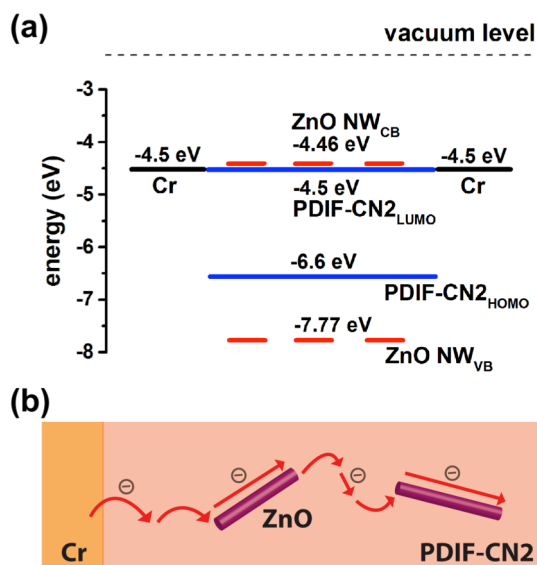
Fig. 4. (a) Energy level diagram of PDIF-CN2 molecule, semiconducting ZnO nanowire, and Cr source/drain contact. (b) Schematic model for charge transfer in a ZnO:PDIF-CN2 blend TFT device with Cr contacts.

electron concentration in the active channel due to the superior semiconducting properties of ZnO nanowires. The OFF current was increased from $7.0 \times 10^{-8}$ A to $5.5 \times 10^{-7}$ A (see the transfer characteristics in Fig. 3b and 3d). Accordingly, this heterogeneous path that serves to enhance the electron carrier transport not only increases the field effect mobility in the blend devices, but also leads to the reduction in the hysteresis of TFT devices.

For an in-depth understanding of the enhancing role of ZnO nanowires, further experiments will examine the effect of different loadings of ZnO nanowires on the field effect characteristics. Optimization will be necessary to reduce the negative threshold voltage and reduce OFF currents seen in the devices. The electrical conductivity of ZnO nanowires can further be adjusted via refined control of the growth process parameters, which is currently in progress in order to determine the optimal conductivity of ZnO nanowire for composite TFT applications.

Experiments are also being conducted to optimize device properties, and to examine the stability of the blend TFTs relative to that in the pristine state. Through addition of adequate nanowire networks with organic conjugated compounds, the flow of electric current can possibly be accelerated and also be tunable, leading to a positive enhancement in transistor performance.

## IV. CONCLUSION

This letter demonstrates a simple and promising approach for enhancement of field effect device characteristics in n-channel solution-processed organic semiconductors. Measurement results of ZnO nanowire:PDIF-CN2 blend TFTs yield significant improvement with respect to device mobility and hysteresis over those of TFTs with pristine PDIF-CN2. While this enhancement in the presence of the ZnO nanowires is significant, there is room for further enhancement through optimization of the electrical properties of the ZnO nanowires, alternative organic host matrices, and refined fabrication/ integration strategies through controlled loading of the ZnO network.

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