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Description	

**Enhancing hole transports and generating hole traps by doping organic hole
transport layers with *p*-type molecules of
2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane**

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Abstract

We investigated the relationship between the hole-transport and hole-trap characteristics of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) doped with *p*-type molecules of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) at various concentrations. The results of our current density-voltage, field-effect transistor, and thermally stimulated current studies revealed that the current densities of hole-only α -NPD devices at a certain driving voltage markedly increased as increasing the F₄-TCNQ concentrations due to the generation of free holes while the hole mobilities of the α -NPD layers decreased as increasing the F₄-TCNQ concentrations due to an increase in hole-trap concentration and deepened hole-trap

energy levels. The optimized doping concentration of F₄-TCNQ was 3 mol%, which provided the highest current density for the hole-only device. On the other hand, since the increase in free-hole concentration was overcome by the decrease in hole mobility, the current density of the hole-only device decreased at the F₄-TCNQ concentration of 4 mol% when compared with the optimized concentration.

Keywords: hole transport; hole trap; *p*-doped organic hole-transport layer; thermally stimulated current; field-effect transistor

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1. Introduction

Doping *p*-type and *n*-type molecules in an organic hole-transport layer (HTL) and an electron-transport layer has been frequently done to obtain a low driving voltage [1], a high power conversion efficiency [2], and a long lifetime [3] in organic light-emitting diodes (OLEDs). The *p*-type dopants used in the HTLs include ferric trichloride [4], 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) [1-3], tris(4-bromophenyl)aminium hexachloroantimonate [5], antimony pentachloride [6], tungsten trioxide [7], molybdenum trioxide [8], and rhenium dioxide [9]. The use of these dopants induces an electron transfer from host to dopant molecules and an increase in free hole concentration. This increase in free hole concentration enhances electrical conductivities in the doped HTLs [10] and induces the formation of nearly ohmic contacts at metal/organic interfaces [11], leading to a marked improvement in OLED performance.

In this study, we fabricated hole-only devices and field-effect transistors (FETs) with an HTL of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD). We investigated how doping the HTL with *p*-type F₄-TCNQ molecules at various concentrations influences its hole-transport and hole-trap characteristics. The hole-trap

characteristics of F₄-TCNQ-doped HTLs have, to date, never been studied. Detailed investigation of the relationship between the hole transports and hole traps of doped HTLs is crucial to developing OLEDs and to clarifying the underlying mechanism of carrier transport in doped HTLs.

2. Experimental details

The structure of the hole-only devices is shown in the inset of Fig. 1. A precleaned glass substrate coated with an indium tin oxide (ITO) anode layer (sheet resistance of 25 Ω/sq) was set in a vacuum evaporator, which was evacuated to $\approx 10^{-4}$ Pa. A 100-nm-thick F₄-TCNQ-doped α -NPD HTL was vacuum-deposited on the ITO surface at a total deposition rate of 0.3 nm/s. The doping concentration of F₄-TCNQ to α -NPD was precisely controlled at 0, 1, 2, 3, or 4 mol% using two quartz crystal microbalances. A 5-nm-thick Ag layer and a 100-nm-thick Al layer were successively vacuum-deposited on the doped HTL at a deposition rate of 0.1 nm/s. The ITO and Ag/Al layers served as an anode and a cathode, respectively. The active area of the devices was 4 mm². The current density-voltage (*J-V*) characteristics of the devices were measured using a semiconductor parameter analyzer (E5250A, Agilent Technology Co.) at room temperature.

To measure the hole mobilities of the α -NPD layers doped with F₄-TCNQ, we fabricated FETs with a doped α -NPD semiconductor layer. Heavily *p*-doped silicon wafers covered with a 300-nm-thick thermally grown SiO₂ insulating layer were used as a gate electrode. A 0.5-nm-thick Cr adhesion layer and a 50-nm-thick Au electrode layer were thermally deposited on the precleaned SiO₂ layer at deposition rates of 0.02 nm/s for Cr and 0.1 nm/s for Au under a background pressure of $\approx 10^{-4}$ Pa. The Cr/Au layers were patterned by using conventional photolithography and lift-off techniques to form Au source and drain electrodes with a channel length of 25 μ m and a channel width of 76 μ m. To complete the FETs, a 50-nm-thick composite layer of α -NPD and F₄-TCNQ was prepared in the conditions similar to those mentioned previously. The FET characteristics of the doped α -NPD layers were measured using a semiconductor device analyzer (B1500A, Agilent Technologies Inc) at room temperature.

The thermally stimulated current (TSC) spectra of the hole-only devices were measured using a TSC measurement system (TSC-FETT EL2000, Rigaku Co., Ltd.) to investigate hole traps in the HTLs [12,13]. The device was cooled to 80 K using liquid nitrogen, and then biased with a current density of 5 mA/cm² for 1 min to charge its

traps with injected holes. Its temperature was increased to room temperature at a heating rate of 0.17 K/s. During this process, holes were released from the traps and the hole current was measured using a femtoammeter to obtain the TSC spectra.

3. Results and discussion

Fabricating the hole-only devices is important for making it simple to investigate their hole-transport and hole-trap characteristics. When an Al cathode layer was directly prepared on the α -NPD layer, we observed weak electroluminescence (EL) at a high bias voltage from the device, indicating that both electrons and holes can be injected in the device with the Al cathode. Since the work function of Ag (-4.6 eV) is lower than that of Al (-4.4 eV) [14], a thin Ag layer (5 nm) was inserted between the α -NPD layer and the Al layer to prevent electron injection from the Al cathode. In fact, we observed no EL from the device with the Ag/Al cathode, meaning that only holes can be injected in the device with the Ag/Al cathode.

The J - V characteristics of the hole-only devices with the Ag/Al cathode are shown in Fig. 1. The current densities at a driving voltage of 3 V are plotted as a function of the F₄-TCNQ doping concentrations in Fig. 2. The current densities markedly increased as

the F₄-TCNQ doping concentrations from 0 to 3 mol%. We obtained the highest one when the F₄-TCNQ concentration was 3 mol%. However, we observed a decrease in the current density at the concentration of 4 mol% when compared with the concentration of 3 mol%. The cause of this decrease will be discussed later.

The increase in the current density is attributable to an increase in the number of free holes in the doped HTLs, resulting from an electron transfer from α -NPD to F₄-TCNQ molecules [1-3,10,11]. Since the ionization potential energy level of α -NPD (-5.5 eV) [1] slightly lies below the electron affinity energy level of F₄-TCNQ (-5.2 eV) [15,16], the electron transfer from α -NPD to F₄-TCNQ is probably less efficient when compared with a F₄-TCNQ-doped zinc phthalocyanine (ZnPc) film [15,16] and a F₄-TCNQ-doped alpha-sexithiophene (α -6T) film [1]. The electron affinity energy level of F₄-TCNQ (-5.2 eV) is closer to the ionization potential energy levels of ZnPc (-5.2 eV) [15,16] and α -6T (-5.1 eV) [1] than the ionization potential energy level of α -NPD (-5.5 eV).

We investigated that how doping the α -NPD layers with F₄-TCNQ affects the hole mobilities of the α -NPD layers. We tried measuring the hole mobilities of the doped α -NPD layers using a conventional time-of-flight (TOF) technique [17-19]. However,

we obtained highly dispersed TOF signals and no TOF hole mobility from the doped α -NPD layers. The large density of hole traps in the doped layers would make obtaining a TOF hole mobility difficult [19]. However, when we fabricated the doped α -NPD FETs, we were able to observe FET signals and calculate FET hole mobilities (μ_{FET}) of the doped layers.

Figures 3(a), 3(b), 3(c), 3(d), and 3(e) show the output characteristics, depicted as source-drain voltage (V_{sd}) vs drain current (I_{d}) as a function of gate voltages (V_{g}), for the α -NPD FETs doped with F₄-TCNQ at 0, 1, 2, 3, and 4 mol%, respectively. The undoped α -NPD layers showed typical *p*-type FET characteristics (Fig. 3(a)). The results showed that I_{d} increases linearly with V_{sd} , and, at a high V_{sd} , the I_{d} becomes saturated as the accumulation of holes in the α -NPD layer is pinched off. Doping the α -NPD layers with F₄-TCNQ induced a gradual increase in off-current, indicating the generation of free holes in the doped α -NPD layers. Using the transfer characteristics, depicted as V_{g} vs $I_{\text{d}}^{0.5}$ at a constant V_{sd} of 100 V, we estimated the μ_{FET} of the doped α -NPD layers using the conventional metal-oxide semiconductor equation, $I_{\text{d,sat}} = \{\mu_{\text{FET}}WC(V_{\text{g}}-V_{\text{th}})^2\}/(2L)$ [20] (3), where $I_{\text{d,sat}}$ is the saturated drain current, W is the channel width, L is the channel length, C is the capacitance per unit area of the SiO₂ insulator, and V_{th} is the

threshold voltage.

The FET hole mobility of the undoped α -NPD layer was $1.6 \times 10^{-5} \text{ cm}^2/\text{V s}$. This value is about one order of magnitude lower than that of an undoped α -NPD layer measured by a TOF technique $((3.0\text{-}10.0) \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s})$ [17,18] due to the contact resistance between the Au layer and the α -NPD layer. The hole injection barrier height at the Au/ α -NPD interface was estimated to be 0.3 eV from the difference between the work function energy level of Au (-5.2 eV) [14] and the ionization potential energy level of α -NPD (-5.5 eV).

The measured μ_{FET} of the α -NPD layers are also plotted as a function of the F₄-TCNQ doping concentrations in Fig. 2. We found that the μ_{FET} monotonically decreased with increasing the F₄-TCNQ concentrations. Thus, since the increase in the free-hole concentration overcame the decrease in the μ_{FET} , the current densities of the hole-only devices gradually increased as increasing the F₄-TCNQ concentrations from 0 to 3 mol% (Fig. 2). On the other hand, since the increase in the free-hole concentration was overcome by the decrease in the μ_{FET} , we observed the decrease in the current density at the concentration of 4 mol% when compared with the optimized

concentration of 3 mol% (Fig. 2).

The TSC spectra of the hole-only devices doped at various concentrations are shown in Fig. 4. Although undoped HTLs have a small TSC spectrum area, this area was markedly increased by the F₄-TCNQ doping. Since the TSC spectrum area corresponds to the hole-trap concentration (N_t), this increase means an increase in N_t . On the assumption that all holes being released from the traps were collected by the electrode and that they all contributed to the TSC currents, the N_t of the HTLs can be calculated using $N_t = Q/qAL$ [13] (1), where Q is the total charge (equal to the area under the TSC peak), q is the electronic charge, A is the active area, and L is the cathode-anode spacing. The N_t , which was calculated using Eq. 1 with the TSC spectra shown in Fig. 4, is plotted as a function of the F₄-TCNQ doping concentrations in Fig. 5. We observed a marked increase in N_t in the low concentration region (0 - 1 mol%) and a very slight increase in the high concentration region (1 - 4 mol%).

The peak hole-trap depth (d_t) can be calculated using $d_t \approx kT \ln(T^4/\beta)$ [13] (2), where k is Boltzmann's constant, T is the temperature at the TSC peak, and β is the heating rate. The d_t calculated using Eq. 2 with the TSC peak temperature was between 0.22 and

0.24 eV. Moreover, the TSC spectrum gradually extended to a higher temperature as the F₄-TCNQ concentration was increased, indicating that the hole-trap distribution gradually extended to a deeper energy level. The deepest hole-trap energy levels, which were estimated from the TSC spectrum edges, are also plotted as a function of the F₄-TCNQ doping concentrations in Fig. 5. From the results of the TSC study mentioned above, we found that doping the α -NPD layers with F₄-TCNQ induced the increase in N_t and the deepened hole-trap energy levels. These changes of the hole-trap characteristics by the F₄-TCNQ doping are expected to lower a hole-transport ability of the α -NPD layers, resulting in the decrease in the μ_{FET} (Fig. 2).

Finally, we discuss the origin of the hole traps generated by the F₄-TCNQ doping. Although dopant molecules, with ionization potential energy levels above that of host molecules, are known to work as hole traps [21,22], this does not apply to our case of F₄-TCNQ-doped α -NPD because the ionization potential energy levels of α -NPD and F₄-TCNQ are reported to be -5.5 [1] and -8.3 eV [15,16], respectively. The electron transfer from α -NPD to F₄-TCNQ results in the generation of donar-acceptor (D-A) pairs of α -NPD and F₄-TCNQ. The D-A pairs are dissociated by a bias voltage and radical cations (holes) of α -NPD are generated by the D-A dissociation. The generated

holes traverse the HTLs and contribute to the increase in current density (Fig. 2). On the other hand, simultaneously generated negatively charged F₄-TCNQ attracts holes and works as hole traps in the doped HTLs due to Coulomb force. Moreover, since the N_t did not linearly increase as the F₄-TCNQ concentration was increased (Fig. 5), F₄-TCNQ molecules are expected to aggregate in the HTLs. The highly negatively charged F₄-TCNQ aggregation can strongly attract holes, suggesting that the hole-trap energy level deepens (Fig. 5). From these considerations, we can only speculate that the origin of the hole traps is negatively charged F₄-TCNQ, which is generated by the electron transfer from α -NPD to F₄-TCNQ.

4. Conclusion

In this study, we investigated hole-transport and hole-trap characteristics of α -NPD layers doped with *p*-type F₄-TCNQ molecules at various concentrations. From detailed study of *J*-*V*, FET, and TSC characteristics, we found that current densities of hole-only α -NPD devices markedly increased with increasing the F₄-TCNQ concentrations due to the generation of free holes while hole mobilities of α -NPD layers decreased with increasing the F₄-TCNQ concentrations due to an increase in hole-trap concentration and deepened hole-trap energy levels. Thus, when considering the trade-off between the

increase in free-hole concentration and the decrease in hole mobility, the optimized doping concentration of F₄-TCNQ was found to be 3 mol%, which provided the highest current density for the α -NPD device. We emphasize that these findings will be useful for clarifying the underlying mechanism of carrier transport in doped layers and for fabricating high-performance organic (opto)electronic devices.

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Figure captions

Fig. 1. Current density-voltage (J - V) characteristics of α -NPD devices doped with F_4 -TCNQ molecules at various concentrations. Inset shows schematic structure of doped devices.

Fig. 2. Current density at 3 V and FET hole mobility vs. F_4 -TCNQ doping concentration.

Fig. 3. Source-drain voltage (V_{sd}) vs drain current (I_d) as function of gate voltages (V_g) for α -NPD FETs doped with F_4 -TCNQ at (a) 0 mol%, (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, and (e) 4 mol%.

Fig. 4. TSC spectra of α -NPD layers doped with F_4 -TCNQ molecules at various concentrations.

Fig. 5. Hole-trap concentration and deepest hole-trap energy level vs. F_4 -TCNQ doping concentration.

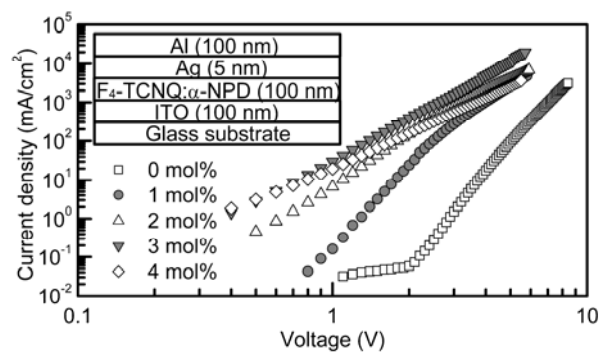


Fig. 1.

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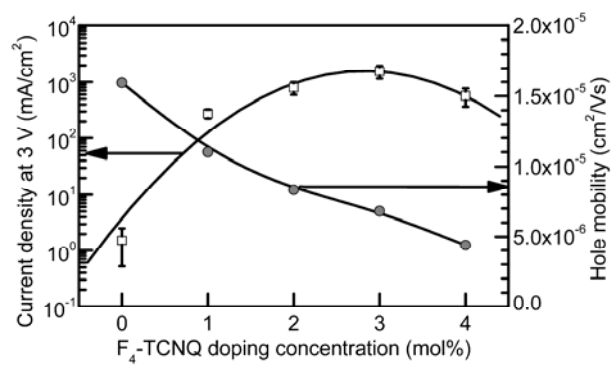


Fig. 2.

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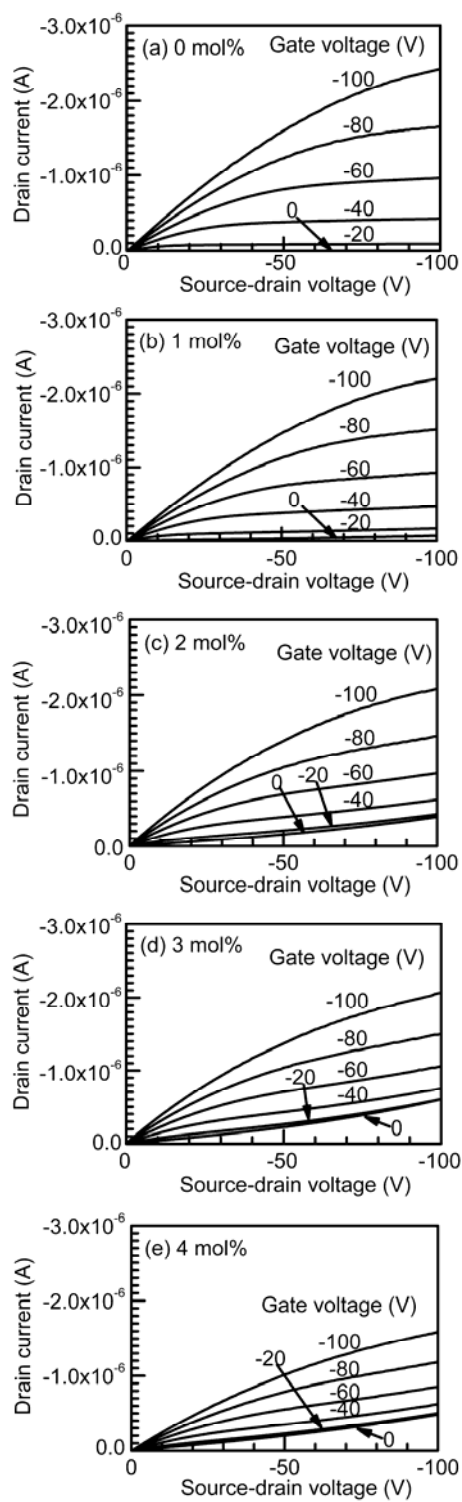


Fig. 3.

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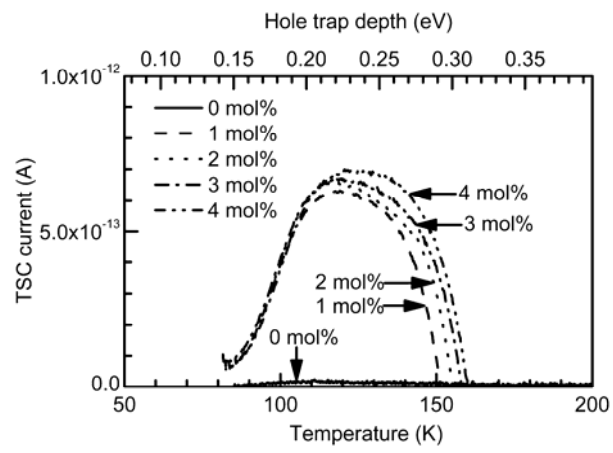


Fig. 4.

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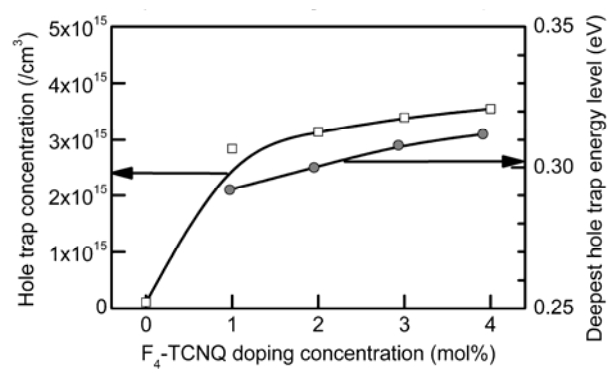


Fig. 5.

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