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Formation of Ohmic Contacts to Organic Semiconductor Films

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Ohmic contacts for both holes and electrons were formed on naphthalene tetracarboxylic anhydride films (NTCDA) at Pt-doped p-type film/metal and Na-doped n-type film/metal junctions, respectively. The injection current density reached $4\,A\,cm^{-2}$ *at a low bias field of* $6 \times 10^4\,V\,cm^{-1}$*. Pt was revealed to be a candidate for a permanent dopant that can act as an electron acceptor in the formation of p-type organic semiconductors.*

Keywords: Fermi level; metal doping; ohmic contacts; organic semiconductor films; platinum; pn-control

INTRODUCTION

The formation of ohmic contacts is a very important issue for semiconductor devices, since their performance is inevitably influenced by charge injection and extraction across semiconductor/metal interfaces [1]. We have previously reported the formation of ohmic contacts to perylene molecular crystals [2]. We revealed that the organic semiconductor surfaces that are in direct contact with the metal electrodes ought to be doped *p* or *n* type, respectively. We believe that this methodology could be extended to organic thin films. We adopted naphthalene tetracarboxylic anhydride (NTCDA) as a test material due to excellent carrier transport ability, namely, NTCDA can be used in

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the form of extremely thick layers reaching 2 μm in organic solar cells without degrading photovoltaic performance [3,4].

Here, we report the formation of ohmic contacts at Pt-doped *p*-type film/metal junctions and Na-doped *n*-type film/metal junctions, that enable free hole and electron injection, respectively.

EXPERIMENTAL

NTCDA films were deposited onto indium tin oxide (ITO) glass substrate using vacuum evaporation technique under 10^{-3} Pa. Pt doping was achieved by the co-evaporation of NTCDA along with metals from an electron-beam source (ULVAC Ltd., EGK-3M). Na doping was achieved by the deposition of Na metal onto the NTCDA films. The energetic position of the Fermi levels (E_F) of the NTCDA films was measured by a Kelvin-Zisman vibrating capacitor apparatus (Riken Keiki, FAC-1) in a pure N_2 atmosphere. We fabricated the sandwich-type cells in which doping was only present in the interfacial regions between NTCDA and the metal electrodes (see Fig. 2). The injection current was measured by applying a voltage between the ITO and the counter metal electrode under 10^{-1} Pa at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the energetic diagram of NTCDA films. The upper edge of the valence band (E_{VB}) and the lower edge of the conduction

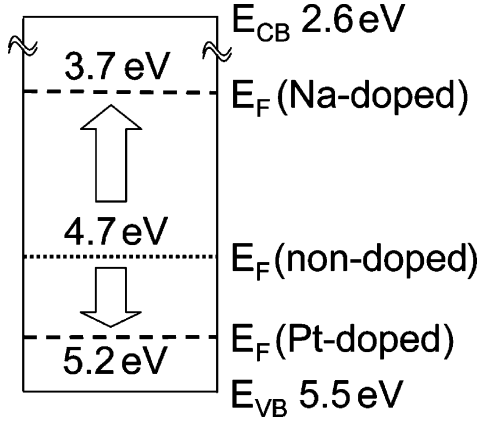

FIGURE 1 Energy diagram of NTCDA films. E_{CB}, E_{VB}, and E_F denote the lower edge of conduction band, the upper edge of valence band, and the Fermi level, respectively.

band (E_{CB}) were determined using atmospheric photoelectron spectroscopy and the optical band gap. Fermi level (E_F) for non-doped films was reproducibly measured at 4.7 eV. When the NTCDA films was doped with 1.6 vol% Pt, the value of E_F shifted in the positive direction towards 5.2 eV, and approached E_{VB} (5.5 eV). When a 23-nm-thick layer of Na metal was deposited on the NTCDA film, all of the deposited Na reacted with NTCDA and no metallic luster of metallic Na remained and E_F shifted towards the negative direction and reached 3.7 eV. Therefore, we concluded that the Pt- and Na-doped NTCDA films became *p* and *n*-type, respectively. It should be pointed out that Pt is a permanent dopant that acts as an electron acceptors, as in the case of F_4-TCNQ [5], which is different from volatile acceptors such as bromine [2,6].

We applied the Pt-doping technique to modify the hole injection characteristics of NTCDA films. Figure 2 shows the dependence of the injection current on the applied electric field. For Pt/nondoped NTCDA/ITO cells, low injection currents (less than several $mA\,cm^{-2}$) were observed at $6 \times 10^4\,V\,cm^{-1}$ (curve B). Interestingly, for cells with doping in the interfacial regions, the current increased along a straight line irrespective of the polarity of the bias (curve A). At $6 \times 10^4\,V\,cm^{-1}$ (4.8 V), the injection current density reached the

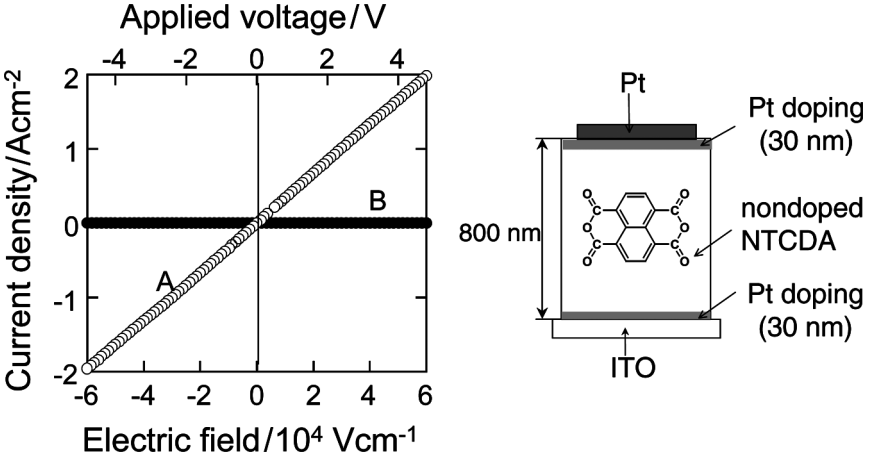

FIGURE 2 Dependence of hole injection current on applied electric field and voltage. Curve A: Pt/Pt-doped NTCDA (30 nm)/nondoped NTCDA (740 nm)/Pt-doped NTCDA (30 nm)/ITO cell. Curve B: Pt/nondoped NTCDA (800 nm)/ITO cell. The positive bias direction corresponds to (+)Pt/NTCDA/ITO(−). Structure of a sandwich-type cell with interfacial doping regions neighboring the NTCDA/metal interfaces and the chemical structure of NTCDA are also shown.

extraordinarily large valued of $2\,A\,cm^{-2}$. The observed currents is obviously no longer dominated by the injection properties at the organic/metal interfaces but is dominated by the hole-transport properties in the nondoped bulk region of the NTCDA film. This result strongly suggests the formation of an ohmic contact for hole injection. Although the thickness of the NTCDA films was nearly of μm order, a current of the order of amperes could be injected by creating an ohmic contact.

Figure 3 shows the dependence of the electron injection current on the applied electric field. For the Ag/Na (3 nm)/NTCDA (600 nm)/ITO cell, almost ohmic behavior was observed (curve A). Since 1-nm-thick layers of Li have been revealed to diffuse deeply into organic film (more than 100 nm) [7], we concluded that the Na penetrated throughout the 600-nm-thick NTCDA film and the doped region reached opposite NTCDA/ITO interface. When annealing was performed at $+80^{\circ}C$ after Na deposition, completely straight ohmic behavior was observed (curve B). Annealing seems to accomplish a uniform distribution of Na in the NTCDA film. At $6 \times 10^4\,V\,cm^{-1}$ (3.6 V), the injection current density reached the extraordinary large value of $4\,Acm^{-2}$. Thus, we have successfully formed ohmic contacts to NTCDA films for both holes and electrons.

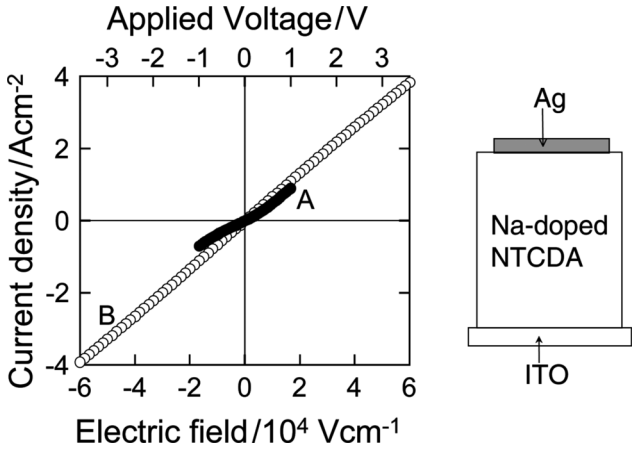

FIGURE 3 Dependence of electron injection current on applied electric field and voltage. Curve A: Ag/Na (3 nm)/NTCDA (600 nm)/ITO cell. Curve B: Ag/Na (3 nm)/NTCDA(600 nm)/ITO cell for which the annealing at $+80^{\circ}C$ for 2.5 h under 10^{-3} Pa was performed after Na deposition. The positive bias direction corresponds to (+)Ag/NTCDA/ITO(–).

The doping concentration in the present study were very high, namely, $1.0 \times 10^{21}\,cm^{-3}$ for Pt doping (0.1 Pt atom peer 1 NTCDA molecule) and $1.3 \times 10^{20}\,cm^{-3}$ for uniform Na doping (Fig. 3, curve B) (0.01 Na atom per 1 NTCDA molecule). Therefore, doped NTCDA can be regarded as a degenerate semiconductor. In this case, the doped NTCDA/metal junctions behaved as ohmic contacts, even when an energetic barrier was expected to be present [8] because of the extremely thin barrier width at the $p+$- or $n+$-NTCDA/metal interfaces. Thus, straight and completely symmetrical ohmic behavior was observed, irrespective of the biasing polarity (Fig. 2, curve A and Fig. 3, curve B). It should be noted that a simple energetic relationship is not a unique condition for fabricating ohmic contacts, i.e., although there is not expected to be a barrier for hole injection at the NTCDA/Pt junction, a very small current limited by injection was observed for nondoped cells (Fig. 2, curve B). Organic semiconductors in direct contact with metal should therefore be doped in order to achieve carrier equilibrium between the organic film and the electrode metal, which makes the contacts ohmic.

CONCLUSION

Ohmic contacts to NTCDA films for both holes and electrons were formed. Pt was revealed to be a candidate for a permanent dopant that acts as an electron acceptor to form *p*-type organic semiconductors. Very large current of several $A\,cm^{-2}$ could easily be injected by applying several volts, although the organic films have a thickness of nearly 1 μm. We believe that the formation of double ohmic contacts for electron injections and holes is crucial for carrier injection in electroluminescent devices [9] and carrier extraction from organic solar cells [4,10,11].

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