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Formation of Ohmic Contacts to Naphthalene Tetracarboxylic Anhydride Films

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Ohmic contacts for holes were formed on naphthalene tetracarboxylic anhydride films (NTCDA) at Pd-doped p-type film/metal junction. The injection current density reached 10 Acm^{-2} at a low bias field of 1.25 × 10^4 Vcm^{-1}. Pd 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; palladium; 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 in order to form ohmic contacts for holes and electrons, 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 the form of

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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 Pd-doped *p*-type NTCDA film/metal junctions, that enable hole injection.

EXPERIMENTAL

NTCDA films were deposited onto indium tin oxide (ITO) glass substrate using vacuum evaporation technique under 10^{-3} Pa. Pd doping was achieved by the co-evaporation of NTCDA along with metals from an electron-beam source (ULVAC Ltd., EGK-3M). The energetic position of the Fermi levels (E_F) of the NTCDA films was measured by a Kelvin vibrating capacitor apparatus (Riken Keiki, FAC-1) in an Ar atmosphere. We fabricated the sandwich-type cells in which doping was only present in the interfacial regions between NTCDA and the metal electrodes as shown in Figure 2. The injection current was measured by applying a voltage between the ITO and the counter Ag 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}; 5.5 eV) and the lower edge of the

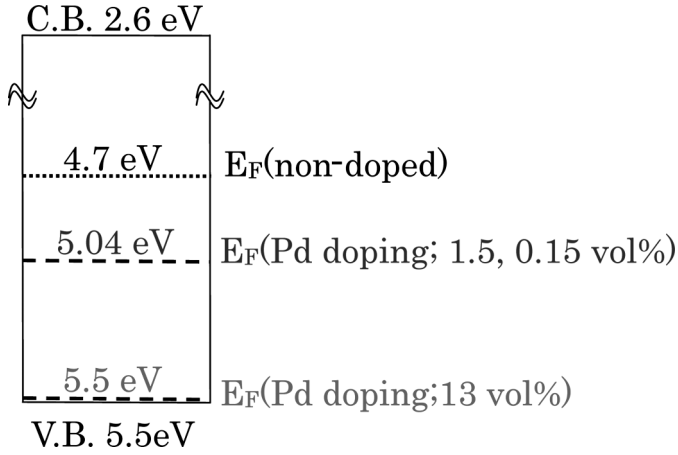

FIGURE 1 Energy diagram of NTCDA films. E_{CB}, E_{VB}, and E_F denote the lower edge of conduction band, the upper edge of valence band, and the Fermi level, respectively.

conduction band (E_{CB}; 2.6 eV) 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 0.15 and 1.5 vol% Pd, the value of E_F shifted in the positive direction towards 5.04 eV. When the concentration of Pd was increased to 13 vol%, the value of E_F shifted to 5.5 eV and reached to E_{VB}. On the other hand, the conductivity measurements using surface-type Au electrode pairs [5] revealed that the specific conductivity (σ) for non-doped NTCDA and Pd-doped (1.5 vol%) NTCDA were $2.1 \times 10^{-9}\,Scm^{-1}$ and $5.0 \times 10^{-3}\,Scm^{-1}$, respectively. σ increased approximately 10^6-fold by Pd doping. This suggests the drastic increase of free carrier concentration in NTCDA film by Pd-doping. Taking these results into consideration, we concluded that the Pd-doped NTCDA films became *p*-type. It should be pointed out that Pd is a permanent dopant that acts as an electron acceptors, as in the case of F_4-TCNQ [6], which is different from volatile acceptors such as bromine [2,7].

We applied the Pd-doping technique to modify the hole injection characteristics of NTCDA films by fabricating the sandwich-type cells shown in Figure 2. Pd-doping was performed only to the interfacial regions neighboring electrodes. Figure 3 shows the dependence of the injection current on the applied voltage. For Ag/non-doped NTCDA/ITO cells, very low injection currents less than several $mAcm^{-2}$ at $1 \times 10^4\,Vcm^{-1}$ (curve C) and the injection-limited behavior, i.e. injection current started to increase above threshold voltage, were observed. Interestingly, for cells incorporating Pd-doped (0.15

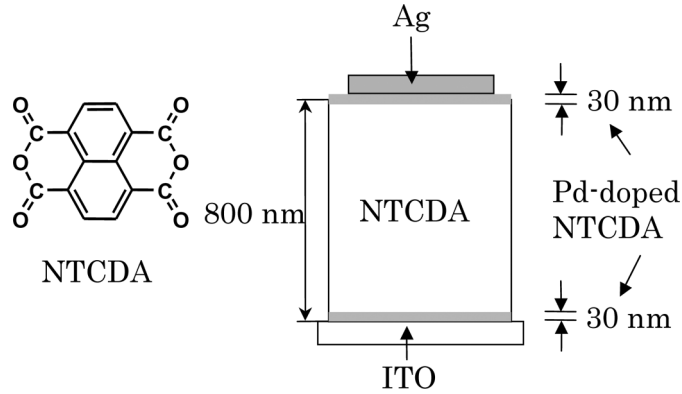

FIGURE 2 Structure of a sandwich-type cell with interfacial doping regions neighboring the NTCDA/metal interfaces and chemical structure of NTCDA.

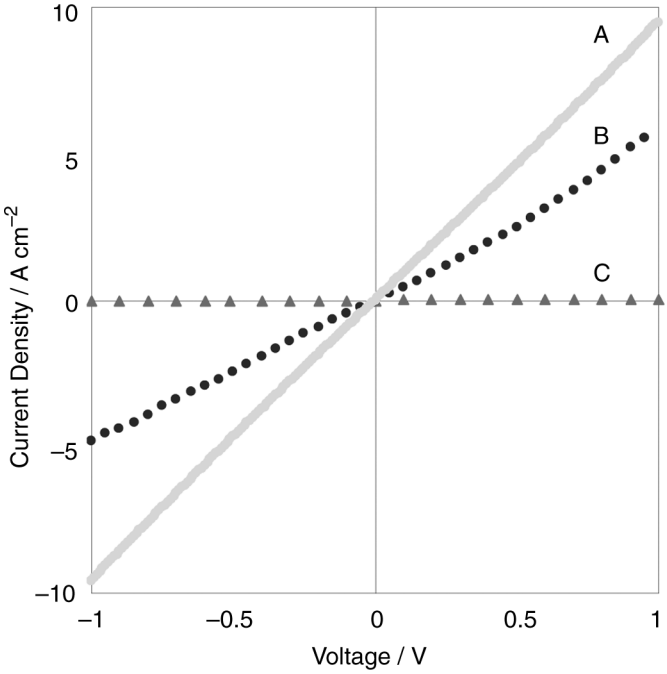

FIGURE 3 Dependence of injection current density on applied voltage for cell shown in Figure 2. Pd concentrations in interfacial doped regions were 0.15 (curve A), 1.5 (curve B), and 0 vol% (curve C). Applied voltage of 0.8 V corresponds to applied electric field of $1 \times 10^4\,\mathrm{Vcm^{-1}}$.

and 1.5 vol%) interfacial regions, the current increased along a straight line irrespective of the polarity of the bias (curves A and B). At $1.25 \times 10^4\,\mathrm{Vcm^{-1}}$ (1 V), the injection current density reached the extraordinarily large value of $10\,\mathrm{Acm^2}$. 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 non-doped 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 and very small amount of Pd (0.045 nm Pd in the interfacial doping region (30 nm-thick NTCDA) for the case of 0.15 vol%), a current of the order of amperes could be injected by creating an ohmic contact.

The doping concentration in the present study were very high, namely, $1.0 \times 10^{21}\,\mathrm{cm^{-3}}$ (0.1 Pd atom per 1 NTCDA molecule) and $1.0 \times 10^{20}\,\mathrm{cm^{-3}}$ (0.01 Pd atom per 1 NTCDA molecule) for Pd doping

of 1.5 vol% and 0.15 vol%, respectively. Therefore, doped NTCDA can be regarded as a degenerate semiconductor irrespective of the present doping concentrations of 1.5 and 0.15 vol%. In these cases, the doped NTCDA/metal junctions behaved as ohmic contacts, even when an energetic barrier was expected to be present between Ag (work function: 4.7 eV) and upper edge of valence band of NTCDA (5.5 eV) because of the extremely thin barrier width at the p^+-NTCDA/metal metal interfaces. Thus, straight and symmetrical ohmic behavior was observed, irrespective of the biasing polarity (Fig. 3, curves A and 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 (work function: 5.65 eV) junction, a very small current limited by injection was observed for non-doped cells. 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.

CONCLUSIONS

Ohmic contacts to NTCDA films for holes were formed by interfacial Pd doping. Pd 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 10 Acm^{-2} could easily be injected by applying 1 V, although the organic films have a thickness of nearly 1 μm. Similar results were observed by Pt doping. In addition, we observed the formation of ohmic contacts to NTCDA films for electrons by Na doping. We believe that the formation of double ohmic contacts for electrons and holes is crucial for carrier injection in electroluminescent devices [8] and carrier extraction from organic solar cells [4,9,10].

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