Electron Injection Behavior from the Magnesium Electrode into a Family of Electron-Transporting Amorphous Molecular Materials, α,ω-Bis(dimesitylboryl)oligothiophene

Fengling Zhang,[a,†] Tetsuya Noda,[a] Hiroshi Kageyama,[a] and Yasuhiko Shirota[a,b*]

[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan, [b] Fukui University of Technology, 3-6-1, Gakuen, Fukui City, Fukui 910-8505, Japan

ABSTRACT

Electron injection behavior from the magnesium (Mg) electrode into a family of electron-transporting amorphous molecular materials, 5,5'-bis(dimesitylboryl)-2,2'-bithiophene (BMB-2T) and 5,5"-bis(dimesityl-boryl)-2,2':5',2"-terthiophene (BMB-3T), in single-layer devices of symmetrical structure was studied. The current density−voltage characteristics of the devices with varying thickness were in agreement with the trap-free space-charge-limited current model. The results suggest that the current is conduction limited and that the contact between BMB-nT (n = 2 and 3) and the Mg electrode is nearly ohmic.

1. INTRODUCTION

Significant progress has been made in the research and development of organic light-emitting diodes (OLEDs) in the past twenty years since the report of Tang and VanSlyke.[1] OLEDs have already been put into practical use as full color, flat-panel displays. Extensive studies on OLEDs have deepened our understanding of materials, operation processes and device physics. [2-9] Both amorphous molecular materials and π-conjugated polymers have been used as materials for use in OLEDs.[7,9]

Achieving high brightness at a low drive voltage is an important requirement for OLEDs. Among various factors that affect the luminous efficiency of OLEDs, both the density and the balance in the number

* Author to whom correspondence should be addressed; electronic mail: shirota@fukui-ut.ac.jp
† Present Address : Biomolecular and Organic Electronics, Department of Physics, Chemistry and Biology, Linköping University, Sweden.

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of holes and electrons injected from the two dissimilar electrodes are of crucial importance. Charge-transporting layers in OLEDs play an important role in facile charge injection from the electrodes into the emitting layer. A number of hole- and electron-transporting materials have been developed.[10]

Charge-injection behavior from the electrode into a charge-transporting layer has been a subject of great importance. Ohmic contact between the organic material and the electrode is ideal for charge injection from the electrode into the organic material. Materials that form Ohmic contact with the indium-tin-oxide (ITO) electrode have been developed, which include the family of 4,4',4"-tris(diphenylamino)triphenylamine (TDATA) amorphous molecular materials with very low solid-state ionization potentials, typically, 4,4',4"-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine (m-MTDATA),[11-13] and copper phthalocyanine.[14] Recently, metal oxides, such as vanadium oxide, molybdenum oxide, and ruthenium oxide, have also been reported to lower the energy barrier for hole injection from the ITO electrode into hole-transporting materials, reducing the operating voltage of OLEDs.[15-17] The use of p-doped hole-transporting layer has also been shown to significantly reduce the drive voltage of OLEDs, which includes a polycarbonate polymer doped with tris(4-bromophenyl)aminium hexachloroantimonate,[18-20] TDATA,[21-23] m-MTDATA,[24] and vanadyl-phthalocyanine[25] doped with tetrafluoro-tetracyanoquinodimethane, m-MTDATA doped with iodine,[26] and α-NPD doped with $FeCl_3$[27] or rhenium oxide.[28]

Likewise, it is desirable to realize an ohmic contact between the cathode and the organic material for electron injection. One method to facilitate electron injection from the cathode into organic materials is to realize better alignment of the energy levels at the contact between the cathode and organic materials. The use of low-work-function metals as the cathode[1,29,30] and the insertion of a buffer layer such as LiF,[31] Al_2O_3,[32] CsF,[33] and poly(methyl methacrylate)[34] between the Al electrode and an adjacent organic layer have been reported to facilitate electron injection from the cathode into organic materials. While electron injection from the magnesium (Mg) cathode into a well-known electron-transporting, green-emitting material, tris(8-quinolinolato)aluminum (Alq_3), has been reported to be injection limited and explained in terms of the Schottky emission model,[35,36] electron injection from LiF / Al into Alq_3 has been shown to be controlled by space-charge-limited current (SCLC).[37] A family of electron-transporting amorphous molecular materials, α,ω-bis(dimesitylboryl)oligothiophene (BMB-nT), have been reported to facilitate electron injection from the magnesium cathode into Alq_3.[38]

In the present study, we have investigated electron-injection behavior from the Mg electrode into the family of BMB-nT amorphous molecular materials, 5,5'-bis(dimesitylboryl)-2,2'–bithiophene (BMB-2T) and 5,5"-bis(dimesitylboryl)-2,2':5',2"-terthiophene (BMB-3T), in electron-only, single-layer devices.

2. RESULTS AND DISCUSSION

Electron-only devices consisting of the single layer of the electron-transporting amorphous molecular materials, BMB-nT (n = 2 or 3), sandwiched between the two Mg electrodes were fabricated by the vacuum-deposition method. First, Mg:Ag alloy was deposited onto a cleaned ITO-coated glass of a sheet resistance of 50 Ω/□ by simultaneous evaporation from the two separate sources (deposition ratio is approximately 10:1). Subsequently, the thin film of BMB-nT (n = 2 or 3) was deposited on the top of the Mg:Ag alloy, followed by the deposition of Mg:Ag onto the BMB-nT layer to form the device of symmetrical structure. The deposition of both Mg and BMB-nT (n = 2 or 3) were carried out at a rate of 2−3 $Å s^{-1}$ at ca. 1×10^{-5} Torr. The current density−voltage characteristics of the devices were measured at room temperature with an electrometer (Advantest TR6143).

BMB-2T and BMB-3T were prepared according to the method described in our previous paper.[38] These materials readily form stable amorphous glasses with glass-transition temperatures of 107 and 115 ºC, respectively,[38] and have been shown to function well as the electron-injection layer in multi-layer OLEDs, ITO / m-MTDATA (30nm) / α-NPD (20nm) / Alq_3 (30nm) / BMB-nT (n = 2 and 3) (20nm) / Mg:Ag.[38]

Figure 1 shows the side view of the fabricated single-layer, electron-only devices of varying thickness, glass / ITO / Mg:Ag (20nm) / BMB-nT(50–260nm) / Mg:Ag (100 nm) and the chemical structures of BMB-nT (n = 2 and 3).

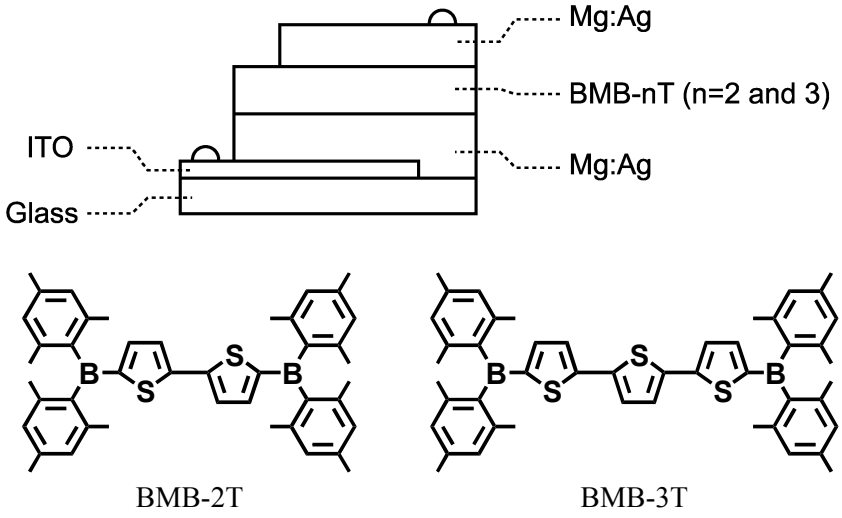

Figure 1 Side view of electron-only, single-layer devices and chemical structures of BMB-2T and BMB-3T.

In order to check the symmetrical structure of the fabricated devices, the current density (J) – voltage (V) characteristics were measured by applying two oppositely driven voltages. The currents were almost the same for both directions. This result indicates that the devices are symmetrical. The solid-state electron affinities (EA) of BMB-nT (n = 2 and 3) are almost the same, being approximately 3.3 eV, as estimated from their reduction potentials ($E_{1/2}$ = −1.76 V vs. Ag/Ag^+ 0.01 mol dm^{-3}) and the reduction potential and the solid-state EA of Alq_3 ($E_{1/2}$ = −2.01V vs. Ag/Ag^+ 0.01 mol dm^{-3} EA: ca. 3.0 eV [35]). The solid-state ionization potential (Ip) of BMB-nT (n = 2 and 3) are ca. 6.2 eV and 6.0 eV, respectively, as estimated from their oxidation potentials and the oxidation potential and the solid-state ionization potential of m-MTDATA ($E_{1/2}$ = 0.06 V vs. Ag/Ag^+ 0.01 mol dm^{-3}, Ip = 5.1 eV).[39,40] The solid-state Ips of BMB-2T and BMB-3T have been determined to be 6.25 and 5.85 eV, respectively, by ultraviolet photoemission spectroscopy, and the solid-state EAs of BMB-2T and BMB-3T have been estimated to be 3.45 and 3.25 eV, respectively, from their optical band gaps.[41] Considering that the work function of the metal Mg:Ag is ca. 3.7 eV, while the energy barrier for electron injection from the Mg electrode into BMB-nT (n = 2 and 3) is approximately 0.25 and 0.45 eV for BMB-2T and BMB-3T, respectively, those for hole injection are 2.15 and 2.55 eV for BMB-2T and BMB-3T, respectively. Since the energy barriers for hole injection are much higher than those for electron injection in the present single-layer devices, hole injection can be neglected, and the current flowing through the devices is considered to be mainly due to electrons injected.

J−V characteristics of the devices using BMB-nT sandwiched between the two Mg electrodes were analyzed in terms of the SCLC (eq.1), thermoionic emission (eq.2), and Fowler-Nordherm tunnelling (eq.3) models.

$$J \times d = \frac{9}{8}\varepsilon_0 \varepsilon \mu E^2 \tag{1}$$

$$J = AT^2 \exp\left[-\frac{\Delta - \left(e^3/4\pi\varepsilon\varepsilon_0\right)^{1/2} E^{1/2}}{kT} \right] \tag{2}$$

$$J = BE^2 \exp\left[-\frac{b}{E} \right] \tag{3}$$

where ε_0 is the permittivity of vacuum, ε is the relative permittivity of the material and μ is the charge carrier mobility, A is the Richardson constant, T is the temperature, k is the Boltsmann constant, e is the elementary charge, and Δ is the energy barrier for charge carrier injection. $B = e^3/8\pi h\Delta$ and $b = [8\pi(2m^*)^{1/2}\Delta^{3/2}] / 3he$, where h the Planck constant, and m* is the effective mass of electron.

Figure 2 shows the J−V characteristics of the devices of varying thickness (from 50 to 260 nm). The results show that the current density of the devices definitely depends on the thickness (d) of the BMB-nT (n = 2 and 3) layer; the current density increased strikingly with decreasing thickness. The plots of ln(J) vs. $E^{1/2}$ in terms of the thermionic emission model and the plots of $\ln(J/E^2)$ vs. 1/E in terms of the tunnelling model did not give any linear relationship. It is indicated that the J−V characteristics of the present single-layer devices are not injection limited. The plots of J times d vs. E were almost independent of the thickness of the electron-transporting layer, as shown in Figure 3. This result is in agreement with the trap-free SCLC model (eq.1.) and suggests that the J–V characteristics of the present devices are conduction limited.

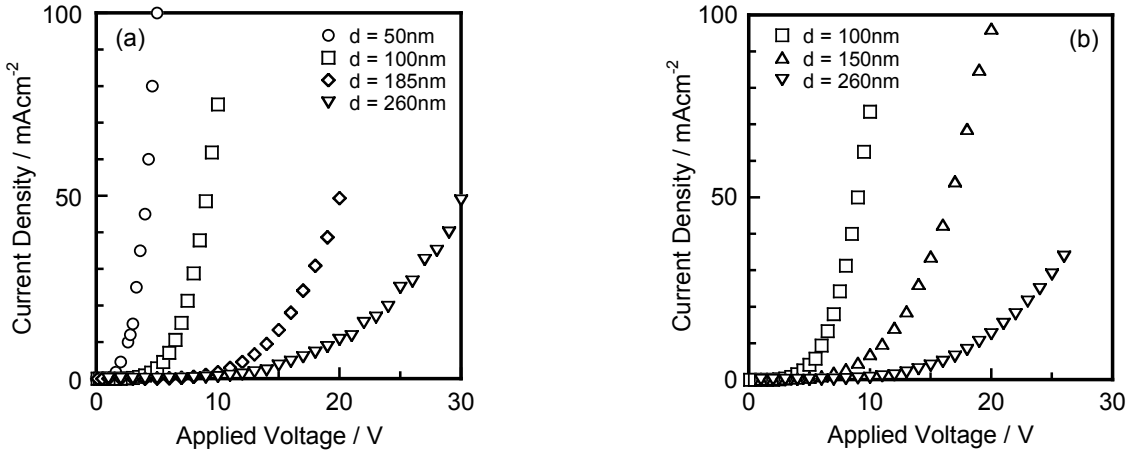

Figure 2 Current density - voltage characteristics of electron-only devices using (a) BMB-2T and (b) BMB-3T.

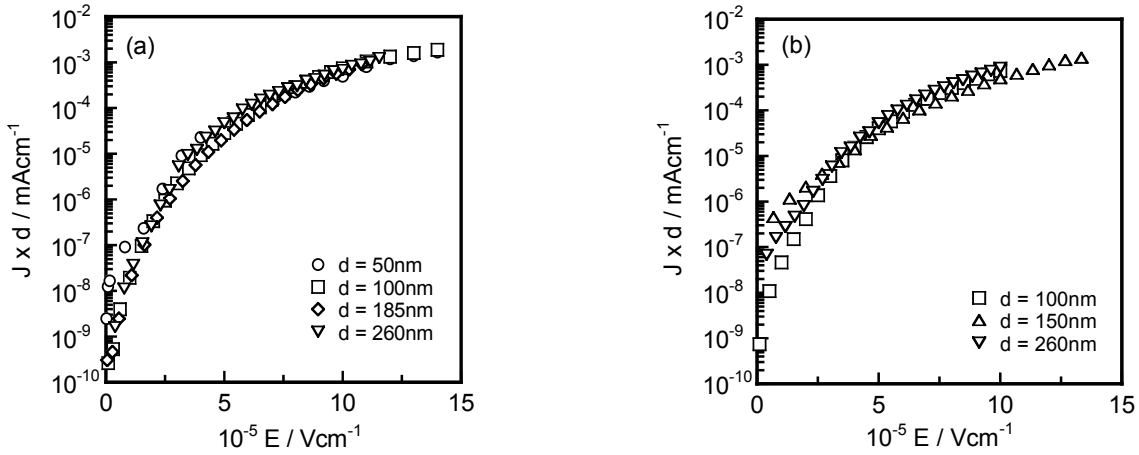

Figure 3 The plots of J × d vs. E for the electron-only devices using (a) BMB-2T and (b) BMB-3T.

The electron mobilities μ_e of BMB-nT (n = 2 and 3) can be estimated from the SCLC according to eq. 1 on the assumption that the relative permittivity ε of BMB-nT is 3. The values of the μ_e of BMB-nT (n = 2 and 3) were approximately 4×10^{-6} $cm^2V^{-1}s^{-1}$ at an electric field of 1×10^6 Vcm^{-1}.

While the energy barrier for electron injection from the Mg electrode into Alq_3 is approximately 0.6 ~ 0.7 eV,[35] that for electron injection from the Mg electrode into BMB-nT (n = 2 and 3) is approximately 0.40 eV as estimated from their cathodic reduction potentials or 0.25 and 0.45 eV for BMB-2T and BMB-3T, respectively, as estimated from their solid-state Ips determined by ultraviolet photoelectron spectroscopy and their optical band gaps. The smaller energy barrier makes electron injection from the Mg cathode into BMB-nT (n = 2 and 3) easier than that from the Mg cathode into Alq_3. The present results suggest that the contact between BMB-nT (n = 2 and 3) and the Mg electrode is nearly ohmic irrespective of the presence of a small energy barrier. It has been reported that the current becomes space-charge limited when the energy barrier for injection is smaller than approximately 0.3~0.4 eV and that the current is injection limited when the energy barrier is larger than the value with regard to the hole injection from the electrodes into poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV).[42,43] Our result is consistent with this report.

3. CONCLUSION

Electron-injection behavior from the Mg electrode into electron-transporting amorphous molecular materials, BMB-2T and BMB-3T, was investigated using electron-only, single-layer devices sandwiched between the two Mg electrodes. The current density − voltage characteristics of the devices of varying thickness can be explained in terms of SCLC. The present result suggests that the contact between BMB-nT (n = 2 and 3) and the Mg electrode is nearly ohmic.

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