Rectification Characteristics of C₆₀-doped 4-(2,2-diphenylethenyl)-N,N-bis(4-methylphenyl)-benzenamine Dual-layer Device

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ABSTRACT
To achieve an efficient hole injection into triphenylamine derivatives cast on an Au electrode, we focused on the use of Fullerene (C₆₀)-doped triphenylamine derivative as a buffer layer. After measuring the current-voltage properties of a layered device with the Au/C₆₀-doped triphenylamine derivative/triphenylamine derivative/Au, hole injection was improved only at the interface where C₆₀ was introduced. In addition, when 1 mol% of C₆₀ was doped, the energy barrier for the hole injection decreased to 0.06 eV from 0.43 eV. Overall, we successfully developed a device with enhanced rectification properties.

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Keywords: Fullerene, Triphenylamine Derivative, Hole Injection, Rectification

1. Introduction

Organic semiconductors are being intensively investigated for application to functional devices and have been developed in recent years for use in organic photovoltaics (OPVs),1 organic light-emitting diodes (OLEDs),2 and organic photodiodes (OPDs).3 Triphenylamine derivatives are p-type organic semiconductors and commonly used in organic photoconductors as hole-transport materials for laser-beam printers.4,5 Furthermore, they are suitable for high-volume production and possess a high chemical stability. However, there are two significant issues to employing them in functional organic devices: (i) they have a low hole mobility and (ii) they have a high hole-injection barrier for metal electrodes.

Regarding the improvement of carrier mobility, single crystallization has been developed as a promising technique. Indeed, single crystals of triphenylamine derivatives exhibited conductivities of magnitudes higher than those of amorphous materials.6-8 However, there has not been an established technique for achieving easy hole injection. Particularly in the case of metal/hole-transport layer/metal devices, these need a high voltage to inject a hole into the hole-transport layer even when the Au electrode (having a large work function) is used.

Fullerene C₆₀ is widely known as an electron acceptor molecule. There are many studies in which C₆₀ has been employed as a hole-injection layer between the organic-semiconductor layer and the electrode.9,10 Lee reported that the interfacial energy barrier of the Al/N,N′-di(1-naphthyl)-N,N′-diphenyl benzidine device decreased to 0.3 eV by inserting a C₆₀ buffer layer at the interface.10

The objective of this study was to investigate the effect of C₆₀ doping on hole-injection properties in a triphenylamine derivative. In order to achieve a more efficient hole injection, a layer with a mixture of C₆₀ and triphenylamine derivative was employed as a hole-injection layer. Therefore, a device of Au/C₆₀-doped triphenylamine derivative/triphenylamine derivative/Au was fabricated and its rectification property was evaluated.

2. Experimental

4-(2,2-Diphenylethenyl)-N,N-bis(4-methylphenyl)-benzenamine (TPA) was used as a triphenylamine derivative and obtained from Ricoh company Ltd. Its purity was ensured to be one spot in the thin-layer chromatography. The chemical structure is depicted in Fig. 1(a). Cyclic voltammetry was conducted on a 5 mmol·dm⁻³ TPA solution in acetonitrile (FUJIFILM Wako Pure Chemical Corp., 99.8%+%), containing a supporting electrolyte of 0.1 mol·dm⁻³ tetraethylammonium perchlorate (Nacalai Tesque, Inc., ≥99.0%) at a scan rate of 50 mV/s. This was achieved in a three-electrode electrochemical cell composed of a φ100 μm Pt disk (working), Ag/AgCl/Saturated KCl (reference), and a Pt plate (counter). The
layered device was prepared as follows. An Au layer was vacuum deposited on a glass substrate with a thickness of approximately 20 nm. Toluene (FUJIFILM Wako Pure Chemical Corp., 99.5+%) solutions containing 10 wt.% of TPA with C60 (molar ratios of C60 to TPA were 0.1 and 1 mol.%) were used to form C60-doped TPA with 0.3 μm thickness on the Au electrode, using a spin-coating technique. C60 with a purity of >99.0% was obtained from Kanto Chemical Co., Inc. Thereafter, a 50 wt.% TPA-tetrahydrofuran (FUJIFILM Wako Pure Chemical Corp., 99.5+%) saturated solution was recast on the C60-doped TPA layer to make a 2.5 μm-thick TPA layer. The thickness of C60-doped TPA and TPA layers were measured using a Surfcom 130A contact-type thickness meter (Tokyo Seimitsu Co., Ltd.). On the TPA layer, a counter Au electrode was vacuum-deposited in the same manner. Thus, the dual-layered organic devices were fabricated as schematically shown in Fig. 1(b). The current-voltage properties of the device were measured at various temperatures in a vacuum chamber connected to a source meter (Keithley 2612A). Hole injection from the bottom Au electrode was defined as the forward direction in this study.

3. Results and Discussion

Figure 2 shows the cyclic voltammogram of TPA. In the positive potential region, two oxidation peak currents are observed at 0.7–1.5 V vs. Ag/AgCl. The first oxidation current is reversible, but the second one is irreversible.11 In contrast, there is no reduction peak current at the negative potential region down to −1.2 V vs. Ag/AgCl. Hence, it was confirmed that TPA is a hole transport material.5 Focusing on the first redox current peak at ~0.85 V vs. Ag/AgCl, the half-wave potential (E1/2) and the ionization potential (IPHOMO) were determined by Eqs. (1) and (2), respectively:12,13

\[
E_{1/2} = \left( E_{pO}^{ox} + E_{pR}^{red} \right) / 2
\]

\[
IPHOMO = E_{1/2} + 4.5 \text{ (eV)}
\]

where \(E_{pO}^{ox}\) and \(E_{pR}^{red}\) are the potentials of the oxidation and reduction current peaks, respectively; \(E_{1/2}\) in Eq. (2) is a potential with reference to a standard hydrogen electrode (SHE). In consequence, the \(E_{1/2}\) for oxidation and \(IPHOMO\) are calculated to be 0.83 V vs. Ag/AgCl (1.03 V vs. SHE) and 5.53 eV, respectively, which correspond to the results of a previous report.13 Therefore, the energy barrier height of hole injection into TPA on the Au electrode is estimated to be 0.43 eV because the work function for Au was reported as 5.1 eV.14 In contrast, the barrier height for electron injection is assumed to be >1.6 eV since \(E_{1/2}\) for reduction is <−1.2 V vs. Ag/AgCl.

We then evaluated the current density-electric field (J-E) properties of the Au/C60-doped TPA/TPA/Au device as shown in Fig. 3. As for the device without the C60-doped TPA layer (for Au/TPA/Au device), a symmetrical J-E property in forward and reverse direction is observed, which shows that the Au electrodes equally interacted with the organic layer. Considering the estimated barrier heights for hole and electron injections, the observed current is identified as originating from the hole injection into the TPA layer. When C60 was doped in the TPA buffer layer, the onset electric field became lower in the forward direction as the C60-doped amount increased, but it did not change for the reverse direction. These results clearly indicate that hole injection is facilitated through the buffer layer by C60 doping. Therefore, it was discovered in this study that the Au/C60-doped TPA/TPA/Au device has rectifying properties although alternative approaches to develop the rectification properties have been reported.15,16

To quantitatively understand the energy barrier height for hole injection into TPA, we performed the Richardson–Schottky plot analysis.17 The barrier height (\(\Phi_0\)) was calculated using the following equation:

\[
\ln(J/T^2) = \ln(A^*A) - \frac{q(\Phi_0 - E_0/n)}{kT} \quad (3)
\]

where \(J\) is the temperature, \(A^*\) is the diode area, \(A^*\) is the Richardson constant, \(q\) is the electronic charge, \(n\) is the diode ideal factor, and \(k\) is the Boltzmann constant. If \(J_0\), which can be obtained by extrapolating the Schottky line (log\(J-E^{0.5}\)) to the zero-electric field (\(E = 0\)), is used as \(J\) in Eq. (3), \(\Phi_0\) is calculated from the slope of the Richardson line (ln\(J_0/T^2-1/T\)). Figure 4(a) shows a Schottky plot of the Au/1 mol% C60-doped TPA/TPA/Au device at various temperatures, which derives \(J_0\) values. Then, we created a Richardson plot as represented in Fig. 4(b) from the obtained \(J_0\) values. Finally, we calculated \(\Phi_0\) values as listed in Table 1. It should be noted that the \(\Phi_0\) of the non-doped device (Au/TPA/Au) is 0.43 eV, which corresponds well to the barrier height estimated from the half-wave potential analysis. The \(\Phi_0\) for 0.1 mol% and 1 mol% C60-doped devices are calculated as 0.35 and 0.06 eV, respectively. Therefore, we achieved a 0.37 eV decrease of hole-injection barrier by applying C60-doped TPA as a buffer layer. However, the reason why the barrier was lowered remains unclear at present. One possible reason may be the effect of the intermolecular interaction between C60 and TPA. In the future, we plan to clarify the barrier reduction mechanism via spectroscopy, atomic force microscopy, and cross-sectional SEM analyses. Moreover, C60-concentration dependence of barrier height will be also investigated in detail in the future.
4. Conclusions

The current density-electric field properties of Au/C$_{60}$-doped TPA/TPA/Au devices were evaluated. The Au/1 mol% C$_{60}$-doped TPA/TPA/Au device exhibited the lowest energy barrier height for hole injection (0.06 eV) while achieving the rectification property. These results may assist in the design of functional devices such as a rectifier diode, although further investigations to elucidate the barrier decrease mechanism and to achieve lower barrier heights will be necessary.

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Figure 4. (a) Schottky and (b) Richardson plots of the Au/1 mol% C$_{60}$-doped TPA/TPA/Au device.

Table 1. Barrier heights of hole injection for C$_{60}$-doped TPA-layered devices.

| Device          | $\Phi_H$/eV |
|-----------------|-------------|
| Non-doped       | 0.43        |
| 0.1 mol% C$_{60}$-doped | 0.35        |
| 1 mol% C$_{60}$-doped | 0.06        |