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A Numerical Device Model and Approach to Degradation Mechanisms in Organic Light Emitting Diodes (OLEDs)

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1. Introduction

Recently, significant progress has been made in the performance of OLED, particularly with regard to their brightness and lifetime. OLEDs are now a viable technology for the manufacture of large-area flat panel displays (FPD) to compete with Liquid Crystal Display (LCD) and plasma technologies. However, the operating mechanisms including charge-injection, -transport, -trapping, and -recombination phenomena in organic semiconductors are still unclear and require further investigation.

A common approach to estimate the barrier height of an organic-conductor interface is to apply the Richardson-Schottky model [1] with the value of the Richardson Factor (A^*) set for a silicon-metal interface. Alternatively, Scott [2] has proposed that the value of A^* for an organic-conductor interface is dependent on the state density and carrier mobility of the organic material.

Several other groups have reported methods for the demonstration of device parameters such as carrier mobility, Density of State (DOS) and barrier height.[3] We have previously shown impedance spectroscopy (IS) is a useful tool for evaluating relaxation, transport and injection in a variety of organic devices.[4-5]

In this paper, we propose a novel Schottky and IS numerical model to evaluate carrier injection and transport behaviour of organic semiconductor materials. Using this method we have obtained values for A^*, the barrier height, interface state density, DOS and carrier mobility of organic materials and interfaces as device parameters. Additionally, we have approached degradation mechanisms of OLED using transient analysis of pulsed luminescence.

2. Theory

2.1. Modified Schottky Model

The current density of a Schottky organic-conductor interface may be expressed as**:**

$$J_{inj} = A^* T^2 \exp\left(\frac{-e\left(\phi_B - \sqrt{eE/4\pi\varepsilon_i}\right)}{k_B T} \right) \tag{1}$$

$$A^* = \frac{16\pi\varepsilon\varepsilon_0 N_0 \mu k_B{}^2}{e^2} \quad [A/cm^2K^2] \tag{2}$$

where, A^*, T, e, $\boldsymbol{\phi}_B$, E, $\boldsymbol{\varepsilon}_0$, $\boldsymbol{\varepsilon}$, k_B, N_0, and μ are the Richardson factor, temperature, electron charge, barrier height, applied electric field, permittivity of vacuum, relative permittivity, Boltzmann constant, state density and carrier mobility, respectively. The value for A^* as proposed by Scott is dependent on N_0 and μ of the organic material. We have modified the Schottky equation to include $\boldsymbol{\phi}_B$ and a non-zero electric field.

2.2. Complex Capacitance Model for IS

Complex permittivity and capacitance are described as follows:

$$\varepsilon_c = \varepsilon_r - i\varepsilon_i \qquad C_R = \varepsilon_r \frac{S}{d}$$

$$C_I = \varepsilon_i \frac{S}{d} = \frac{\sigma S}{\omega d}$$

where, C_R, C_I, $\boldsymbol{\varepsilon}_r$, $\boldsymbol{\varepsilon}_i$, $\boldsymbol{\sigma}$, $\boldsymbol{\omega}$, S, and d are the real part of capacitance, imaginary part of the capacitance, real part of permittivity, imaginary part of the permittivity, conductance, angular frequency, active area and thickness of organic semiconductor, respectively. C_R and C_I are expressed by Naito's model and our model as follows:

$$C_R(\omega) = \frac{1}{2R_i\delta\omega} \frac{B}{(1+A)^2 + B^2} \tag{3}$$

$$C_I(\omega) = \frac{S D_{it}}{2\omega d\delta} v_{th} S_t C_0 V \exp\left(\frac{-q\left(\phi_B - \sqrt{qE/4\pi\varepsilon_i}\right)}{k_B T} \right) ln\left(1+\omega^2\tau^2\right) \tag{4}$$

where, R_i, $\boldsymbol{\delta}$, $\boldsymbol{v}_{th}$, S_t, C_0, V, q, D_{it}, $\boldsymbol{\tau}$ are the low-frequency incremental resistance of the diode, the trapping parameter, the thermal carrier velocity, the capture cross-section, the static electric capacitance of the organic layer, the bias voltage, the electron charge, the interface state density and the time constant for the characteristic time required to fill & empty the interface state, respectively.

The variables A and B are expressed as follows:

$$A = N_t(E_0) S_t v_{th} \frac{k_B T \pi}{2\omega}$$

$$\frac{d\omega B}{d\omega} = N_t(E_0) S_t v_{th} \frac{k_B T \pi}{\omega}$$

$$N_t(E_0) = N_0 \exp\left(-\frac{T_0}{T} \ln \frac{N_V \cdot S_t v_{th}}{\omega} \right)$$

where, $N_t(E_0)$ is the energy distribution of the localized state density at the valence band edge, N_V is the effective density of state in the valence band and N_0 is the density of localized states at the valence band edge (DOS).

3. Experimental

3.1. HOD and EOD

We fabricated hole-only device (HOD) ; glass / ITO (150nm) / TcTa (70nm) / Al (150nm) and electron-only device (EOD) ; glass / ITO (150nm) / TmPyPB (70nm) /LiF (1nm) / Al (150nm).

Temperature dependent I-V characteristics were obtained, under vacuum (1×10^{-2} Pa), with a temperature controlled probe system in order to estimate $\boldsymbol{\phi}_B$ and A^*. Carrier mobility was calculated using the dark injection (DI) – space charge limited current (SCLC) method [6]. A Solartron SI-1255 and 1296 frequency response analyzer system was used for IS measurements.

3.2. Phosphorescent blue OLED

We fabricated a phosphorescent blue OLED having the structure: glass / ITO (150nm) / TcTa (70nm) / mCP:FIrpic (6%,40nm) / TmPyPB (40nm) / LiF (1nm) / Al (150nm). Luminescence and I-V characteristics were obtained with a luminescence colour meter (Topcon MB-7A) and a source-measure unit (Keithley 2400).

4. Results and Discussion

4.1 Determination of Device Parameters

The temperature dependent I-V characteristics of the HOD are shown in the Schottky and Arrhenius plots in Figure 1. Using this data and fits to the numerical model, we have estimated ϕ_B(H)=0.33 [eV] and A^*(H)=1.0×10^{-3} [A/cm^2/K^2] for the injection of hole carriers. The A^* value of the ITO/TcTa interface is much smaller than a metal/Si interface [7]. This suggests that A* is strongly dependent on the combination of materials and its interface.

Figure 2 shows the result of IS measurements and fits to the numerical model. We have estimated D_{it}(H)=5.0×10^8[/cm^2] and H_0(H)=1.0×10^{16}[/cm^3eV] for the hole injection side. However, at low frequencies (<10Hz), the real part of capacitance becomes unstable. We believe that the hole injection interface exhibits a slow trap-and-release phenomenon.

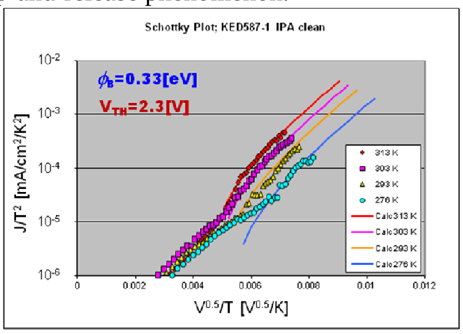

Fig.1. Schottky plot of HOD; Glass/ITO(150nm)/TcTa (70nm)/Al(150nm) and numerical model fittings. Estimated barrier height ϕ_B for injecting hole is 0.33 eV.

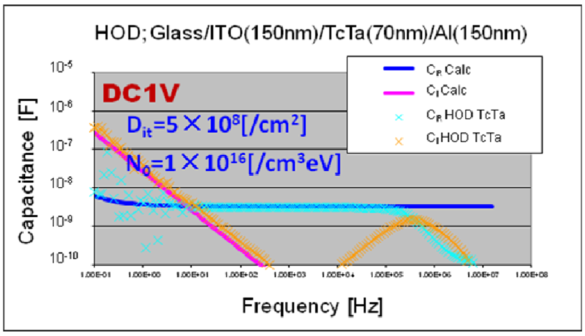

Fig.2. Impedance spectroscopy measurement and model fittings of HOD; Glass/ITO(150nm)/TcTa(70nm)/Al(150nm). Estimated interface state density and density of state (DOS) are 5 × 10^8 /cm^2 and 1 × 10^{16} /cm^3eV at sub-V_{TH} region, respectively.

Likewise, we also obtained the device parameters for the electron injection interface from the temperature dependent I-V characteristics of the EOD. From the measurement data and fits to the numerical model we have estimated ϕ_B(E)=0.65 [eV], A*(E)= 1.0×10^2 [A/cm^2/K^2], $\boldsymbol{D}_{it}$ (E)=5.0×10^{11} [/cm^2] and $\boldsymbol{H}_0$ (E)=2.0×10^{18} [/cm^3eV].

4.2. Characterization of phosphorescent blue OLED

We also obtained highly efficient light blue luminescence (38cd/A and CIE (0.16, 0.31) at 1,000 cd/m^2) .

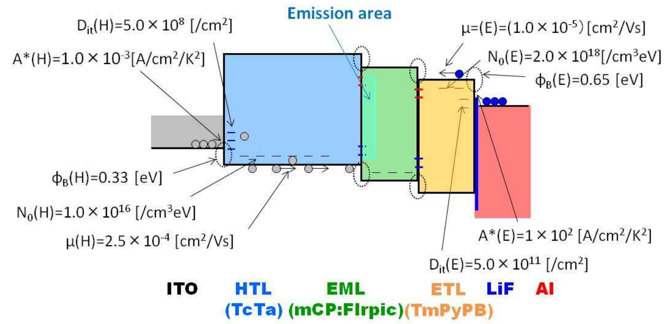

Fig.3. Estimated device parameters of hole and electron injection side are illustrated in standard phosphorescent blue OLED.

The estimated device parameters of the hole and electron injection interfaces and emission area of the FIrpic-doped OLED are shown in Figure 3.

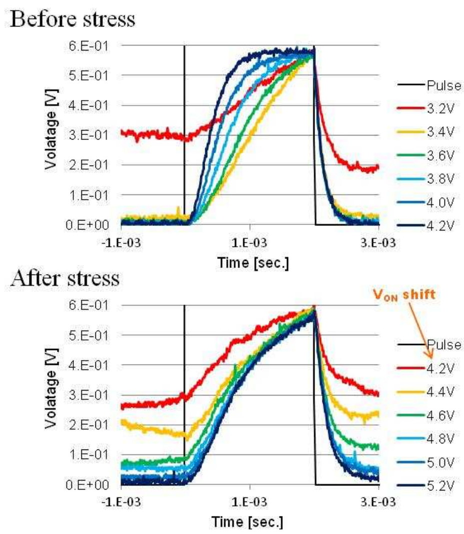

Fig.4. Response of luminescence before/after stress

We tried transient analysis of pulsed luminescence before and after current stress (5mA/cm^2 1hr) as shown Figure 4. A delay of rise time and positive shift of turn-ON voltage (V_{ON}) are observed after stress. We believe the results suggest an increase of interface traps or states at recombination zone as degradation mechanism.

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