# Analysis of Band Structure Near Metal/Organic Semiconductor Junctions Using Impedance Spectroscopy

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# Abstract

A band diagram across a semiconductor device is informative to understand its electrical characteristics. In this work, we propose a method to obtain band diagrams of organic thin-film devices using impedance spectroscopy. Impedance spectrum of a simplified single-layer device was measured and fitted by assuming an equivalent circuit of a multilayer model. The resistivity of each sub-layer obtained was then converted to the relative position of the quasi-Fermi level. By this method, band-bending curves near the Schottky junctions were successfully reconstructed.

## 1. Introduction

Organic photovoltaic (OPV) devices using semiconducting organic molecules or polymers have attracted much attention with increasing energy demand. Organic materials have several benefits against inorganic counterparts such as light weight and flexible nature [1], tunability of photo-absorption spectrum [2], etc. By continuous efforts to improve design of semiconducting molecules and fabrication processes, their photo-conversion efficiency (PCE) is rapidly growing and reached around 12% [3]. To further increase PCE, controlling metal/organic junctions to achieve ideal ohmic contacts of electrodes and reduction of unwanted space charge in organic layers are required. Measurement of the energy band structure through the device is therefore strongly desired to determine the bottle-neck of the device performance. However, because OPVs are composed of many thin layers, measurement of band bending, or electric potential distribution, toward the thickness direction is generally difficult.

There have been several attempts to obtain real band diagrams. For example, direct mapping of band bending by cross-sectional Kelvin probe force microscopy (KPFM) has been reported [4]. However, spatial resolution of KPFM is insufficient to resolve potential distribution in a real OPV devices. In recent years, impedance spectroscopy (IS), which measures the frequency dependence of the complex impedance of a device, has been also applied to OPVs [5]. In most cases of IS analyses, each organic thin-film layer constituting the multiple-layered device is assigned to a pair of resistor and capacitor and the wide-frequency-range spectrum is fitted by changing the circuit parameters.

In our previous study, impedance spectra of blue-light-absorbing OPVs were measured to determine the bias dependence of the circuit parameters and unexpected

negative space charge was found in the p-layer [6]. However, due to the complicity of the OPV devices, it was difficult to resolve the potential distribution within a single layer and therefore fitting to the spectra was not complete. In this study, we apply a multi-layer model to a simplified single-layer device to resolve potential distribution within a single organic layer to reveal the band bending near the Schottky junctions.

# 2. Experimental

Figure 1 shows the sample structure used in this work. A patterned indium tin oxide (ITO) on a glass substrate was used as a bottom electrode. The substrate was cleaned with acetone and UV/O<sub>3</sub>-treated at 150°C. Dibiphenyl-benzothienobenzothiophene (BPh-BTBT, Nippon Kayaku), and tetrafluoro-tetracyanoquinodimethane (F4TCNQ, Tokyo Chemical Industry), and aluminum (Al, Nilaco) were used as a large-ionization-energy p-type semiconductor, an acceptor dopant, and a top electrode material, respectively. Each layer was deposited at 24°C in a vacuum chamber of which background pressure is  $2 \times 10^{-4}$  Pa. The deposition rates were 0.1 and 0.2 nm/s for p- and Al-layers, respectively. During the deposition of p-layer, F<sub>4</sub>TCNQ was co-evaporated by controlling the molar ratio to BPh-BTBT:  $F_4TCNQ = 9:1.$ 

*J-V* characteristics were measured in a dark and nitrogen atmosphere by a parameter analyzer (*Agilent*, *E5272A*). Impedance spectra were measured in the same atmosphere by an LCR meter (*NF circuit*, *ZM2375*) with an applied AC voltage of 10 mV while DC bias voltage was approximately set to the forward-current condition of each device so as to make the current density constant, 10  $\mu$ A/cm<sup>2</sup>. The frequency was sweped from 5.5 MHz to 20 mHz.

## 3. Results and discussion

Figure 2 shows the Cole-Cole impedance plots for the samples of which thicknesses of the doped p-layers are 200 and 300 nm. Curve fitting to the spectra was performed by a



Fig. 1 Sample structure used for impedance spectroscopy and chemical structures of BPh-BTBT and  $F_4TCNQ$ .



Fig. 2 The Cole-Cole impedance plot for different thickness samples under a current density of  $10 \ \mu\text{A/cm}^2$ : the experimental values (circles) and the fitted curves (lines).

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Fig. 3 Equivalent circuit of the multi-layer model. An organic layer is sliced into four (200 nm) or six (300 nm) sub-layers.

least square method using the equivalent circuit for multilayers (Fig. 3). In the multilayer model, the real (Re Z) and the imaginary (Im Z) parts of the impedance are given by Re  $Z = \sum_{i=1}^{n} \frac{R_i}{1 + (\omega C_i R_i)^2} + R_s$  (1)

and

-Im 
$$Z = \sum_{i=1}^{n} \frac{\omega C_i R_i^2}{1 + (\omega C_i R_i)^2}$$
, (2)

where  $\omega$  is the angular frequency,  $R_s$  is the series resistance due to the electrode and lead wires,  $R_i$  and  $C_i$  are the resistance and capacitance components of *i* th sub-layer, and *n* is the number of sub-layers. The total capacitances of the sample (*C*) were determined from the low-frequency limit of -Im Z to be 6.58 and 4.16 nF for 200 and 300 nm samples, respectively. Since the dielectric constant of the p-layer can be regarded as uniform,  $C_i$  was set to *nC* for each sample to simplify the curve fitting. By changing the total number of equal-thickness sub-layers, the equivalent circuits with at least four and six *RC* parallel pairs were found to be necessary for better fitting to the spectra of the 200 and 300 nm samples, respectively. This suggests that the doped p-layer is not uniform along the thickness direction.

From the  $R_i$ s obtained by the fitting, the energy difference between the quasi-Fermi level under the forward bias condition and the valance band edge for each sub-layer was calculated by the following equation:

$$E_{\rm F} - E_{\rm v} = k_{\rm B} T \ln(\rho q \mu_{\rm p} N_{\rm v}), \qquad (3)$$

where  $E_{\rm F}$  is the quasi-Fermi level of holes,  $E_{\rm v}$  is the valance band edge,  $k_{\rm B}$  is the Boltzmann constant, T is the absolute temperature,  $\rho$  is the resistivity, q is the elementary charge,  $\mu_{\rm p}$  is the mobility,  $N_{\rm v}$  is the effective density of states. The mobility was determined on the basis of steady-state space-charge-limited current (SCLC) method to be 6.64× 10<sup>-7</sup> cm<sup>2</sup>/Vs by curve fitting with the Mott-Gurney law,

$$J = \frac{9}{8}\mu_p \varepsilon_r \varepsilon_0 \frac{V^2}{d^3} , \qquad (4)$$



Fig. 4 Reconstructed band diagrams for the organic layers with (a) 200 and (b) 300 nm thicknesses under the hole current injected from ITO. The DC bias voltages applied to ITO are 1.22 and 1.04 V, respectively.

where  $\varepsilon_{\rm f}$  is the relative permittivity,  $\varepsilon_0$  is the permittivity of vacuum, *d* is the thickness of the sample. The  $\varepsilon_{\rm f}$  was calculated to be 70.5 from *C* of the sample. Obtained  $E_{\rm F} - E_{\rm V}$  values for the set of sub-layers are then reordered by assuming Schottky junctions on both ends of two samples and smooth distribution of space charge because the order of the *RC* parallel circuit is arbitrary during the curve fitting.

The final results are summarized in Fig. 4. Note that this graph does not indicate a usual band diagram but a relative position of valance-band edge against quasi-Fermi energy of each sub-layer. Although these are only part of more systematic experiments in the next step, we already notice that the 200 nm device is almost fully depleted. In this case, carrier density in the p-layer is nearly uniform and much smaller than expected from the acceptor concentration. When the thickness is increased to 300 nm, band bending becomes apparent. Its asymmetric shape will be due to the difference of barrier height between ITO and Al electrodes.

#### 4. Conclusions

The energy band structures were depicted by analyzing impedance spectra of single-layer organic devices. The multilayer model successfully reproduced the complex impedance curves. The 200 nm sample was almost uniform but the 300 nm one was explained with the band-bending due to asymmetric Schottky junctions. Further analyses by changing organic layer thickness and electrode materials will be shown in the presentation.

#### References

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