Evaluation of Hole Mobility in Non-peripherally Alkyl-substituted Tetrabenzotriazaporphyrin Thin Films Utilizing MIS-CELIV Method

Yusuke Nakayama, WooJin Kim, Yuki Nishikawa, Akihiko Fujii, and Masanori Ozaki

Graduate School of Engineering, Osaka Univ.
2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

Abstract

Charge carrier mobility measurement of donor materials for organic thin-film solar cells, alkyl-substituted tetrabenzotriazaporphyrin (CnTBTAPH$_2$), was carried out by using metal-insulator-semiconductor charge carriers extraction by the linearly increasing voltage (MIS-CELIV) method. The carrier mobility based on the hopping process between the molecular columns composed with CnTBTAPH$_2$ was estimated from the current transient signal of MIS-CELIV. The alkyl substituent length dependence of the mobility was demonstrated, and the relationship with the inter-column spacing was discussed by taking the evaluated activation energy into consideration.

1. Introduction

Tetrabenzotriazaporphyrin (TBTAP) derivatives, which are organic semiconductor materials and soluble in typical organic solvents, are expected to be applied to solution-processable thin film devices, such as solar cells [1]. The TBTAP molecules tend to form the columnar structure in the thin film by their self-organization, and the excellent carrier transport along the column axis was reported [2]. However, the column axis tends to be parallel to the substrate in the thin film device, such as solar cell, and the carrier transport towards inter-column direction is predominant rather than that along the column axis. Since charge transfer between molecules is based on the overlap of molecular orbitals in general, the carrier transport strongly depends on the inter-molecular distance. Therefore, the substituent length of TBTAP derivatives should affect the carrier mobility in the vertical direction to the substrate.

In this study, the carrier transport properties in thin films of 1,4,8,11,15,18,22,25-octaalkyltetrabenzotriazaporphyrin (CnTBTAPH$_2$), the molecular structure of which is shown in Fig. 1, were investigated. As a measurement method for the carrier mobility in CnTBTAPH$_2$ thin films, "metal-insulator-semiconductor carrier extraction by the linearly increasing voltage" (MIS-CELIV) [3] was adopted, and the substituent-length dependence of carrier mobility was discussed.

2. Experimental

MgF$_2$, which was used as an insulating material, was evaporated onto indium-tin-oxide (ITO)-coated glass substrates in vacuum, and the film thickness was controlled to be 100 nm. CnTBTAPH$_2$ (n = 5, 6, 7, 8), which were synthesized according to the literature [4], were dissolved in chloroform at 20 g/L with 1,8-diiodooctane (DIO) of 0.02 wt%. CnTBTAPH$_2$ layers, the thickness of which was 330-380 nm, were spin-coated. The solution preparation and spin-coating were carried out in an inert gas. 3.0-nm-thick MoO$_3$ and 40-nm-thick Au top-electrode were evaporated through a shadow mask onto the CnTBTAPH$_2$ layer under vacuum below 10^{-4} Pa, resulting in the device structure of ITO/MgF$_2$/ CnTBTAPH$_2$/MoO$_3$/Au.

In the electrical measurement by MIS-CELIV method, the negative offset voltage (V_{off}) from 0 to -5 V was applied to the ITO electrode for injecting holes, then linearly increasing voltage was applied by using a function generator (NF Corporation WF1973). The current transient was measured by a digital oscilloscope (Teledyne LeCroy HDO4054) as a drift current based on holes extracted from the MoO$_3$/Au electrode.
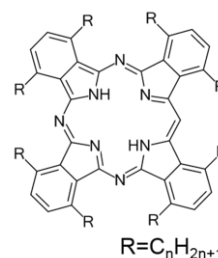

Fig. 1 Molecular structures of CnTBTAPH$_2$

3. Results and discussion

MIS-CELIV current transient consists of the capacitive current density j_0 and extraction current density Δj. Figure 2 shows typical MIS-CELIV current transients of the C6TBTAPH$_2$ thin film device at voltage rising speed A = 333.3 kV/s with various V_{off} as an example. The current density was enhanced depending on V_{off}, and almost saturated at V_{off} = -5 V. The hole mobility μ in the C6TBTAPH$_2$ thin film was evaluated to be 1.3×10^{-3} cm^2/Vs from the current transient at V_{off} = -5 V by using Eqs. (1) and (2).
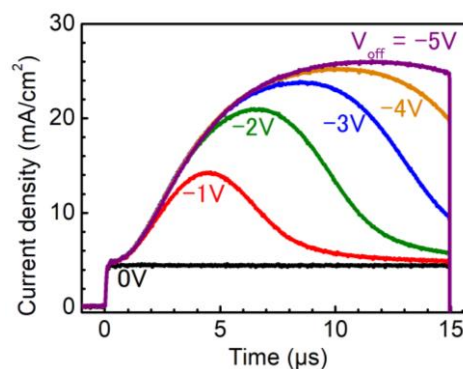

Fig. 2 MIS-CELIV current transients of C6TBTAPH$_2$ thin film device at A = 333.3 kV/s with various V_{off}.

$$\mu = \frac{2d_s^2}{At_{tr}^2}\left(1 + \frac{\varepsilon_s d_i}{\varepsilon_i d_s}\right) \qquad (1)$$

where ε_s (ε_i) is dielectric permittivity of semiconductor (insulator), and d_s (d_i) is thickness of semiconductor (insulator) layer. The time taken for the current to reach $2j_0$ is defined as t_{2j0}, which is related to the carrier transit time (t_{tr}) written by

$$t_{tr} = \frac{4}{\pi}t_{2j0} \qquad (2)$$

under the condition that C_i (capacitance of the insulator) is considerably larger than that of the semiconductor C_s ($C_i/C_s \gg 1$).

The hole mobilities for CnTBTAPH$_2$ with different length of alkyl chains, that is C5TBTAPH$_2$, C7TBTAPH$_2$, and C8TBTAPH$_2$, were also evaluated by MIS-CELIV method. The hole mobility was markedly reduced depending on the alkyl chain length as shown in Fig. 3, that seemed to be strongly related to the inter-molecular distance, and regards a typical characteristic originating from hopping conduction.
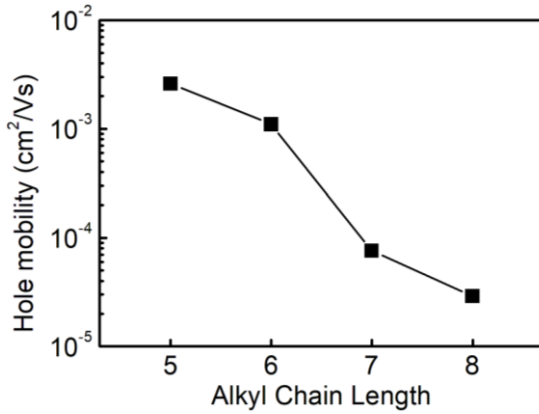

Fig. 3 Alkyl chain length dependence of hole mobility of CnTBTAPH$_2$.

Table 1 Inter-column spacing of CnTBTAPH$_2$ in the spin-coated thin films.

Alkyl chain length n	5	6	7	8
Inter-column spacing (nm)	16.7	19.2	20.3	22.8

In the X-ray diffraction patterns of CnTBTAPH$_2$ spin-coated thin films, strong and sharp peaks appeared at the low angles, and the inter-column spacing could be determined as shown in Table 1. The alkyl chains substituted at non-peripheral positions should surround the molecular core of TBTAP and locate between the columns, therefore, the longer alky chains contribute to the large inter-column spacing. The higher mobility of C5TBTAPH$_2$ shown in Fig. 3 can be explained by the shorter inter-site distance in the hopping conduction.

In order to determine the activation energy (E_a) of the hopping conduction in CnTBTAPH$_2$ thin films, the temperature dependence of hole mobility in the CnTBTAPH$_2$ thin films was investigated. Figure 5 shows the hole mobility in C6TBTAPH$_2$ thin film at 300-390 K, and actually indicates a thermal activation type behavior, namely, Arrhenius-type behavior [5], that also indicates a feature of hopping conduction. The Arrhenius activation energy E_a was successfully evaluated to be $E_a = 25$ meV by using Eq. (3).

$$\mu = \mu_0 \exp\left(-\frac{E_a}{k_B T}\right) \qquad (3)$$

where k_B is Boltzmann constant, T is temperature, and μ_0 is the parameter of mobility prefactor.

The further results including the alkyl chain length dependence of E_a and the detailed discussion about the carrier transport mechanism in CnTBTAPH$_2$ thin film will be demonstrated in our presentation of the conference.
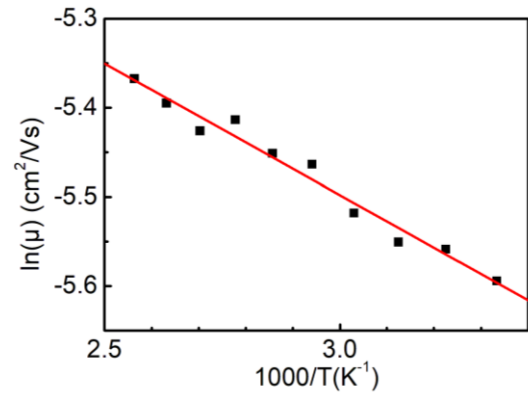

Fig. 4 Temperature dependence of hole mobility in the C6TBTAPH$_2$ spin-coated thin film

4. Conclusions

The hole mobility of CnTBTAPH$_2$ was successfully estimated by MIS-CELIV method, and the alkyl chain length dependence of the mobility was demonstrated. The carrier transport in the CnTBTAPH$_2$ thin films could be explained by the hopping process towards the inter-column direction, and the activate energy of C6TBTAPH$_2$ was evaluated to be 25 meV. The detailed studies are now in progress to clarify the carrier transport mechanism regarding different length of alkyl chains and would be reported in our presentation.

References
[1] J. C. Swarts *et al.*, J. Mater. Chem. **11** (2001) 434.
[2] Y. Miyake *et al.*, Appl. Phys. Express **4** (2011) 021604.
[3] G. Juška *et al.*, J. Non-Cryst. Solids **358** (2012) 748.
[4] A. Fujii *et al.*, Mol. Cryst. & Liq. Cryst **653** (2017) 22.
[5] I. Fishchuk *et al.*, Phys. Rev. B **81** (2010) 045202.