# 耐熱性を有する塗布型有機半導体材料の開発

福　田　　　貴[*1]
渡　辺　真　人[*1]
羽　村　　　敏[*1]

## A Soluble Thermally-Stable Organic Semiconductor Material for Field-Effect Transistors

Takashi FUKUDA
Makoto WATANABE
Satoshi HAMURA

A novel solution-processable low molecular weight organic semiconductor material TS-5, which has high thermal stability and solubility with various aromatic solvents, was developed. Field effect transistors (FET) fabricated using TS-5 as an active layer, exhibited p-type transistor responses with mobilities greater than 1.0 $cm^2$/Vs and are stable at 150℃ in air condition.

### 1. Introduction

Organic field-effect transistors (OFETs) are particularly attractive as their fabrication processes are simple compared with conventional silicon technology, which involve high-temperature and high-vacuum deposition processes. The low process temperature of OFETs enables the compatibility with plastic substrates for lightweight and flexible products.

For high performance OFETs, organic semiconductors with a high mobility, stability, and processability are needed. The solution-processed organic materials in transistors have to be stable for practical applications. Recently, low molecular weight organic semiconductors, such as bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), have been shown to yield high performance devices [1]. Although the possibility of photooxidation of pentacene analogs cannot be completely excluded [2], polyacene compounds give high performances because of increased $\pi$-stacking. It is known that TIPS-pentacene undergoes a structural phase transition at 124℃ and the mobilities are reduced after heat treatment at 120℃ [3]. Benzene-thiophene fused heteroacene compounds such as 2,7-dialkyl[1]benzothieno[3,2-b]benzothiophenes (Cn-BTBTs) show hole mobilities greater than 1.0 $cm^2$/Vs [4]. Furthermore Cn-BTBTs are highly stable to oxidation because of their low lying highest occupied molecular orbitals (HOMOs). However, low HOMO levels lead to high injection barriers for carriers from electrodes and such materials are thermally unstable because of their low melting points (ca. 130℃ ). Therefore, there is a demand for thermally stable organic materials with high mobilities. Here we report the properties of a novel low molecular-weight fused ring compound TS-5, and electrical characteristics of FETs.

### 2. Experimental

FET Fabrication

Field effect transistors were fabricated in top-contact configuration on a doped n+-Si wafer with a thermally

＊1　四日市研究所

grown oxide layer (200 nm). A TS-5 thin film (50 nm) was deposited using the drop cast method from a 0.2 wt% toluene solution onto the Si/$SiO_2$ substrate in air. The solvent was evaporated under atmospheric pressure. On top of the organic thin film, gold drain and source electrodes were deposited in vacuo to yield devices with a channel length (*L*) of 15–20 μ m and a channel width (*W*) of 500 μ m (**Fig. 1**).

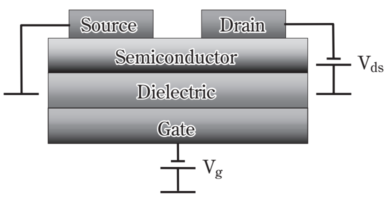


**Fig. 1** FET device structure

The electrical characteristics of TS-5 were measured in ambient conditions. The field-effect mobilities were achieved in the saturation region from the square root of the drain current versus gate voltage curve, using

$$I_d = \frac{C \mu_{sat} W}{2L} (V_g - V_{th})^2$$

where $I_d$ is drain current, C is capacitance per unit area, $V_g$ is gate voltage, and $V_{th}$ is threshoud voltage. The current on/off ratios were determined from the $I_d$ between $V_g$ = 0 V and -50 V.

## 3. Results and Discussion

### [1] Characteristics of TS-5

Molecular orbital (MO) calculations were carried out using the DFT method at the B3LYP/6-31G* level. The calculated HOMO and LUMO levels for TS-5, pentacene, and BTBT are shown in **Fig. 2**. The HOMO level of TS-5 is -5.15 eV, while that of pentacene is -4.60 eV and BTBT is -5.54 eV. Since the work function of gold is 5.1 eV, a smooth carrier injection from the gold electrode to TS-5 is expected. As TS-5 has a large band gap, it is stable in air.

**Figure 3** shows a tracing differential scanning calorimetry (DSC) measurement. No signal could be assigned to a structural phase transition, and only a melting point (ca. 190℃) was observed. This indicates that TS-5 is thermally stable.

Since TS-5 is soluble in various aromatic solvents

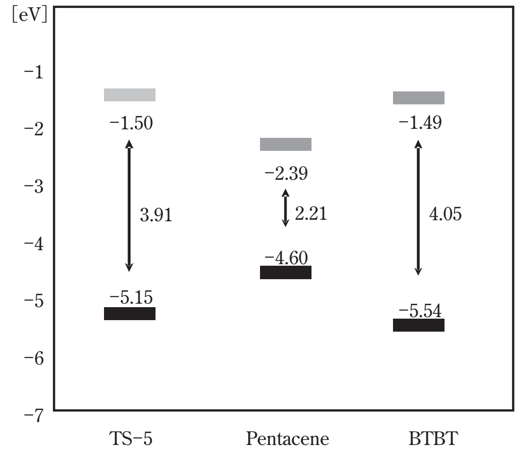


**Fig. 2** HOMO and LUMO energy levels of TS−5, pentacene and BTBT

at room temperature (**Table 1**), solution processed techniques can be used to incorporate it as the active layer in OFETs. Liquid chromatography analysis revealed that no oxidized compounds of TS-5 were formed after 2 weeks in air.

### [2] Electrical Characteristics of FET

The FETs exhibited typical p-type transistor behavior, with hole mobilities as high as 1.27 $cm^2$/Vs and on/off ratios of $3.6 \times 10^7$ (**Fig. 4**). When the FETs were heated at 150℃ for 15 min in air, the electrical performances did not change. These results indicate that TS-5 FETs are stable.

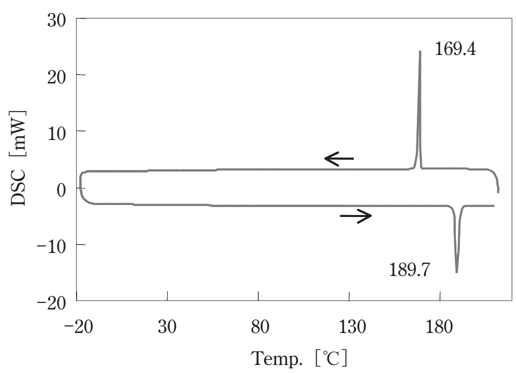


**Fig. 3** DSC trace of TS−5

**Table 1** TS−5 solubility in aromatic solvents

| Solvent | Solubility (wt%), 25℃ |
|---|---|
| toluene | 1.13 |
| tetraline | 1.10 |
| m−xylene | 0.971 |
| mesitylene | 0.749 |
| pentylbenzene | 0.479 |

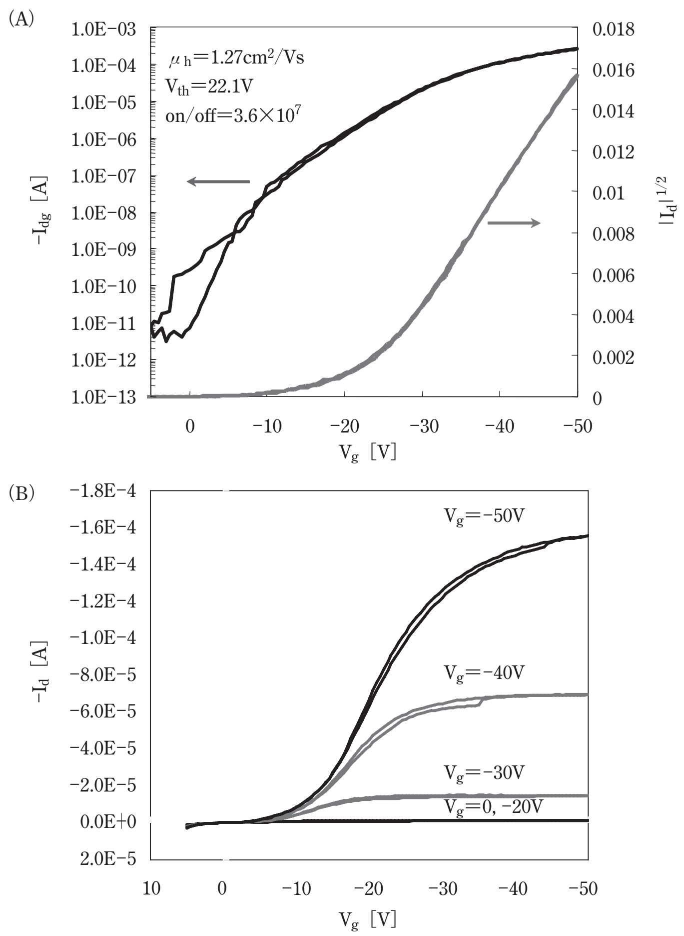


**Fig. 4**　(A) Transfer characteristics ($V_d$=−50V) and (B) output characteristics of a TS-5 FET

## ［3］Characterization of TS-5 thin films

The X-ray diffraction (XRD) spectrum of the TS-5 thin film on a $Si/SiO_2$ substrate is shown in **Fig. 5**. A series of 12 diffraction peaks, assigned to the (00l) reflections, indicate the film's high crystallinity. The inter layer distance (d-spacing) calculated from these reflections is 17.8 Å, which correlates with the dimensions of the c axis. The c axis is oriented perpendicular to the substrate and the ab plane is parallel to the substrate.

**Figure 6** shows the AFM image of the thin film. A series of flat terraces were observed over a range of micrometers on the surface. The height of the step is 1.8 nm, which is consistent with the d-spacing from the XRD pattern. The flat surface and the well-defined molecular steps indicate that TS-5 forms a molecularly flat thin film extending across a micrometer area on the

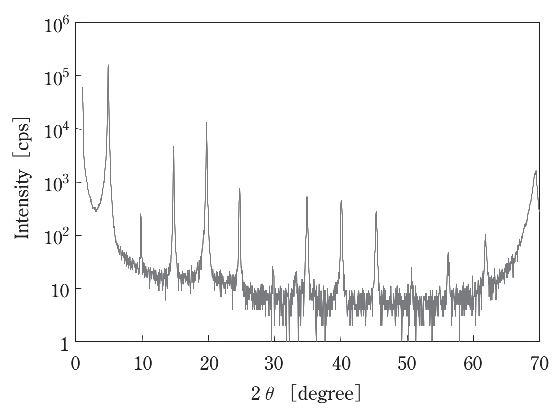


**Fig. 5**　XRD reflections for a drop-casted TS-5 thin film

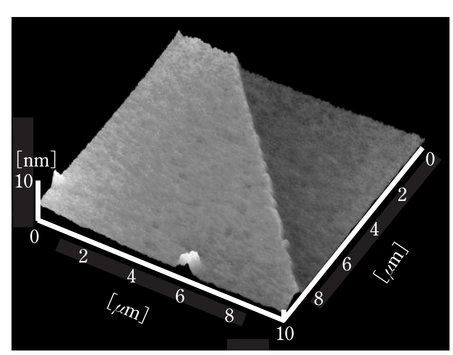


**Fig. 6**　AFM image of a TS-5 thin film

$SiO_2$ surface. This structure enhances the charge carrier mobilities.

## 4. Conclusion

A novel low molecular-weight semiconductor material TS-5 was developed. The compound is soluble in various aromatic solvents with an oxidation resistance in air, and useful using as an active layer of FET devices by solution process. FETs fabricated with TS-5 exhibited p-type transistor responses with mobilities greater than 1.0 $cm^2/Vs$ and on/off ratios $3.6 \times 10^7$. In addition, TS-5 thin films have high thermal stabilities in an atmosphere. As a highly oriented TS-5 crystalline thin film was obtained using the simple drop casting method under ambient conditions, TS-5 is highly promising for practical usage. We will continue to examine other coating methods and ink formulation of TS-5 to further improve electrical FET performances.

## 5. Acknowledgment

The authors would like to appreciate Dr. Satoshi Hoshino of National Institute of Advanced Industrial Science and Technology (AIST) for helpful suggestion and discussion.

## 6. References

[1] M. M. Payne, S. R. Parkin, J. E. Anthony, C.–C. Kuo, T. N. Jackson, J. Am. Chem. Soc., 127, 4986-4987 (2005); b) S. K. Park, T. N. Jackson, J. E. Anthony, D. A. Mourey, Appl. Phys. Lett., 91, 063514 (2007).
[2] K. Ono, H. Totani, T. Hiei, A. Yoshino, K. Saito, K. Eguchi, M. Tomura, J. Nishida, Y. Yamashita, Tetrahedron, 63, 9699-9704 (2007).
[3] J. Chen, C. K. Tee, J. Yang, C. Shaw, M. Shtein, J. Anthony, D. C. Martin, J. Polym. Sci., Part B : Polym. Phys., 44, 3631-3641(2006).
[4] H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, T. Yui, J. Am. Chem. Soc., 129, 15732-15733 (2007).