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Evaluation of Seebeck Coefficients of Organic Thin Films toward Flexible Thermoelectric Power Generators

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1. Introduction

A thin flexible power generator is strongly desired for the wearable electronics that is one of the future images of the organic electronics. The thermoelectric power generator that uses the human-body-originated heat is one of the candidates. In general, the ability of the thermoelectric conversion material is determined by how small the thermal conductivity is and how large the Seebeck coefficient is. Many of organic conducting and semiconducting materials are, in this sense, promising as thermoelectric conversion materials because they have very large Seebeck coefficient, over 1 mV/K, and small thermal conductivity. However, there are only a limited number of studies on the thermoelectricity of organic materials[1-3] and very few especially on small molecules. Therefore, what is necessary now are to precisely evaluate the Seebeck coefficients of various organic conductor/semiconductor thin films and to examine what kind of material is the most promising as a thermoelectric conversion material.

To carry out such experiments, it is necessary to measure the samples in ultra-high vacuum with strictly controlled purity because their electrical characters are greatly influenced by the oxygen and water in the atmosphere. Since there is no commercial instrument that meets such a demand, an original one has been developed in this study to precisely evaluate both the Seebeck coefficient and the electric conductivity of an organic thin film under strict purity control. In this presentation, we present the detail of the instrument and some examples of the evaluation of thermoelectric ability.

2. Development of Seebeck Coefficient Measurement System for Organic Thin Films

The requirements for the instrument are as follows: (1) a thin film of the mixture of the host and dopant materials can be deposited in ultrahigh vacuum and the Seebeck coefficient and the electrical conductivity can be measured in-situ, (2) the base temperature and the thermal gradient of the thin film can be precisely controlled, and (3) the input impedance of the voltage measurement circuit must be very high so as to measure the high resistance sample.

Figure 1 shows the schematic illustration of the developed instrument. The numbers with brackets corresponds to the parts designed to meet above requirements. A copper sample holder {marked by number (2)} is set on a large-thermal-capacity heating/cooling stage where the base temperature can be controlled by liquid nitrogen and a programmable thermoegulator. The temperature difference between two gold electrodes on the substrate (ΔT) is controlled by the input electric power to the ΔT heater that is integrated in the sample holder. It was confirmed that ΔT can be proportionally controlled by the input power to the ΔT heater within 0−10°C range and that the temperature gradient obtained between the two electrodes is uniform and one directional. The laboratory-made differential amplifier {marked by number (3)} had nearly 10^{15} Ω input impedance, of which value is sufficient to simultaneously measure the temperatures at two electrodes and the thermopower between them at the same time even for highly resistive materials.

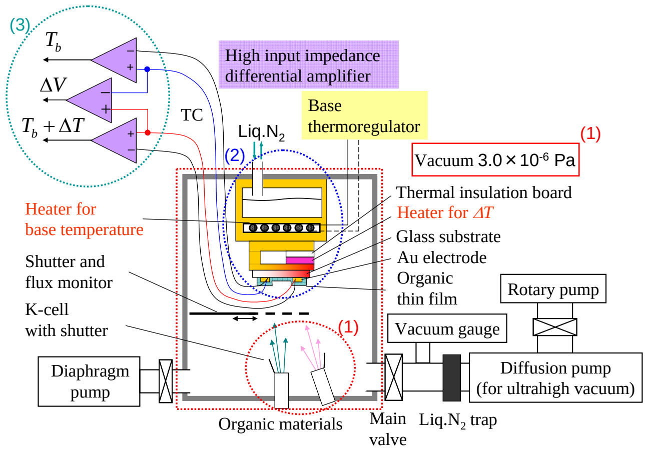

Fig. 1 Schematic illustration of the developed instrument.

3. Test Measurements

For the test of the instrument and also for preliminary study of the thermopower of organic thin films, we have measured the Seebeck coefficients (α) and electrical conductivities (σ) of pure pentacene representing intrinsic semiconductors, acceptor-doped DPh-BTBT[4]:$C_{60}F_{36}$ (10 vol%) representing heavily doped semiconductors, and TTF-TCNQ representing organic conductors.

Glass substrates with Au parallel electrodes (10 mm gap width) were used as substrates, and organic materials were deposited onto the substrates through a shadow mask to bridge the

Table I Summary of the test measurements.

Material	α (mV/K)	σ (μS/cm)	κ (W/Kcm)	Z (K^{-1})	ZT@25℃
Pure pentacene	-0.066	0.50	5.1×10^{-3} [5]	4.3×10^{-13}	1.3×10^{-10}
DPh-BTBT: $C_{60}F_{36}$(10%)	1.2	6.5	5.1×10^{-3} [5]	1.8×10^{-9}	5.5×10^{-7}
TTF-TCNQ	-0.03	65000	5.1×10^{-3} [5]	1.1×10^{-8}	3.4×10^{-6}

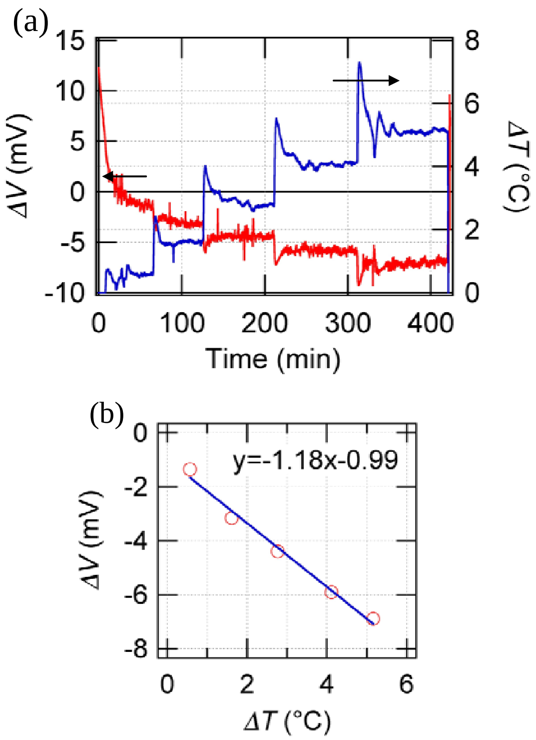

Fig. 2 Typical result of the thermopower measurement at 25°C obtained with DPh-BTBT: $C_{60}F_{36}$(10%)

electrodes. The base temperature (T_b) was then adjusted to 25°C, and potential difference (ΔV) between the electrodes was measured while changing ΔT stepwise as shown in Fig. 2(a). Seebeck coefficient ($\alpha = -\Delta V/\Delta T$) of the material was finally calculated from the linear slope of the ΔV-ΔT plot {Fig. 2(b)} subtracted by the offset Seebeck coefficient of the measurement system, which was premeasured using a Pt thin film.

The results for the three materials are summarized in Table I. Here, the thermal conductivity (κ) of pentacene thin-films[5] was used for all materials to derive the performance index ($Z = \alpha^2\sigma/\kappa$). The majority carrier of pure pentacene in high vacuum was found to be electrons because the Seebeck coefficient was negative. Besides, α is small because it is almost intrinsic. The success of this measurement implies that the developed instrument has a sufficient ability to evaluate highly resistive materials. On the contrary, α of DPh-BTBT:$C_{60}F_{36}$ was positive which indicates that the mixed material is p-type as expected. In this case, it is notable that α is large even though it is a highly doped semiconductor. α of TTF-TCNQ is very small because it can be regarded as an extremely doped semiconductor, although it must be a metal when it is in a perfect crystalline state. If the TTF-TCNQ thin film is assumed to be a semiconductor, the majority career is electrons.

From Table I, the value of ZT still small. For the semiconductors, the carrier density should be optimized. Because the contribution of the electric conductivity to Z or ZT is extremely large in Z and ZT, an organic conductor is also promising as a thermoelectric material.

4. Summary

A specially designed instrument to evaluate Seebeck coefficient and electrical conductivity of the organic material has been developed. Its ability to measure the Seebeck coefficients of highly resistive materials was confirmed. By using the instruments, Seebeck coefficients and Z values of three typical organic functional materials were preliminary evaluated. To find promising organic thermoelectric materials and to know the influence of carrier doping for maximization of Z value, various organic materials will be studied in future using this instrument.

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