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An accurate method to determine the through-plane electrical conductivity and to study transport properties in film samples

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ABSTRACT

The through-plane conductivity of a film sample is critically important because it largely affects the performance of batteries, capacitors, and thermoelectric devices. In this study, we developed a modified four-probe through-plane electrical conductivity measurement method using a coaxial structure. This method is general and works for free-standing film samples. We studied different samples including a steel sheet, highly oriented pyrolytic graphite, and conducting polymers. We confirmed metallic transportation in the steel sheet and hopping transportation in graphite in the through-plane direction by conducting low temperature measurements at 100 K. In the case of a conducting polymer poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate, the conductivity anisotropic ratio decreases with increasing in-plane conductivity. Temperature dependent measurements show two distinct activation energy regimes in the through-plane direction in PEDOT/PSS but almost no change in the in-plane electrical conductivity activation energy. This could be due to additional carrier paths that occur through the more disordered region (the PSS-rich region) in the through-plane direction. We also examined the Meyer–Neldel rule in PEDOT/PSS and concluded that PEDOT/PSS follows the anti-Meyer–Neldel rule, likely due to the high carrier density in the film.

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1. Introduction

Solution processable conductive materials, such as conducting polymers and carbon nanotubes, have attracted considerable attention recently due to their potential applications in energy storage, energy conversions, and flexible electronics [1–3]. In-plane electrical conductivity is generally used to evaluate the performance of these materials. With the development of organic semiconductors and the synthesis and separation of carbon nanotubes, in-plane electrical conductivity has improved significantly over the past years and has already reached the requirements for practical device applications [4–14]. Nevertheless, for most electronic devices, such as batteries, capacitors, and thermoelectric devices, the through-plane electrical conductivity is even more important because the through-plane electrical conductivity greatly affects the device performance when considering the working mechanisms of these devices. Although it is generally recognized that the electric conduction in the in-plane direction and the through-plane direction should be different because most one dimensional materials and polymers have a preferred molecular orientation during film formation, attempts to measure through-plane electrical conductivity are very limited [15]. The primary reason is that two-probe electrical conductivity measurements are dominated by the contact resistance between the electrode and the samples, and therefore it only works for a film with relatively low electrical conductivity. The typical four-probe electrical conductivity measurement is an ideal approach; however, it requires a thick block, which is difficult to make from solution-processed materials.

Recently, we reported the anisotropic thermoelectrical properties of conducting polymer films [16]. In our previous study, a

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typical four-probe in-plane electrical conductivity measurement (Fig. 1a) and a modified four-probe through-plane electrical conductivity measurement using a coaxial structure were conducted on the same film (Fig. 1b). We observed a highly anisotropic ratio in the electrical conductivity and the thermal conductivity of a conducting polymer poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT/PSS). Note that the modified four-probe through-plane electrical conductivity measurement assumes that there is no significant voltage drop between the source and sense probes. This may not always be true depending on the sample properties and the geometric structure. It is necessary to understand the potential errors using this approach. In this study, we successfully improved the measurement protocols by using an electrical finite element method (FEM) simulation and controlling the distance between the source and the sense probe. This method also allowed us to conduct low temperature measurements to understand the transport mechanisms for different materials and for the same material in different directions.

2. Experimental methods

2.1. Materials

Highly Oriented Pyrolytic Graphite (HOPG, 10 × 10 × 1.2 mm^3) was purchased from NT-MDT. Graphite Sheet (PGS EYG-S091210) was purchased from Panasonic. PEDOT:PSS (PH1000, Clevios) was purchased from H.C. Starck. Ethylene glycol (>99.5%) was purchased from TCI Chemicals.

2.2. Film preparation

A 1-mm-thick cross-linked poly(dimethylsiloxane) (PDMS) (SILPOT 184, Toray) film was prepared in a 20 mL polystyrene bottle. PEDOT:PSS solution (10 mL), with or without the addition of ethylene glycol, was added and the polystyrene bottle was heated on a hot plate at 70 °C. After all the solvent was gone, the PEDOT:PSS film was easily detached from the PDMS substrate. The as-prepared free-standing PEDOT:PSS film was annealed at 150 °C for 30 min.

2.3. Characterization

The film thickness was measured using a high-resolution Digimatic measuring unit (VL-50-B, Mitsutoyo). Both the temperature-dependent in-plane conductivity and the through-plane conductivity measurement set-up were constructed in-house. For the in-plane conductivity measurements, the sense and source probes were made of gold wire with a diameter of 0.5 mm. The channel length between the sense probes was fixed to 4.5 mm. The room temperature in-plane conductivity of different samples was cross checked with a four-probe conductivity test meter (MCP-T600, Mitsubishi Chemical Corporation). For the through-plane conductivity measurement, all the probes were made of copper plated with 2 μm of gold. The diameter of the outer source probe was 1 cm. The distance between the source probe and the sense probe was varied from 25 μm to 750 μm. The side surface of the sense probe was coated with 10 μm of insulating polymers (polyvinyl alcohol) to avoid shorting between the source and sense probes. The current was controlled using a source measure unit (Yokogawa GS820), and the voltage and temperature were monitored using a memory data logger (LR8400, Hioki).

3. Results and discussion

To understand the potential errors when using the modified four-probe conductivity measurement method, we performed a FEM simulation using conventional software (EStat, Advance Science Laboratory). Because target samples such as conducting polymers do not have a very high through-plane conductivity value, to simplify the simulation, we fixed the dielectric constant of the sample ($\varepsilon = 3$), made the sample size infinite, and didn't consider the effect of the inner probes (the sense probes) on the electrical field distribution. As shown in Fig. 2, the electric potential drops with increasing distance from the source probe. For a film with a thickness of 100 μm, the potential drops significantly to approximately half at the center of the hole. With increasing film thickness, the potential drops become smaller. For a film with a thickness larger than 1 cm, the potential drops by only approximately 7%. For the sample anisotropic dielectric constant, the voltage drop could be smaller, as shown in Fig. 2d. This simulation demonstrates how we can accurately measure the through-plane electrical conductivity. The most important consideration is to control the distance between the source and sense probes and to measure the voltage drops with distance. In principle, if the source/sense probes are very close, the potential error should be very small. For a 100 μm thick film, using a measurement device with a source/sense probe distance smaller than 25 μm, the voltage drop should be smaller than 20%.

Based on the simulation results, we designed a series of measurement devices. Fig. 3a shows a typical image of a through-plane four-probe electrical conductivity measurement setup bonded inside a stainless steel vacuum chamber. The top view of the device is shown in Fig. 3b. The outer electrodes are used as source probes and the size is fixed in all the devices. The inner electrodes are used as sense probes and the diameter of the probes is varied. All the probes were made of copper plated with 2 μm of gold and were polished after plating. The diameter of the outer source probe was 1 cm. The distance between the source probe and the sense probe

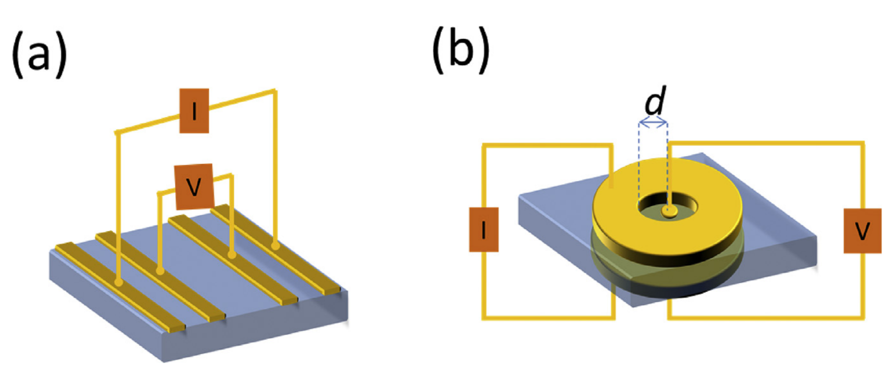

Fig. 1. Schematic of the (a) in-plane and (b) through-plane four-probe electrical conductivity measurement setup.

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