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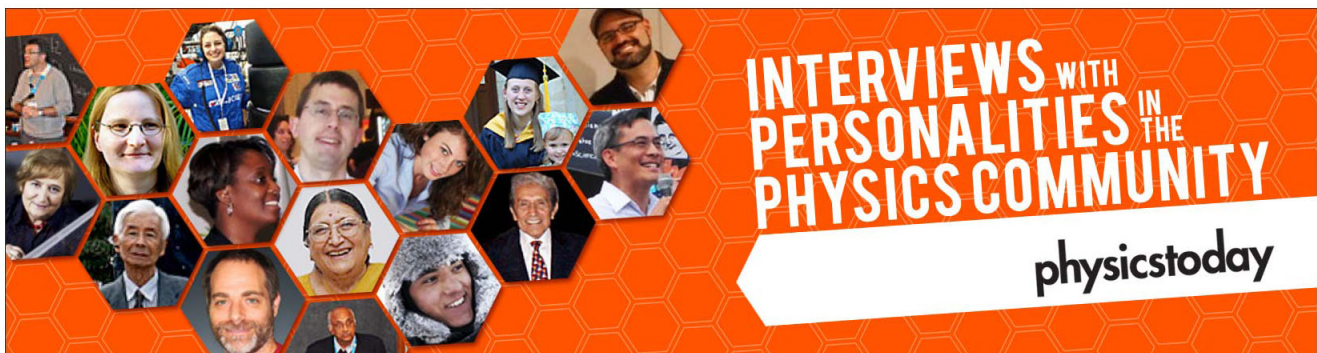
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## ADVERTISEMENT



# High Seebeck effects from conducting polymer: Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) based thin-film device with hybrid metal/polymer/metal architecture

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Conductive polymers are of particular interest for thermoelectric applications due to their low thermal conductivity and relatively high electrical conductivity. In this study, commercially available conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) was used in a hybrid metal/polymer/metal thin film design in order to achieve a high Seebeck coefficient with the value of  $252 \mu\text{V}/\text{k}$  on a relatively low temperature scale. Polymer film thickness was varied in order to investigate its influence on the Seebeck effect. The high Seebeck coefficient indicates that the metal/polymer/metal design can develop a large entropy difference in internal energy of charge carriers between high and low-temperature metal electrodes to develop electrical potential due to charge transport in conducting polymer film through metal/polymer interface. Therefore, the metal/polymer/metal structure presents a new design to combine inorganic metals and organic polymers in thin-film form to develop Seebeck devices. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4761954>]

Organic materials have attracted much attention in the studies of thermoelectric properties.<sup>1–9</sup> The interest in thermoelectric properties of organic materials has been sparked for several reasons. First, organic materials can exhibit tunable electrical and thermal conductivities towards the development of thermoelectric functions through convenient molecular design and morphological control. Second, organic materials are usually less expensive to process and prepare thermoelectric devices. Third, Seebeck effect forms a principle for the development of heat sensors in a broad infrared spectral range. In addition, Seebeck effect is an important parameter in the determination of thermoelectric functions. The Seebeck coefficient is normally defined as

$$S = \frac{\Delta V}{\Delta T}, \quad (1)$$

where  $\Delta V$  is the electrical potential difference created by the temperature gradient,  $\Delta T$ , within the material. In essence, Seebeck effect is established by electrical potential driven by entropy difference in internal energy of charge carriers between high- and low-temperature surfaces. It has been shown that optimizing thermal and electrical conductivity can usually lead to an enhancement on Seebeck effect.<sup>10–12</sup> It has been reported that composites<sup>13–18</sup> and heterojunctions<sup>19–23</sup> can offer effective approaches to control thermal and electrical conductivities in the development of thermoelectric functions. Specifically, polymer composites can also limit the thermal conductivity while still permitting electrical conductivity via combining materials that exhibit high electrical conductivity with insulating polymers that have a low thermal conductivity. Hetero-junctions can be effectively used to lower thermal conductivity by phonon

scattering at the interfaces of separate materials due to boundaries and imperfections. This interface also causes Kapitza resistance due to the acoustic mismatch model.<sup>24,25</sup> In this study, the conducting poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was made into a metal/polymer/metal thin-film device to explore its Seebeck performance. The chemical structure of PEDOT:PSS is shown in Figure 1. The PEDOT:PSS is particularly interesting because of properties such as thermal stability and tunable electrical conductivity.<sup>26</sup> The hybrid metal/polymer/metal thin-film device takes advantage of a structure that restricts thermal conductivity by polymer film while allowing ample electrical conductivity through ohmic interfacial contact. This creates an entropy difference in internal energy of charge carriers across the polymer film within the device thus causing the charge diffusion (holes in this case) from high to low temperature metal.

The metal/polymer/metal structure was made in a sandwich-like architecture with a polymer layer sandwiched between the two metal layers. A 40 nm thick aluminum (Al) layer was evaporated onto a glass substrate at the vacuum of  $2 \times 10^{-6}$  Torr. The PEDOT:PSS layer was then spin cast (at a thickness of 200 nm and 300 nm) on top of the Al layer in a nitrogen atmosphere. In this study, we used commercially available PEDOT:PSS aqueous solutions purchased from H. C. Starck. The purchased solution was Clevios P CH 8000. The PEDOT is conducting contrary to PSS which acts as an insulator, therefore, changing the PEDOT:PSS ratio can largely tune the electrical conductivity of the polymer. The conducting PEDOT:PSS has an electrical resistivity of approximately  $2 \times 10^5 \Omega\text{cm}$ .<sup>27</sup> A top Al layer of 40 nm was then evaporated on the PEDOT:PSS film under the same conditions as the first Al layer. To characterize a hybrid metal/polymer/metal thin-film device, electrical leads and k-type thermocouples were attached to each Al film in order to

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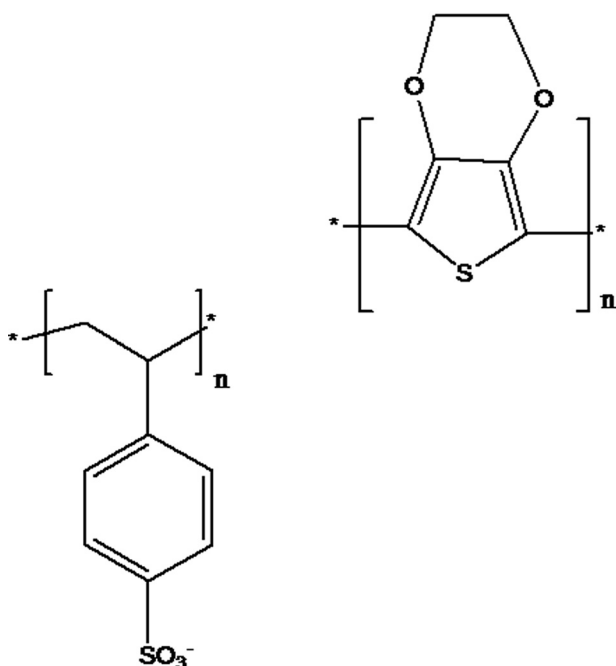


FIG. 1. Chemical structure for conducting polymer PEDOT:PSS.

measure the temperature and potential difference between the two metal layers. This device architecture is illustrated in Figure 2.

A Fisher Scientific Isotemp hot plate and an aluminum heat sink were used to obtain a stable temperature difference within the devices for the Seebeck measurements. The hybrid metal/polymer/metal devices were placed on the heat plate and heated at a rate of 4 °C/min. The top Al layer was connected to a heat sink in order to stabilize temperature difference across the PEDOT:PSS film sandwiched between two Al layers. The voltage difference and temperature gradient were measured using an InstruNet Model 100 Input/Output System. The data were used to calculate the Seebeck Coefficient ( $\Delta V/\Delta T$ ) in which  $\Delta V = V_{HT} - V_{LT}$  and  $\Delta T = T_{High} - T_{Low}$ . The current-voltage (I-V) measurement of the hybrid thin-film device was also taken in order to characterize the electrical conduction at the polymer/metal interface. LAB TRACER software along with a Keithley 2400 power supply were used to take these measurements.

Figure 3(a) shows the Seebeck coefficient as a function of temperature in the metal/polymer/metal hybrid thin-film device with two different PEDOT:PSS film thicknesses. These Seebeck coefficients prove to be high as compared to

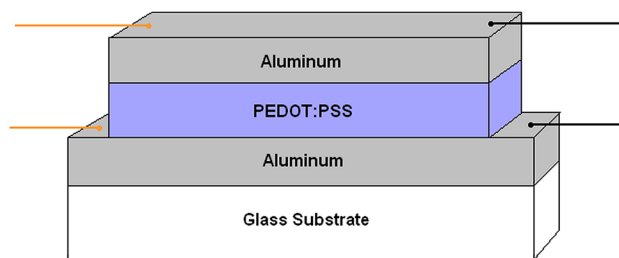


FIG. 2. Schematic structure for Al/PEDOT:PSS/Al device.

the bulk and nanostructure of many organic materials.<sup>28–31</sup> The I-V curve shown in Figure 3(b) indicates that the PEDOT:PSS/Al interface forms an ohmic contact to allow charge transport for the generation of electric potential between high and low temperature Al electrodes. We notice that in Figure 3(a) that the Seebeck coefficient for the hybrid device increases from 14  $\mu\text{V/K}$  to 252  $\mu\text{V/K}$  over the given temperature range from 30 °C to 110 °C for the 200 nm sample. As the film thickness is increased to 300 nm, the Seebeck coefficient increases from 20  $\mu\text{V/K}$  to 158  $\mu\text{V/K}$  over the given temperature range. Therefore, it is clear that thinner and thicker PEDOT:PSS films have different Seebeck coefficients in lower (30 °C–85 °C) and higher (85 °C–110 °C) temperature ranges. At a lower temperature range, the thicker film device exhibits a larger Seebeck coefficient. At a higher temperature range, the thinner film device shows a larger Seebeck coefficient. Clearly, the polymer film thickness can change the Seebeck coefficient in the metal/polymer/metal device. This experimental result implies that a thicker polymer film can lead to a larger entropy difference in internal energy of charge carriers between two Al layers in a lower temperature range. But, a thinner polymer film can generate a larger entropy difference in internal energy of charge carriers at a higher temperature range. We know that a polymer film consists of surface and bulk components with different electron-phonon coupling strengths. Therefore, changing polymer film thickness can vary the overall electron-phonon coupling and consequently changes the entropy difference in internal energy of charge carriers between two Al layers in an Al/polymer/Al device. Our experimental results indicate that thinner and thicker films can exhibit a larger entropy difference between two metal layers at high and low temperature ranges, respectively, towards the development of high Seebeck effect.

In summary, we observe a high Seebeck performance from the commercially available conducting polymer

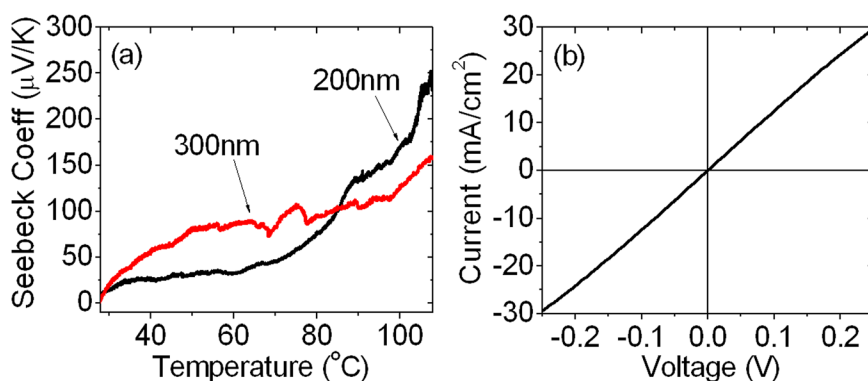


FIG. 3. (a) Seebeck coefficient as a function of temperature measured from Al/PEDOT:PSS/Al device with two different PEDOT:PSS thicknesses: 200 nm and 300 nm. (b) Current-voltage characteristics for Al/PEDOT:PSS/Al device.

PEDOT:PSS used in a hybrid metal/polymer/metal thin film device. The observed high Seebeck effect indicates that the metal/polymer/metal design can develop a large entropy difference in internal energy of charge carriers between high and low-temperature metal electrodes under a temperature difference. This large entropy difference can lead to a sufficient electrical potential for the development of Seebeck effect due to charge transport through ohmic Al/PEDOT:PSS interfaces and bulk PEDOT:PSS film. On the other hand, the low thermal conductivity of bulk PEDOT:PSS film together with phonon scattering at Al/PEDOT:PSS interfaces forms a bottleneck to limit the thermal conduction from high to low-temperature metal electrode in the Al/PEDOT:PSS/Al device. This limited thermal conduction can maintain the entropy difference between high and low-temperature metal electrodes towards the development of Seebeck effect. Therefore, the Al/PEDOT:PSS/Al device can exhibit a significant Seebeck effect. The temperature-dependent Seebeck coefficient suggests that increasing temperature can largely boost electrical conduction through charge density but still limits thermal conduction through interfacial phonon scattering in the Al/PEDOT:PSS/Al device. As a consequence, a high Seebeck effect can be developed at a high temperature. In addition, changing polymer film thickness can vary the Seebeck coefficient in the Al/PEDOT:PSS/Al device through surface and bulk electron-phonon coupling. Clearly, the hybrid metal/polymer/metal thin-film design presents an effective structure to combine high-electrical conducting metals and low-thermal conducting polymers for the development of efficient Seebeck devices.

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