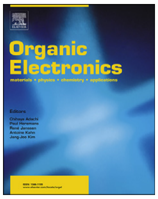
Organic Electronics 31 (2016) 31–40

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Processing and doping of thick polymer active layers for flexible organic thermoelectric modules

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ARTICLE INFO

Article history:
Received 16 October 2015
Received in revised form
16 December 2015
Accepted 5 January 2016
Available online 16 January 2016

Keywords:
Organic thermoelectric generators
P3HT
F_4-TCNQ
Fe^{3+}-$tos_3 \cdot 6H_2O$
Uni-leg-type flexible module

ABSTRACT

While the majority of research on organic thermoelectric generators has focused on individual devices with organic films having thicknesses of several hundred nanometers (nano-films), films with micrometer-scale thicknesses (micro-films) provide a longer thermal conduction path that results in a larger temperature gradient and higher thermoelectric voltages in modules. In this study, the properties of solution-processed nano- and micro-films of the p-type semiconductor P3HT doped with two different dopants, F_4-TCNQ and Fe^{3+}-$tos_3 \cdot 6H_2O$, were investigated. While doping with F_4-TCNQ resulted in high electrical conductivity only in nano-films, doping with Fe^{3+}-$tos_3 \cdot 6H_2O$ from a 25 mM solution yielded power factors of up to ~30 $\mu Wm^{-1} K^{-2}$ with a conductivity of 55.4 Scm^{-1} in micro-films. Changes in the molecular packing were compared based on X-ray diffraction, and the best operational stability in air was found for the Fe^{3+}-$tos_3 \cdot 6H_2O$-doped micro-films. Using Fe^{3+}-$tos_3 \cdot 6H_2O$ as dopant, flexible thermoelectric modules with solution-processed micro-films patterned by a photo-etching technique that does not require alignment and assembly of individual devices were demonstrated, exhibiting a maximum power output of 1.94 nWK^{-2} for a uni-leg module with 48 elements. Analysis of the flexible module performance showed that the performance is limited by the contact resistance, which must be taken into consideration when optimizing module structure.

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1. Introduction

Organic thermoelectric generators (OTEGs) replace the traditional inorganic active materials in thermoelectric generators (TEGs) with organic compounds and have advantages such as low thermal conductivity, light weight, and high flexibility that enable the potential to easily cover large heat exchanger surfaces of any shape and size [1]. Organic materials also offer the prospect of low-temperature solution processing, which could enable the roll-to-roll mass printing of large-area, integrated modules resulting in cost reduction [2]. Thus, OTEGs are poised to become versatile distributed power sources in the near future with applications from wearable electronics to power supplies for mobile devices and distributed sensor networks [3].

The performance of TEGs is often compared based on the figure of merit $ZT = \sigma S^2 T/\kappa$. For high performance with an average temperature between the hot and cold surfaces of T, high electrical conductivity (σ) and Seebeck coefficient (S) are required while maintaining a low thermal conductivity (κ) [4]. Pristine or lowly-doped organic semiconductors can have high S [5,6] and some of the lowest κ among known materials, but generally suffer from low σ. Because of trade-offs between S, σ, and κ, controlling the carrier density in the active materials to increase σ while maintaining high S and low κ is key for optimizing and improving OTEG performance [1,7–10]. In particular, reducing the decrease in S with increasing σ is of great importance since many reported organic thermoelectric materials already have low κ of less than 0.5, which is attributed to poor phonon transport in the amorphous layers [10].

Conducting polymers are good candidates for OTEGs because

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http://dx.doi.org/10.1016/j.orgel.2016.01.007
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the carrier density can be controlled by modifying the chemical oxidation levels [8]. In fact, recent progress using poly(3,4-ethylenedioxythiophene) (PEDOT) has yielded remarkably high thermoelectric performance comparable to that of inorganic materials because of a low κ (0.2–0.4 Wm^{-1} K^{-1}) and high σ (more than several hundred Scm^{-1}) [8,11–13]. Furthermore, conducting polymers can be soluble in many common organic solvents and are viscoelastic, making them suitable for the mass-production of flexible OTEGs [3].

An important consideration for the design of flexible OTEGs is having the longest thermal and electrical conduction paths (*i.e.*, the thickest active layer) possible while maintaining flexibility to obtain the largest temperature gradient and highest thermoelectric voltage. However, the organic thin films used in common organic devices such as light-emitting diodes [14], field-effect transistors [15], and solar cells [16] usually have thicknesses of several tens to a few hundred nanometers (nano-films). To increase power output, fabrication and processing methods for films with micrometer-scale thicknesses (micro-films) must be developed. In particular, the control of carrier density by doping the films is important for optimizing device performance [4]. While doping processes for OTEGs have been widely tested and studied in nano-films [6,8,11,17–21], few investigations of the doping of micro-film OTEGs exist.

In addition to the development of individual devices, the connection of many devices, in series electrically and in parallel thermally, to create modules is necessary to get practically useful thermoelectric voltages [1,4]. A typical thermoelectric module consists of a series of alternately connected p-type and n-type elements forming a π-shape that must be balanced to account for differences in S, σ, and κ and avoid power losses [1,4]. Inorganic thermoelectric modules are generally fabricated by the assembly of individual pieces of the inorganic materials cut from a slab, resulting in expensive and rigid devices with a limited number of existing industrial and natural environments to which they can be easily applied [22].

To overcome these drawbacks, flexible organic thermoelectric modules with the elements simultaneously fabricated directly onto the substrate by solution processing are highly desired [2,22–24]. However, the scarcity of good candidates for organic n-type materials and the complexity of the module design makes the adoption of a π-leg structure difficult [23,25]. Alternatively, the design and fabrication can be simplified by using a uni-leg architecture, in which the top electrode is directly connected to the bottom electrode of the adjacent device, enabling the generation of power by using only one type of thermoelectric material (p-type or n-type) [2,26]. For both types of modules, ink-jet and screen printing have been studied as solution processes to realize the mass production of large-area modules [23,25,26]. However, viscosity and solvent limitations make ink-jet printing slow for fabricating thick active layers [25,26], and controlling the crystal orientation of deposited materials is difficult by screen printing. Thus, alternative fabrication techniques are desirable.

In this paper, the effects of two different dopants on the properties of nano- and micro-films of the polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) fabricated by solution processing, using spin coating and drop casting with drying in a solvent vapor environment, respectively, are studied to realize flexible, solution-processed OTEGs based on micro-films. The polymer P3HT (Fig. 1A) was chosen because it is a commonly used p-type semiconductor polymer and is soluble in many organic solvents. As dopants, the well-known electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4-TCNQ, Fig. 1B) and the Lewis acid iron(III) p-toluenesulfonate hexahydrate (Fe^{3+}-$tos_3 \cdot 6H_2O$, Fig. 1C) were used. The effects of doping concentration on thermoelectric properties, performance, and air-stability of individual OTEGs are investigated and compared for both dopants in nano- and micro-films.

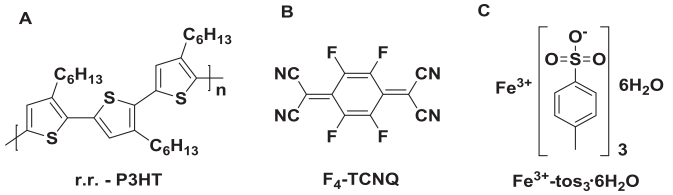

Fig. 1. Chemical structures of (A) region-regular (r.r.) P3HT, (B) F_4-TCNQ, and (C) Fe^{3+}-$tos_3 \cdot 6H_2O$.

Furthermore, we develop a fabrication method for flexible uni-leg OTE modules using a photo-etching technique to directly pattern a micrometer-thick active layer into individual elements without the need for alignment and assembly of the elements. The thermoelectric properties of the modules are investigated in detail to better understand module design principles. This solution processing method is a step toward roll-to-roll mass production that could significantly reduce the complexity, time, and cost of thermoelectric module production compared to conventional processes such as ink-jet and screen printing.

2. Experimental

Regio-regular P3HT (MERCK, regio-regularity > 94.7%, molecular weight of 34 kg/mol), F_4-TCNQ (TCI), and Fe^{3+}-$tos_3 \cdot 6H_2O$ (Sigma–Aldrich) were purchased commercially and used without further purification. The substrates and bottom electrodes were prepared as follows. The glass substrates (700 μm thick) were first immersed in a *Piranha* solution (hydrogen peroxide: sulfuric acid vol. ratio of 1:3) in a petri dish heated at 125 °C for 30 min. Next, the substrates were cleaned by ultrasonication in successive baths of pure water, acetone, and iso-propanol, with each bath lasting 5 min and being repeated using fresh solvent twice, followed by UV/O_3 treatment for 15 min. The flexible PET substrates (100 μm thick, LINTEC) were cleaned in the same way but without the *Piranha* treatment. After cleaning, the substrates were immediately transferred into a vacuum deposition chamber, and patterned bottom electrodes (chromium 10 nm/gold 150 nm) were deposited by vacuum evaporation through metal shadow masks at a base pressure of ca. 5×10^{-4} Pa.

The organic layers were fabricated and doped using solution processing in ambient air. Nano- and micro-meter films were fabricated using spin coating and drop casting, respectively. Before film fabrication, solutions of P3HT in o-dichlorobenzene (oDCB, >98% Wako) were stirred at 80 °C for 1 h. The nano-films samples were spin coated from a 25 mg/mL solution at 2000 rpm for 90 s (see Fig. S1A). After spin coating, the samples were annealed at 150 °C for 15 min. The micro-films were fabricated by dropping high concentration P3HT solutions in oDCB (40–80 mg/mL) onto the substrate and annealing at 100 °C under a saturated solvent atmosphere for 1 h to suppress the formation of a highly convex surface, which is usually caused by a higher viscosity at the surface during drying because of a local reduction in solvent. (see Fig. S1B). After the fabrication, the samples were annealed at 150 °C for 30 min.

The P3HT films were patterned using the photo-etching process described in Fig. S3. After patterning, the films were p-doped by immersing them in an acetonitrile solution (>98% Wako) containing a dopant (F_4-TCNQ or Fe^{3+}-$tos_3 \cdot 6H_2O$) for 1 h. To prevent the solution concentration from changing because of solvent

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