



Enhanced thermoelectric properties of germanium powder/poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) composites

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ABSTRACT

We herein report on the enhanced thermoelectric properties of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS)/Ge composite films fabricated by drop-casting of a solution of Ge powder in PEDOT:PSS. The power factor of the fabricated PEDOT:PSS/Ge composite films with 29.6 wt.% Ge was $165 \mu\text{W m}^{-1}\text{K}^{-2}$, and they exhibited an extremely low thermal conductivity. The maximum thermoelectric figure of merit was anticipated to be ~ 0.1 at room temperature for the PEDOT:PSS/Ge composite films with 29.6 wt.% Ge, suggesting that their heterostructure was effective in enhancing their thermoelectric efficiency.

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1. Introduction

Over the past few decades, the enhancement of thermoelectric efficiency of materials has been a challenging issue of great scientific and technological concern for realizing thermoelectric heat-to-electrical-energy conversion systems [1]. Generally, the thermoelectric efficiency is characterized by the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where, S , σ , κ , and T are the Seebeck coefficient (V K^{-1}), electrical conductivity (Scm^{-1}), thermal conductivity ($\text{W m}^{-1}\text{K}^{-1}$), and absolute temperature (K), respectively [2,3]. Judging from the definition of ZT , the best thermoelectric materials should have low thermal conductivity and high Seebeck coefficient and electrical conductivity. However, the three parameters, which constitute ZT , are interdependent on each other and are related to the carrier concentration of a given material; increasing one parameter results in the decrease of another parameter or parameters. Recent advances in high- ZT thermoelectric materials have been mostly achieved by optimizing material composition and modifying the nanostructure of inorganic materials such as Bi_2Te_3 [4], PbTe [5], and SiGe [6]. However, these inorganic thermoelectric

materials are generally less abundant, expensive, and toxic. Consequently, it is difficult to scale-up processes or build micro-devices based on these materials [7]. In order to overcome these limitations of inorganic materials, recent research has been focused on polymer-based thermoelectric materials. In particular, conducting polymers have attracted great attention as promising thermoelectric materials owing to their unique advantages such as low thermal conductivity, flexibility, low cost, and ease of synthesis [8–26]. Thermoelectric properties of conducting polymers with various shapes and structures were reported such as thin film, pellet and nanowire [13–15]. However, the typical ZT value of the conducting polymer-based materials are on the order of 10^{-2} – 10^{-3} , much lower than those of inorganic materials [16–18]. For polymer-based thermoelectric materials to achieve a ZT that is comparable to that of inorganic thermoelectric materials, it is essential to enhance the Seebeck coefficient without decreasing the electrical conductivity. For this reason, numerous researchers have suggested organic/inorganic composites such as poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS)/carbon nanotubes (CNTs) [16], PEDOT:PSS/Te nanorods [19], PEDOT:PSS/ $\text{Ca}_3\text{Co}_4\text{O}_9$ [20], PEDOT:PSS/ PbTe [21], PEDOT:PSS/ Bi_2Te_3 [7,22], $\text{P}_3\text{HT}/\text{Bi}_2\text{Te}_3$ [25], and polyaniline (PANI)/CNTs [26] to achieve better thermoelectric performance. We herein suggest a quick, simple, and high-yielding synthesis method for preparing PEDOT:PSS/Ge composite films for use as thermoelectric

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materials. Additionally, we report on their enhanced thermoelectric properties depending on the amount of Ge in the films. By drop-casting a solution of Ge powder in PEDOT:PSS, PEDOT:PSS/Ge composite films were fabricated. A power factor of $165 \mu\text{W m}^{-1}\text{K}^{-2}$ was achieved by the PEDOT:PSS/Ge composite films with 29.6 wt.% Ge. The ZT value was anticipated to be approximately 0.1 at room temperature based on the thermal conductivity obtained by out-of-plane measurements. These results indicate that the PEDOT:PSS/Ge composite films are likely to be used in a heat-to-electrical-energy conversion system.

2. Experimental details

2.1. Fabrication of PEDOT:PSS/Ge composite films

In order to fabricate the PEDOT:PSS/Ge composite films, CLEVIOS PH1000 (1 ml PEDOT:PSS solution containing 0.01 g PEDOT:PSS, Heraeus) and Ge (99.99%, Sigma Aldrich) were used as base materials. Prior to preparing the PEDOT:PSS/Ge composite films, Ge powder was prepared by ball-milling Ge in a jar with stainless steel balls in a nitrogen atmosphere for preventing oxidation. The milled Ge powder particles were found to have a non-uniform size distribution, from sub-micrometer to several micrometers. Various amounts of Ge powder (i.e., 0.0 wt.%, 17.4 wt.%, 29.6 wt.%, 38.7 wt.%, 51.4 wt.%, 71.6 wt.%, 80.8 wt.%, 95.5 wt.% and 98.4 wt.%) were mixed to PEDOT:PSS solutions and stirred for 24 h at room temperature to achieve precise control of the composition of the PEDOT:PSS/Ge composite films [27]. The PEDOT:PSS/Ge composite films were drop-cast on a fused silica substrate, which had been cleaned with oxygen plasma, as shown in Fig. 1(a). Then, the films were dried using a vacuum oven at 60°C for 30 min under a base pressure of 0.13 Pa (1.0×10^{-3} Torr) in order to remove the organic solvent from the PEDOT:PSS/Ge composite films. Then, annealing was performed using a hot plate at 150°C for 5 min.

2.2. Micro-structure of PEDOT:PSS/Ge composite films

X-ray diffraction (XRD, model: Rigaku Ultima IV/ME 200DX) analysis was utilized to examine the crystal structure of the PEDOT:PSS/Ge composite films at $\text{Cu K}\alpha$ radiation = 0.15406 nm (45 kV, 40 mA). Fig. 1(b) shows the XRD pattern of the PEDOT:PSS/Ge composite films and pure Ge powder, indicating that the diffraction peaks of the PEDOT:PSS/Ge composite were perfectly indexed to the fcc crystal structure of pure Ge, with the lattice constant $a = 5.65754 \text{ \AA}$. The microstructure and morphology of the PEDOT:PSS/Ge composite films were investigated by scanning electron microscopy (SEM, model: Jeol JSM-6701F) at 15 kV. The top and cross-sectional SEM images are shown in Fig. 2(a) and (b), respectively. It was confirmed that the Ge powder was well distributed uniformly throughout the PEDOT:PSS/Ge composite films. The thickness of PEDOT:PSS/Ge composite films was approximately 5–7 μm . Fig. 2(c) shows the SEM-energy dispersive spectroscopy (EDS) mapping images of a selected area of a cross-section of a PEDOT:PSS/Ge composite film. As shown in Fig. 2(c), we also observed the elemental distribution of C, S, and Ge, confirming that the Ge powder was uniformly dispersed in the composite films without segregation.

3. Results and discussion

3.1. Enhanced thermoelectric power factor of the PEDOT:PSS/Ge composite films

Electric properties of the PEDOT:PSS/Ge composite films with different wt.% of Ge powders are shown in Fig. 3. Electrical conductivities and Seebeck coefficients of the PEDOT:PSS/Ge composite films were measured at room temperature along the in-plane direction. All measurements were carried out in a thermo-isolated glove box to prevent experimental errors arising from thermal agitation. Electrical

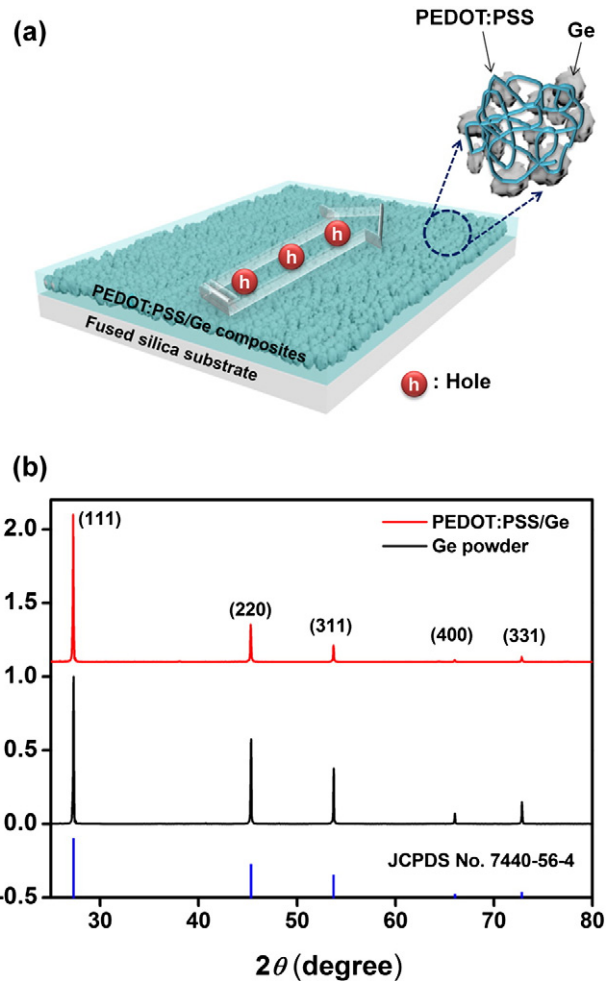


Fig. 1. (a) An illustration of Ge powder-embedded PEDOT:PSS composite films on fused silica substrate. (b) XRD patterns of PEDOT:PSS/Ge composite films (red), pure Ge powder (black), and major peak of pure Ge (blue, JCPDS file no. 7440-56-4).

conductivity measurements were carried out using the Van der Pauw method, a commonly used method for measuring sheet resistivity, with a nano-voltmeter (Keithley Instruments Inc., Model 2182) and a current source (Keithley Instruments Inc., Model 236). As shown in Fig. 3(a), the electrical conductivity decreased monotonically with increasing wt.% of the Ge powder, which can be explained with a simple parallel model: $\sigma = \sigma_{\text{PEDOT:PSS}} \cdot (1 - x) + \sigma_{\text{Ge}} \cdot x$, where x is the volume ratio of Ge [22]. It should be noted that the PEDOT:PSS/Ge composite films with 98.4 wt.% Ge powder were almost completely electrically insulating. This result reveals that the role of PEDOT:PSS is to mainly allow conduction of charge carriers in the PEDOT:PSS/Ge composite films unlike Ge, which has a low electric conductivity of Ge ($<0.1 \text{ Scm}^{-1}$). The Seebeck coefficients of the PEDOT:PSS/Ge composite films were obtained using a custom-made Seebeck coefficient measurement system, which consisted of peripheral component interconnect extensions for instrumentation flat form, two Peltier devices, two thermocouples, and a nano-voltmeter (Keithley Instruments Inc., Model 2182). Detailed description of the Seebeck coefficient measurement is available in a previous study [18]. The two Peltier devices were both heated up with a constant temperature gradient. A certain amount of heat, which was generated by heating one end of the Peltier devices, was transported to the other cold side through the PEDOT:PSS/Ge composite films along the in-plane direction with negligible heat loss. The temperature difference (dT) and voltage difference (dV) between the hot

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