



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

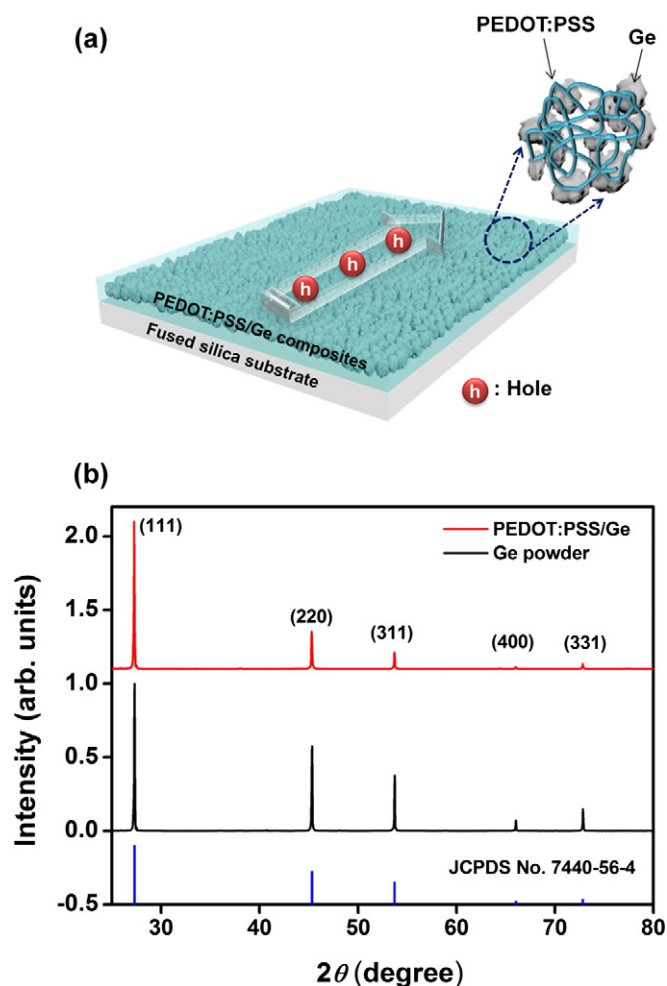


Fig. 1. (a) An illustration of Ge powder-embedded PEDOT:PSS composite films on fused silica substrate. (b) XRD patterns of PEDOT:PSS/Ge composite films (red), pure Ge powder (black), and major peak of pure Ge (blue, JCPDS file no. 7440-56-4).

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

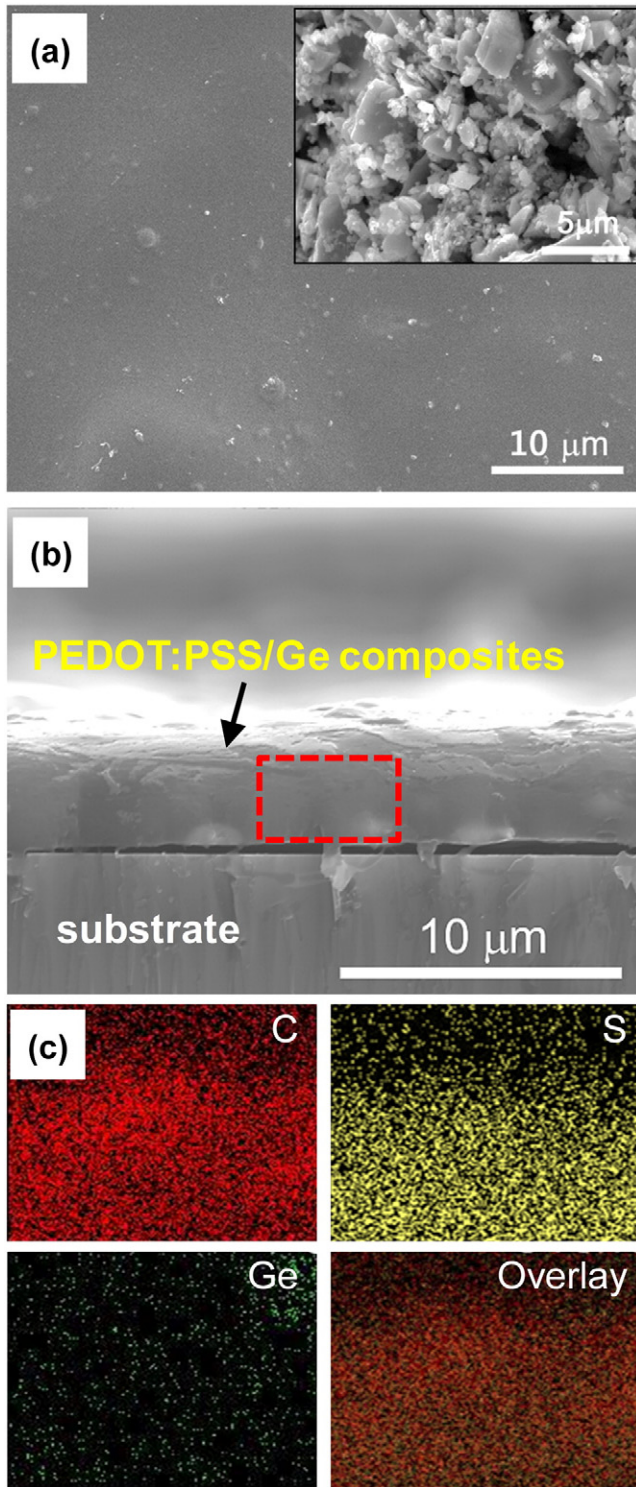


Fig. 2. SEM images of PEDOT:PSS/Ge composite films (29.7 wt.% of Ge). (a) Top view (inset: Ge powders at higher magnification) and (b) cross sectional view. (c) EDS mapping images of C, S, and Ge, and overlay image of the selected area of (b).

and the cold sides were measured using the thermocouples and the nano-voltmeter, respectively. The Seebeck coefficient was calculated from the equation $S = dT / dV$. As shown in Fig. 3(a), in contrast to the direct dependency of electric conductivity, the Seebeck coefficient increased with increasing wt.% of the Ge powders until it reached a maximum. This result is consistent with the dependency of the Seebeck

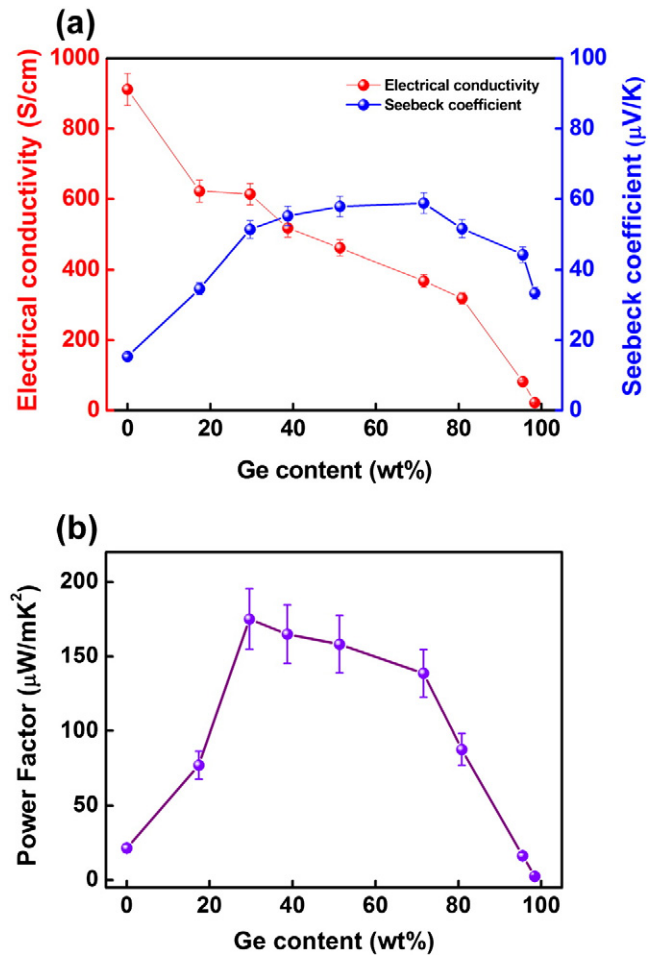


Fig. 3. (a) Measured electrical conductivities and Seebeck coefficients of PEDOT:PSS/Ge composite films with various Ge amounts at room temperature. (b) Calculated power factors of PEDOT:PSS/Ge composite films with various Ge amounts at room temperature.

coefficient on the mixture-content of other organic–inorganic composite systems [20,25,28,29]. The Seebeck coefficients were measured to be higher than $50 \mu\text{V K}^{-1}$ for the samples with 29.6 wt.% to 80.8 wt.% Ge powder. The Seebeck coefficient of the 71.6 wt.% Ge powder sample was measured to be $58.9 \mu\text{V K}^{-1}$. This value is almost four times larger than that of pure PEDOT:PSS, considering that pure PEDOT:PSS generally has a Seebeck coefficient of $12\text{--}16 \mu\text{V K}^{-1}$ at room temperature. The positive sign of the Seebeck coefficient and its significantly larger values indicate that holes are the majority charge carriers [19]. The power factor was calculated from the measured values of electric conductivity and Seebeck coefficient as shown in Fig. 3(b). The maximum power factor at room temperature was calculated to be $165.1 \mu\text{W m}^{-1}\text{K}^{-2}$ for the sample with 29.6 wt.% Ge powder. This power factor value is eight times larger than that of pure PEDOT:PSS thin films. Considering that the power factors of polymer-based thermoelectric materials are less than $100 \mu\text{W m}^{-1}\text{K}^{-2}$, this large enhancement of power factor for the organic matrix/inorganic powder composites is attributed to the high positive Seebeck coefficient of the Ge powder ($>300 \mu\text{V K}^{-1}$). However, this enhancement cannot be explained with only a simple parallel model as in the case of electrical conductivity, because the PEDOT:PSS/Ge composite films are a mixture of series and parallel connections of the two components [22]. Furthermore, the fact that the Ge powder was composited well with the PEDOT:PSS resulted in the destruction of connecting junctions between the particles of Ge [20]. Therefore, the Seebeck coefficient exhibited a non-monotonic dependency on the wt.% of the Ge powder.

3.2. Strong reduction of thermal conductivities in the PEDOT:PSS/Ge composite films

Thermal conductivities of selected samples (i.e., 0.0 wt.%, 17.4 wt.%, and 29.6 wt.%) were investigated using Nanoflash LFA 447 (Netzsch Instruments Inc.) with a xenon flash lamp. The heat pulse from the xenon flash lamp was irradiated on the front side of the PEDOT:PSS/Ge composite films, and the heat was conducted in the direction of thickness, thus increasing the temperature of the back side. Thermal diffusivity (D) was measured using time-dependent temperature change of the back side. Thermal conductivity was calculated from thermal diffusivity by the following equation:

$$D = \kappa / (\rho \cdot C_p),$$

where ρ is the density of the composite films and C_p is the specific heat capacity at constant pressure. The thermal conductivity of the pure PEDOT:PSS films was measured to be $\sim 0.33 \text{ W m}^{-1}\text{K}^{-1}$, which is comparable to the results stated in previous reports [23,30]. As shown in the inset of Fig. 4, the thermal conductivity (κ) of the PEDOT:PSS/Ge composite films increased with increasing Ge content, until the Ge amount reached 17.4 wt.%. This result indicates that the Ge powder in the composite films could have been a pathway for heat, resulting in the increase in thermal conductivity. After reaching the maximum peak of thermal conductivity, the excess Ge powder acted as a phonon scattering source causing a decrease in thermal conductivity [31]. The ZT value was anticipated from the measured values of electrical conductivity, Seebeck coefficient, and thermal conductivity. Considering that the ZT value of a conducting polymer is normally between 10^{-2} and 10^{-3} [18], we did expect the PEDOT:PSS/Ge composite films with the Ge powder content of 29.6 wt.% to have a ZT value of 0.1, a value at least ten-times higher than that of pure polymers at room temperature. This result is mainly attributed to the enhancement of power factor caused by the Ge powder. Moreover, the wide size distribution of the Ge powder and the interface between organic and inorganic materials possibly effectively scattered the long-wavelength phonons, which conduct most of the heat in solid-state materials [32–34].

4. Conclusions

In summary, PEDOT:PSS/Ge composite films were fabricated by homogeneously mixing PEDOT:PSS and Ge powder. The maximum power factor at room temperature was measured to be $165 \mu\text{W m}^{-1}\text{K}^{-2}$ for the sample with 29.6 wt.% Ge powder. The anticipated maximum ZT value based on thermal conductivity, which was obtained by out-of-plane measurements, was found to be about 0.1 at room temperature,

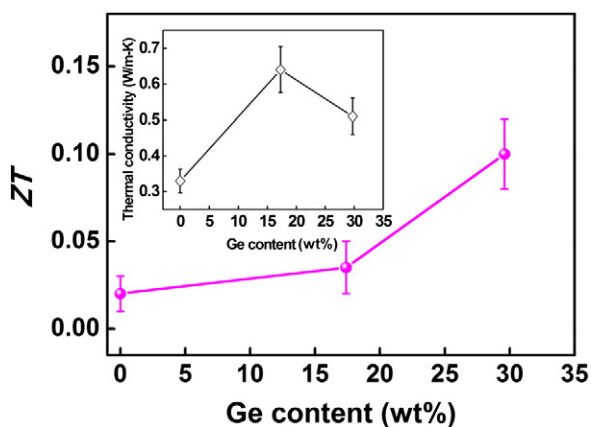


Fig. 4. The anticipated ZT value of PEDOT:PSS/Ge composite films with various Ge amounts at room temperature. The inset shows measured thermal conductivity of PEDOT:PSS/Ge composite films along the out-of-plane direction.

a value ten-times higher than that of pure conducting polymers. Our results demonstrate that the PEDOT:PSS/Ge composite films show a very significant feasibility for application as polymer-based thermoelectric materials.

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