공학석사학위논문

건식 스프레이 증착 시스템을 이용한 유연 열전소자 발전기 상온 제작

Room-temperature fabrication of

flexible thermoelectric generator

using dry-spray deposition system

2016년 2월

서울대학교 대학원

기계항공공학부

송 대 섭

Abstract

Room-temperature fabrication of flexible thermoelectric generator using dry-spray deposition system

Dae-Seob Song

Department of Mechanical and Aerospace Engineering

The Graduate School

Seoul National University

We present a flexible thermoelectric (TE) generator with titanium dioxide (TiO_2), antimony (Sb), and tellurium (Te) powders fabricated by a nanoparticle deposition system (NPDS). NPDS is a novel low-energy consumption dry-spray method that enables the deposition of inorganic materials on substrates at room temperature and under low vacuum. TiO_2 nanopowders were dispersed on a TE powder for improved adhesion between TE films and the substrate. Film morphologies were investigated using field-emission scanning electron microscopy, and the phase structure was analyzed by X-ray diffraction. A TE leg, deposited with 3 wt% TiO_2 content, had the largest Seebeck coefficient of approximately 160 μV/K. The prototype TE generator consisted of 16 TE legs linked by silver interconnects over an area of $20 \times 60\ mm^2$. The prototype produced a voltage of 48.91 mV and a

maximum power output of 0.18 μW from a temperature gradient of 20 K. The values are comparable to that of conventional methods. These results suggest that flexible TE generators can be fabricated by energy efficient methods, although internal and contact resistances must be decreased.

Keywords: nano-particle deposition system, flexible thermoelectric generator, dry-spray deposition, room temperature.
Student Number: 2014-21841

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Chapter 1. Introduction

1.1 Background

Thermoelectric (TE) power generators convert a thermal differential into electrical power and can be used to improve energy consumption efficiency. Moreover, flexible TE power generators can be used in self-powered portable electronic systems, such as wearable electronics, biometric sensors, and autonomous robots [1–4].

1.2 Fabrication of flexible TE generator

Recently, various TE materials and manufacturing methods have been developed for the fabrication of flexible TE generators. TE materials based on tellurium (Te) and antimony (Sb) have typically been used for this purpose, due to their high figure of merit values, ZT, where $ZT = \alpha^2 \cdot T/\rho \cdot \lambda$, λ is the thermal conductivity, ρ is the electrical resistivity, α is the Seebeck coefficient, and T is the temperature; the printing methods utilized (e.g., screen printing [5], inkjet printing [6], metal organic chemical vapor deposition (MOCVD) [7], co-sputtering [8], and flash evaporation [9]) significantly improved the energy conversion efficiency of the TE generators. A glass fabric-based flexible TE generator, which was recently optimized and developed for wearable mobile electronic systems, showed remarkable output power, but also high energy consumption and cost [10]. Pastes which contain TE and binder materials for screen printing and inkjet printing must be annealed. Also, MOCVD consumes a large amount of energy, due to the high growth temperatures required. Co-sputtering and flash evaporation methods require a post-annealing process to improve the TE generator's performance. These high-energy processes negate the benefits of TE generators; thus, more efficient fabrication processes are required for widespread adoption.

1.3 Objectives

The nanoparticle deposition system (NPDS), which can deposit metal and ceramic particles using a dry-spray process at room temperature and under low-vacuum conditions, was developed by Ahn et al. in 2006. NPDS is similar to the aerosol deposition method (ADM); however, NPDS is a relatively low-energy consumption process, compared with alternative dry-spray processes [11]. NPDS requires a low-pressure gas carrier and a low vacuum, which reduces energy consumption and the complexity of the facilities needed. NPDS has been used to deposit TiO_2 and WO_3 particles on a substrate for energy applications, such as dye-sensitized solar cells (DSSC) and electrochromic displays [12,13], which suggests the use of a NPDS for efficient fabrication of flexible TE generators.

According to a recent study, microparticles with a TiO_2 nanopowder deposited by NPDS adhered well to the substrate and exhibited a greater film density than other pure microsized particles [14]. In addition, TiO_2 nanopowders dispersed in TE materials may result in remarkable phonon scattering, reducing thermal conductivity [15].

In the present work, we fabricated 16 Sb_2Te_3 TE film (p-type) legs, with a TiO_2 nanopowder, dispersed on a polyvinyl chloride (PVC) flexible substrate by NPDS, for a TE generator. Here, we focused on the fabrication and characterization of the flexible TiO_2/Sb_2Te_3 TE generator.

Chapter 2. Experimental procedures

2.1 Nanoparticle deposition system

A NPDS was used to deposit TE powders by spraying nano- or microsized particles at room temperature and under low vacuum conditions. Figure 2.1 shows the NPDS system and nozzle used to deposit the TE powder. The nozzle was a slit-type, and the deposition area was 10 × 1 mm^2 without moving the nozzle. The deposition parameters are listed in Table 2.1.

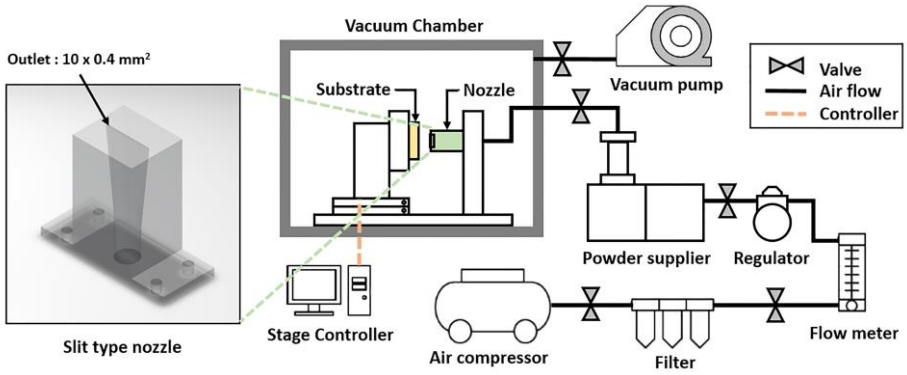

Figure 2.1. Schematic diagram of the nanoparticle deposition system (NPDS).

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In the field of TE generator research, TE semiconductor materials with a band structure, high electrical conductivity, and low thermal conductivity have been used to optimize ZT; TE powders commonly used include Bi_2Te_3, Sb_2Te_3, and ZnO. In this research, Sb powder (99.9 % metal basis, -200 mesh, Alfa Aesar) and Te powder (99.8 % metal basis, -200 mesh, Acros Organics) were mixed by agitation with a TE powder. The mixing ratio of Sb and Te was 43:57 by weight. TiO_2 nanopowder (anatase phase, 15 nm, Nanoamor) was included in the TE powder to improve the adhesion and TE properties. Transparent PVC was used as the flexible substrate and was cut into 60 × 20 mm^2 piece, having a thickness of 0.23 mm.

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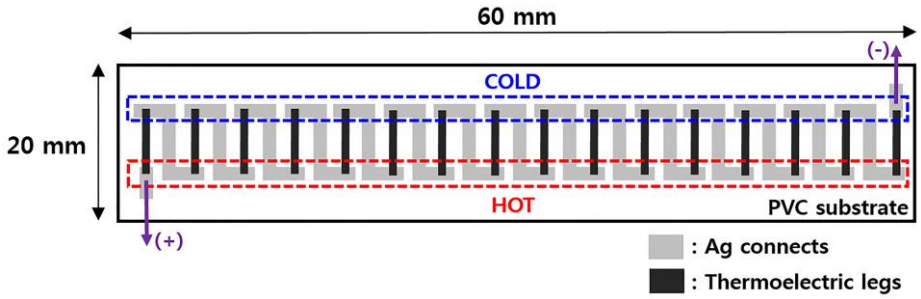

Figure 2.2. Schematic diagram of the thermoelectric (TE) generator.

2.4 Characterization

The morphology of the TiO_2/Sb_2Te_3 TE films was examined using field-emission scanning electron microscopy (FE-SEM, SUPRA 55VP), and the phase structure was analyzed by an X-ray diffraction system with monochromatic Cu-Kα radiation. The Seebeck coefficient of one TE leg was calculated from output voltage and the gradient of the temperature differential which included influence of the thermal conductivity of the TE films. The temperature difference, current, and output voltage were measured by thermocouples and an electrometer (Keithley 6514).

Chapter 3. Results and Discussion

3.1 Field-emission scanning electron microscopy

Figure 3.1 shows SEM images of the surface and cross-section of the TiO_2/Sb_2Te_3 TE films. The images show that particles of varying size and color agglomerated in the film. Following deposition, the white TiO_2 particles were dispersed between Sb_2Te_3 films. The thicknesses of the films were approximately 60 μm.

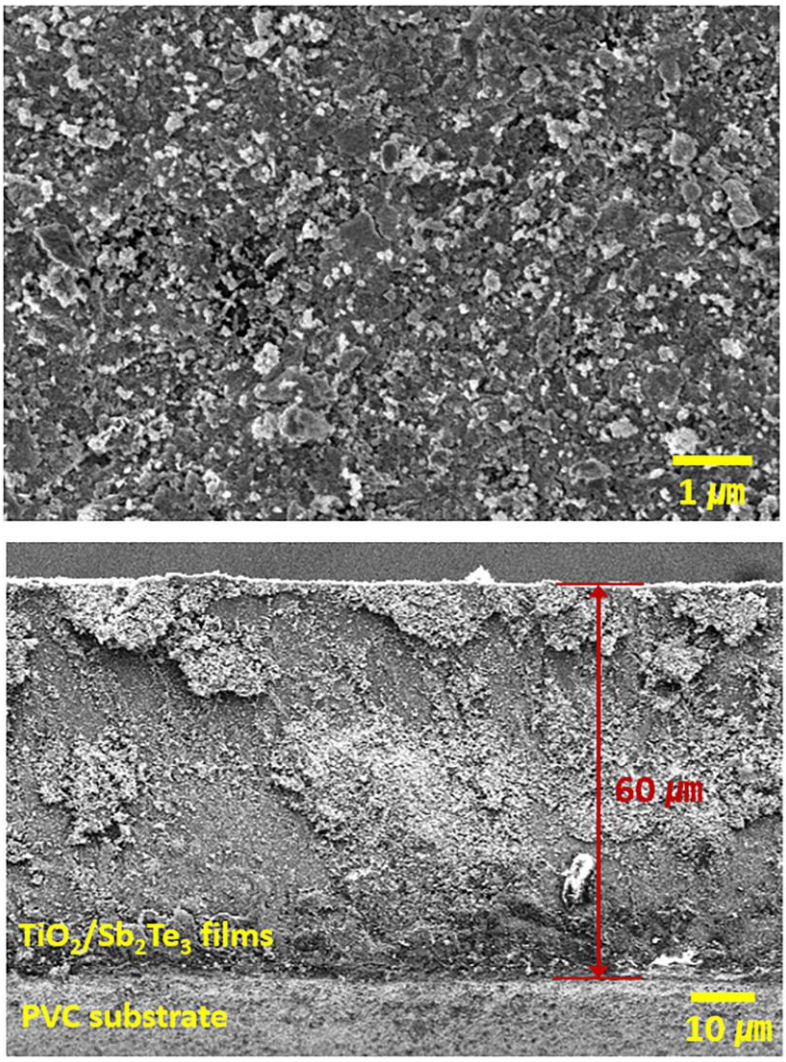

Figure 3.1. Scanning electron microscopy (SEM) images of the surface (top) and cross-section (bottom) of the TiO_2/Sb_2Te_3 films.

3.2 X-ray diffraction

The XRD analysis presented in Fig. 3.2 indicates that the TE powder contained Sb, Te, and TiO_2 particles. The TE films deposited by NPDS were composed of Sb_2Te_3 compound and TiO_2 particles. Moreover, the XRD peaks of the TE films were broader than those of the TE powder. These results show that the consolidation and fracture of the TE powder during deposition process resulted in a formation of Sb_2Te_3 compound and a reduction of the crystallite size in the TE film.

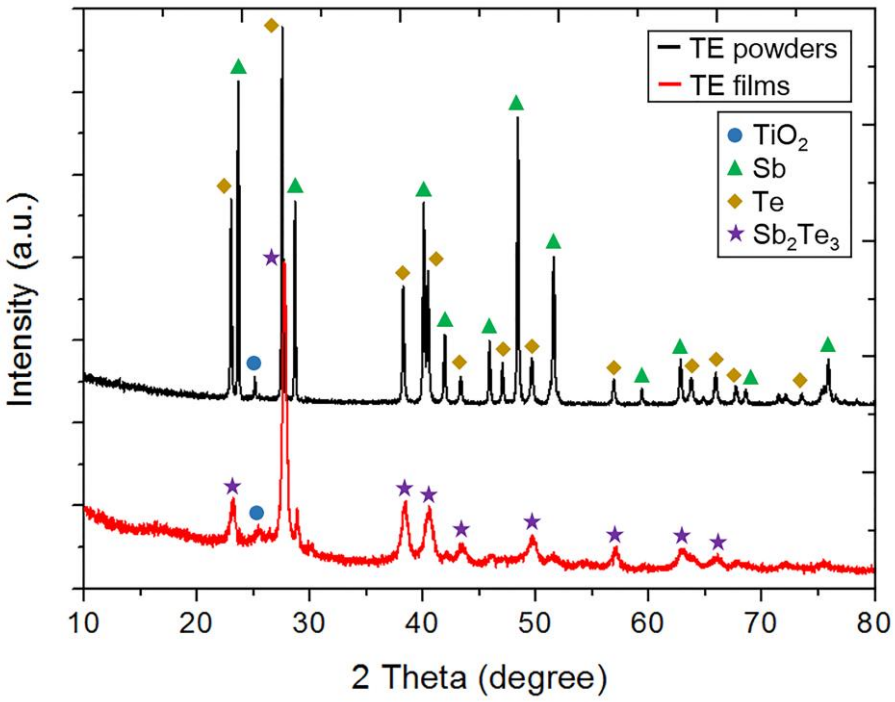

Figure 3.2. X-ray diffraction (XRD) patterns of the TE powder and the TE films.

3.3 Seebeck coefficient and internal resistance

Figure 3.3 shows the composition ratio of the TiO_2 dependence of the Seebeck coefficient and internal resistance of one TE leg. The Seebeck coefficient and internal resistance were inversely proportional. At 3 wt% TiO_2 content, the largest Seebeck coefficient was approximately 160 μV/K, and the lowest internal resistance of 0.832 kΩ was identified. These results demonstrate that an optimal volume of TiO_2 enhances the TE properties of the TE film. However, above 3 wt%, the TiO_2 composition decreased the TE properties owing to its high electrical resistivity. The TE legs of the TE generator were fabricated by TE powder with 3 wt% TiO_2 contents.

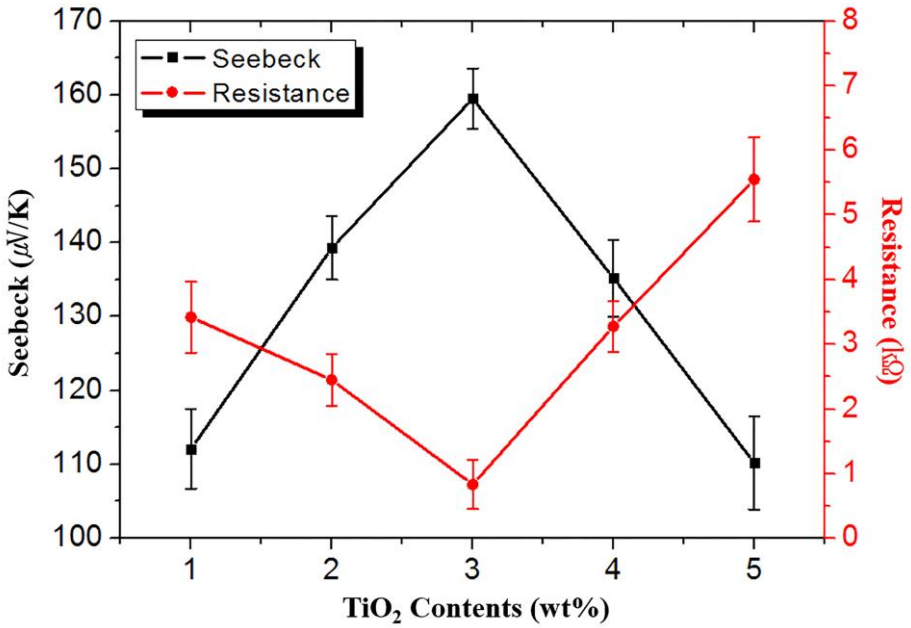

Figure 3.3. Seebeck coefficient and internal resistance of one TE leg as a function of the TiO_2 ratio.

3.4 Prototype flexible TE generator

A prototype flexible TE power generator was successfully fabricated, as shown in Fig. 3.4. Sixteen TE legs were connected by Ag connects; the flexible PVC substrate could be bent perpendicular with respect to the TE direction, and the TE legs had sufficient adhesion to the PVC substrate to endure bending.

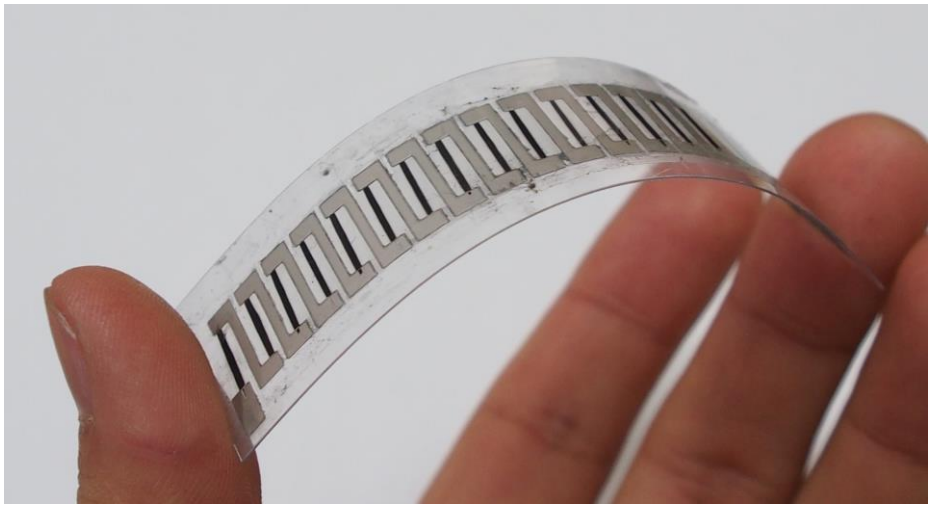

Figure 3.4. Image of the flexible TE generator under bending stress.

3.5 Voltage and power output

The voltage and power output for the prototype flexible TE power generator were measured as a function of the temperature difference in Fig. 3.5. The inset shows how voltage and current were measured, and how the temperature differential gradient was applied to the end of each leg by a heat sink and hot plate. According to Fig. 3.5, the maximum voltage was 48.91 mV, and the maximum power output was 0.18 μW at $\Delta T = 20$ K.

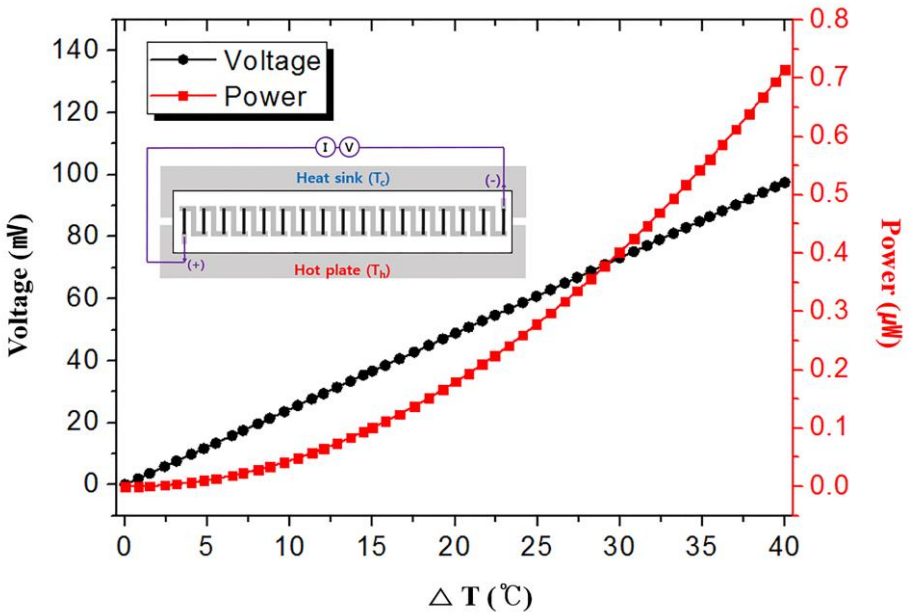

Figure 3.5. Voltage and power output for the flexible TE power generator as a function of the temperature differential. The inset shows a schematic of the measurement setup.

3.6 Comparison

Various fabrication processes for flexible TE generators were compared in Table 3.1. Screen printing consume a large amount of energy due to the high annealing temperatures (250℃) and high pressing pressure (250 × 106 Pa) [16], and inkjet printing also need high annealing temperature (400℃) [6]. CVD uses a large amount of energy, due to the growth temperature required (400℃) [7]. Although NPDS operates at room temperature and under low-vacuum conditions (10000 Pa), the TE properties of a generator fabricated by NPDS were comparable to that of a TE generator fabricated by high-energy consumption processes. Therefore, NPDS is a promising new, energy-efficient method for TE generator fabrication.

Table 3.1. Comparison of various fabrication processes for flexible TE generators.

Process	**NPDS**	Screen printing	Inkjet printing	CVD
Materials	**TiO_2/Sb_2Te_3**	$Bi_{1.8}Te_{3.2}$, Sb_2Te_3	$Sb_{1.5}Bi_{0.5}Te_3$, $Bi_2Te_{2.7}Se_{0.3}$	Bi_2Te_3, $Bi_{0.4}Sb_{1.6}Te_{3.0}$
Substrate	**PVC**	Polyimide	Polyimide	SiO_2/GaAs
Temperature (℃)	**RT**	RT	60	400
Pressure (Pa)	**10000 (low vacuum)**	250×10^6 (high pressure)	Atmosphere	High vacuum
Annealing (℃)	**None**	250	400	None
Thickness (μm)	**60**	78.4	Not specified	4
Seebeck coefficient (μV/K)	**160**	104	139	230
Maximum power output at ΔT = 20 ℃	**0.18 μW of power by 16 TE legs**	40.3 nW of power by 16 TE junctions	Not specified	0.2 μW of power by 20 pairs of TE legs

NPDS: nanoparticle deposition system; CVD: chemical vapor deposition; PVC: polyvinyl chloride.

Chapter 4. Conclusions

Sixteen TiO_2/Sb_2Te_3 TE legs were patterned on a flexible PVC substrate using NPDS at room temperature and under low-vacuum. To improve the TE properties and adhesion between the film and substrate, TiO_2 nanopowders were dispersed on the starting TE powders with 3 wt% content. A TE leg, deposited with 3 wt% TiO_2, had the highest Seebeck coefficient (about 160 μV/K) and the lowest internal resistance of 0.832 kΩ. The prototype TE generator produced 0.18 μW at 48.91 mV and 3.68 μA for a temperature difference of 20 K. This value is similar to those of high-energy consumption methods. Therefore, the NPDS provides a novel, energy-efficient means of TE film deposition for eco-friendly fabrication of TE generators. Our future work will focus on decreasing the internal resistance of the module and the contact resistance between the element and electrode for optimizing the power output of the TE generator.

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Abstract (Korean)

본 연구에서는 나노 입자 적층 시스템으로 티타늄 다이옥사이드, 안티몬, 그리고 텔루륨 분말을 사용한 유연 열전소자 발전기를 제시하였다. 나노 입자 적층 시스템은 작은 에너지 소비를 갖는 새로운 건식 스프레이 방법으로서, 상온과 저 진공 상태에서 무기물 재료들을 기판에 증착할 수 있다. 티타늄 다이옥사이드 나노 분말들은 열전소자 층과 기판 사이의 접착을 향상시키기 위해 열전소자 분말들에 분산되었다.

증착된 열전소자 층의 모폴로지는 주사전자현미경에 의해 조사하였으며, 상의 구조는 엑스레이 분산을 이용하여 분석하였다. 질량비가 3 w%인 티타늄 다이옥사이드로 증착된 하나의 열전소자 구간은 최대 약 160 μV/K의 제백 계수를 가졌다. 제작된 열전소자 발전기의 프로토 타입은 은 배선으로 연결된 16개의 열전소자 구간들로 이루어졌으며 이 면적은 $20 \times 60\,\mathrm{mm}^2$ 였다. 프로토 타입은 20 K의 온도 구배 차이에서 48.91 mV의 전압과 최대 0.18 μW의 전력을 만들 수 있었다. 이 수치들은 기존의 열전소자 발전기 제작 방법으로 제작된 열전소자 발전기의 수치들과 비교할 만하였다. 이 결과들은 유연 열전소자 발전기가 보다 에너지 효율적인 방법으로 제작될 수 있음을 제시하였으나, 내부와 접촉 저항은 개선되어야 한다.

주 요 어: 나노 입자 적층 시스템, 유연 열전소자 발전기, 건식 스프레이 증착, 상온.

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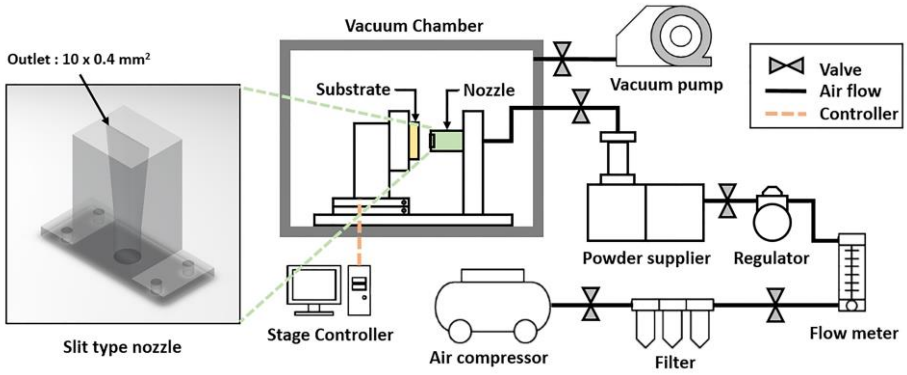

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2.3 TE generator fabrication process

PVC substrates were cleaned by sonication in ethyl alcohol, and TE film legs were prepared using the dry-spray method (NPDS). Sixteen TiO_2/Sb_2Te_3 TE film legs (length: 10.5 mm; width: 1.2 mm) were deposited at regular intervals by NPDS. Silver (Ag) contacts were used as the electrical interconnects between the legs, which were patterned in series, as shown in Fig. 2.2, using a commercial Ag paste with patterned polyimide masking tape and a scalpel. The series TE legs generate electrical power via the temperature differential between both ends of them.

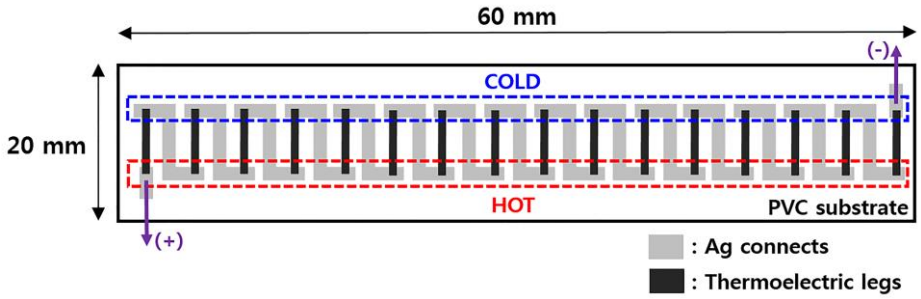

Figure 2.2. Schematic diagram of the thermoelectric (TE) generator.

2.4 Characterization

The morphology of the TiO_2/Sb_2Te_3 TE films was examined using field-emission scanning electron microscopy (FE-SEM, SUPRA 55VP), and the phase structure was analyzed by an X-ray diffraction system with monochromatic Cu-Kα radiation. The Seebeck coefficient of one TE leg was calculated from output voltage and the gradient of the temperature differential which included influence of the thermal conductivity of the TE films. The temperature difference, current, and output voltage were measured by thermocouples and an electrometer (Keithley 6514).

Chapter 3. Results and Discussion

3.1 Field-emission scanning electron microscopy

Figure 3.1 shows SEM images of the surface and cross-section of the TiO_2/Sb_2Te_3 TE films. The images show that particles of varying size and color agglomerated in the film. Following deposition, the white TiO_2 particles were dispersed between Sb_2Te_3 films. The thicknesses of the films were approximately 60 μm.

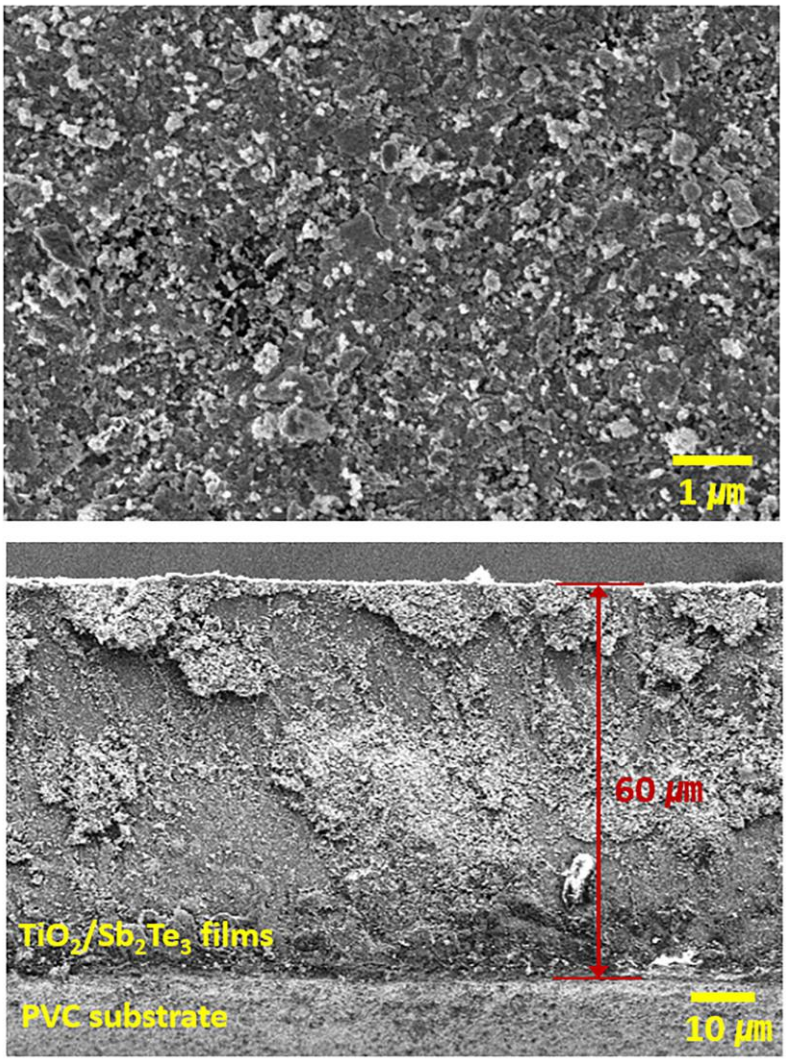

Figure 3.1. Scanning electron microscopy (SEM) images of the surface (top) and cross-section (bottom) of the TiO_2/Sb_2Te_3 films.

3.2 X-ray diffraction

The XRD analysis presented in Fig. 3.2 indicates that the TE powder contained Sb, Te, and TiO_2 particles. The TE films deposited by NPDS were composed of Sb_2Te_3 compound and TiO_2 particles. Moreover, the XRD peaks of the TE films were broader than those of the TE powder. These results show that the consolidation and fracture of the TE powder during deposition process resulted in a formation of Sb_2Te_3 compound and a reduction of the crystallite size in the TE film.

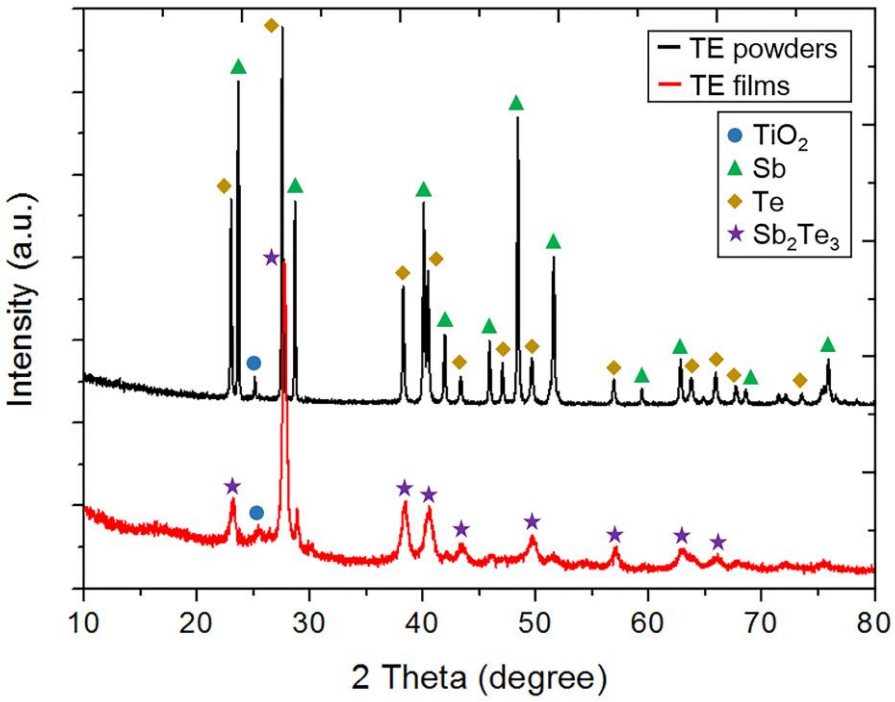

Figure 3.2. X-ray diffraction (XRD) patterns of the TE powder and the TE films.

3.3 Seebeck coefficient and internal resistance

Figure 3.3 shows the composition ratio of the TiO_2 dependence of the Seebeck coefficient and internal resistance of one TE leg. The Seebeck coefficient and internal resistance were inversely proportional. At 3 wt% TiO_2 content, the largest Seebeck coefficient was approximately 160 μV/K, and the lowest internal resistance of 0.832 kΩ was identified. These results demonstrate that an optimal volume of TiO_2 enhances the TE properties of the TE film. However, above 3 wt%, the TiO_2 composition decreased the TE properties owing to its high electrical resistivity. The TE legs of the TE generator were fabricated by TE powder with 3 wt% TiO_2 contents.

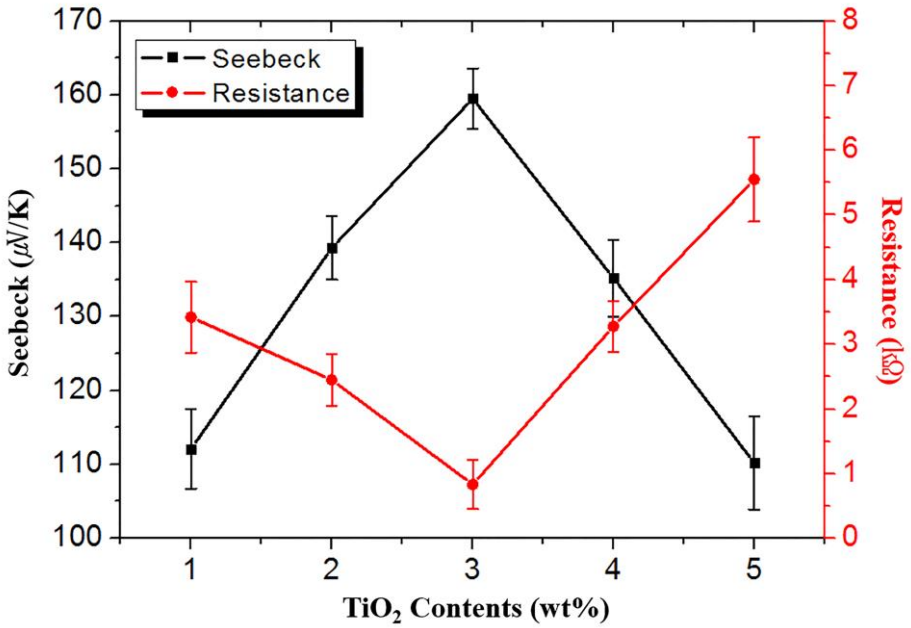

Figure 3.3. Seebeck coefficient and internal resistance of one TE leg as a function of the TiO_2 ratio.

3.4 Prototype flexible TE generator

A prototype flexible TE power generator was successfully fabricated, as shown in Fig. 3.4. Sixteen TE legs were connected by Ag connects; the flexible PVC substrate could be bent perpendicular with respect to the TE direction, and the TE legs had sufficient adhesion to the PVC substrate to endure bending.

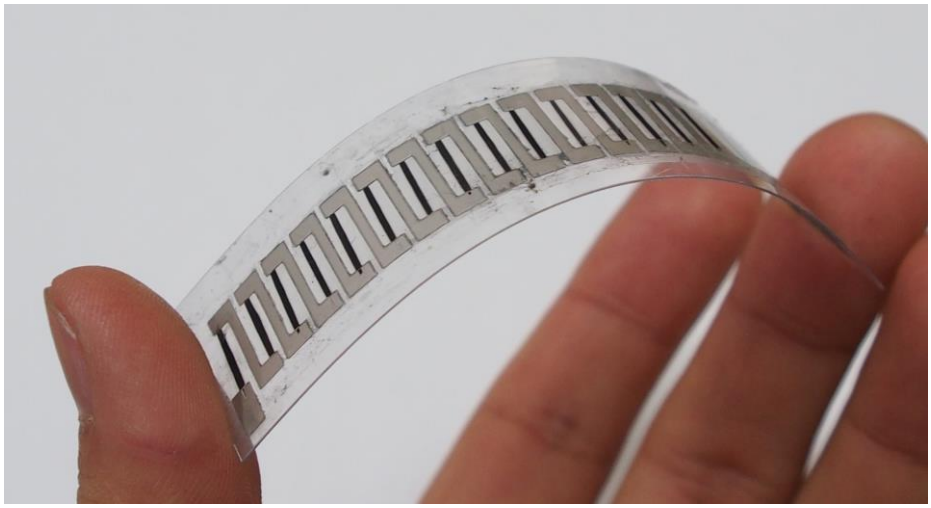

Figure 3.4. Image of the flexible TE generator under bending stress.

3.5 Voltage and power output

The voltage and power output for the prototype flexible TE power generator were measured as a function of the temperature difference in Fig. 3.5. The inset shows how voltage and current were measured, and how the temperature differential gradient was applied to the end of each leg by a heat sink and hot plate. According to Fig. 3.5, the maximum voltage was 48.91 mV, and the maximum power output was 0.18 μW at $\Delta T = 20$ K.

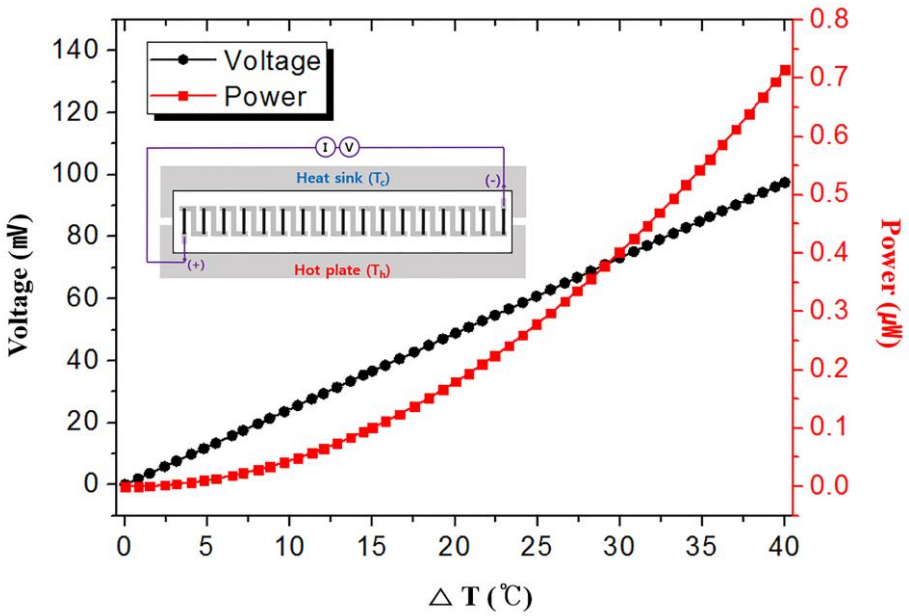

Figure 3.5. Voltage and power output for the flexible TE power generator as a function of the temperature differential. The inset shows a schematic of the measurement setup.

3.6 Comparison

Various fabrication processes for flexible TE generators were compared in Table 3.1. Screen printing consume a large amount of energy due to the high annealing temperatures (250℃) and high pressing pressure (250 × 106 Pa) [16], and inkjet printing also need high annealing temperature (400℃) [6]. CVD uses a large amount of energy, due to the growth temperature required (400℃) [7]. Although NPDS operates at room temperature and under low-vacuum conditions (10000 Pa), the TE properties of a generator fabricated by NPDS were comparable to that of a TE generator fabricated by high-energy consumption processes. Therefore, NPDS is a promising new, energy-efficient method for TE generator fabrication.

Table 3.1. Comparison of various fabrication processes for flexible TE generators.

Process	**NPDS**	Screen printing	Inkjet printing	CVD
Materials	**TiO_2/Sb_2Te_3**	$Bi_{1.8}Te_{3.2}$, Sb_2Te_3	$Sb_{1.5}Bi_{0.5}Te_3$, $Bi_2Te_{2.7}Se_{0.3}$	Bi_2Te_3, $Bi_{0.4}Sb_{1.6}Te_{3.0}$
Substrate	**PVC**	Polyimide	Polyimide	SiO_2/GaAs
Temperature (℃)	**RT**	RT	60	400
Pressure (Pa)	**10000 (low vacuum)**	250×10^6 (high pressure)	Atmosphere	High vacuum
Annealing (℃)	**None**	250	400	None
Thickness (μm)	**60**	78.4	Not specified	4
Seebeck coefficient (μV/K)	**160**	104	139	230
Maximum power output at ΔT = 20 ℃	**0.18 μW of power by 16 TE legs**	40.3 nW of power by 16 TE junctions	Not specified	0.2 μW of power by 20 pairs of TE legs

NPDS: nanoparticle deposition system; CVD: chemical vapor deposition; PVC: polyvinyl chloride.

Chapter 4. Conclusions

Sixteen TiO_2/Sb_2Te_3 TE legs were patterned on a flexible PVC substrate using NPDS at room temperature and under low-vacuum. To improve the TE properties and adhesion between the film and substrate, TiO_2 nanopowders were dispersed on the starting TE powders with 3 wt% content. A TE leg, deposited with 3 wt% TiO_2, had the highest Seebeck coefficient (about 160 μV/K) and the lowest internal resistance of 0.832 kΩ. The prototype TE generator produced 0.18 μW at 48.91 mV and 3.68 μA for a temperature difference of 20 K. This value is similar to those of high-energy consumption methods. Therefore, the NPDS provides a novel, energy-efficient means of TE film deposition for eco-friendly fabrication of TE generators. Our future work will focus on decreasing the internal resistance of the module and the contact resistance between the element and electrode for optimizing the power output of the TE generator.

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Abstract (Korean)

본 연구에서는 나노 입자 적층 시스템으로 티타늄 다이옥사이드, 안티몬, 그리고 텔루륨 분말을 사용한 유연 열전소자 발전기를 제시하였다. 나노 입자 적층 시스템은 작은 에너지 소비를 갖는 새로운 건식 스프레이 방법으로서, 상온과 저 진공 상태에서 무기물 재료들을 기판에 증착할 수 있다. 티타늄 다이옥사이드 나노 분말들은 열전소자 층과 기판 사이의 접착을 향상시키기 위해 열전소자 분말들에 분산되었다.

증착된 열전소자 층의 모폴로지는 주사전자현미경에 의해 조사하였으며, 상의 구조는 엑스레이 분산을 이용하여 분석하였다. 질량비가 3 w%인 티타늄 다이옥사이드로 증착된 하나의 열전소자 구간은 최대 약 160 μV/K의 제백 계수를 가졌다. 제작된 열전소자 발전기의 프로토 타입은 은 배선으로 연결된 16개의 열전소자 구간들로 이루어졌으며 이 면적은 $20 \times 60\,\mathrm{mm}^2$ 였다. 프로토 타입은 20 K의 온도 구배 차이에서 48.91 mV의 전압과 최대 0.18 μW의 전력을 만들 수 있었다. 이 수치들은 기존의 열전소자 발전기 제작 방법으로 제작된 열전소자 발전기의 수치들과 비교할 만하였다. 이 결과들은 유연 열전소자 발전기가 보다 에너지 효율적인 방법으로 제작될 수 있음을 제시하였으나, 내부와 접촉 저항은 개선되어야 한다.

주 요 어: 나노 입자 적층 시스템, 유연 열전소자 발전기, 건식 스프레이 증착, 상온.

학 번: 2014-21841