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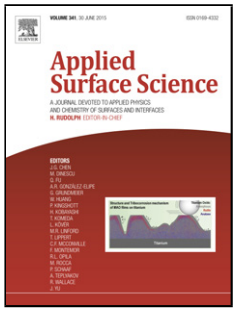

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Thermoelectric performance of electrophoretically deposited *p*-type Bi_2Te_3 film

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Highlights

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- Fabrication of uniform, crack-free *p*-type Bi_2Te_3 films using a fast, cost-effective, EPD method for TE applications.
- The microstructures of the surface and thickness of the green and sintered films have been investigated using SEM.
- An in-plane Seebeck coefficient of 237μV/K has been recorded for the sintered film at 500K.

Abstract

In this study, *p*-type Bi_2Te_3 films were fabricated using a fast, cost-effective, electrophoretic deposition method for thermoelectric applications. The sintering process was carried out at 693K, which resulted in compact, dense coatings. SEM investigations showed the uniform and even thicknesses across the green and sintered films. In addition, their microstructures were examined in more depth. Furthermore, the Seebeck coefficient measurements of the green and sintered films were compared and the highest in-plane Seebeck coefficients of 239μV/K have been recorded for the sintered film at 500 K.

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Keywords—Electrophoretic deposition; Bi_2Te_3 Thick Films; Microstructure; Sintering; Seebeck coefficient; Thermoelectric materials.

Introduction

A temperature gradient can generate an electricity current i.e. potential differences in thermoelectric (TE) materials [1, 2]. One major source to provide the temperature difference is the enormous amount of waste heat (approximately 2/3 of the total energy production in the world [3, 4]) released every day into the atmosphere from different sources such as industrial processes, almost all of the energy production methods, cars, planes, computers or even stovetops [5, 6]. Transforming even a small portion of this huge amount of waste heat into electricity could contribute towards a reduction in global warming through lower fossil fuel consumption and, most importantly, provide a solution for energy uncertainties [2, 7].

However, thermoelectric materials have found limited applications, because of some serious challenges such as their low specific power factor [8, 9] and the high production cost of thermoelectric generators [5, 10]. Thermoelectric devices are currently used in restricted applications and specific cases such as deep-space satellites because they have no moving parts and present zero vibration [1, 4, 6, 11]. The objective of this research is to provide some solutions for those important issues by fabricating high-quality thermoelectric film using a fast cost-effective film fabrication method called Electrophoretic deposition (EPD) [12].

In EPD, the charged powder particles of a suspension are attracted and deposited onto a substrate with the opposite charge under a DC electric field [13, 14]. A coherent, crack-free film with a uniform microstructure can be achieved with requiring simple equipment [15]. In addition, EPD presents a number of advantages, which is especially important for TE applications. For instance, the stoichiometry of the film is determined by the starting powder because there is no chemical reaction

during the film fabrication process which helps to accomplish and maintain high TE characteristics [13]. Furthermore, EPD can increase the grain boundaries of the microstructure and therefore enhance the TE properties [16].

The EPD method has been used for research in countless areas, such as solid oxide fuel cells [17], superconductors [18], etc.; it has also been utilized for various medical and industrial applications, such as corrosion protection, for many years [13]. However, a limited amount of research has been reported on various TE materials such as Bi_2Te_3, which is the focus component of this investigation [19-23].

This article reports on fabrication of coherent high-quality crack-free microstructures of *p*-type Bi_2Te_3 films deposited on Cu-substrates using the EPD method. In addition, the thermoelectric properties of the green (not sintered) and sintered films have been measured.

Methodology

A *p*-type Bi_2Te_3 powder was used to deposit the films on Cu-substrates. The average particle size of the powder was 10µm. To prepare Bi_2Te_3 films, the time and voltage of the EPD process were 100V and 10 minutes, respectively. More details about the starting powder, the EPD process and film preparations have been reported elsewhere [21, 22]. The media of the EPD suspensions were 100% vol. tetrahydrofuran (THF) with a purity of 99%. THF was selected via a thorough research process, which will be discussed in future publications. The sintering of the as-deposited (green) films was conducted in an Ar-controlled environment tube furnace at 693K for 1 hour. The optimum conditions for the EPD technique, as well as the sintering processes such as temperature and time, were determined through systematic investigation and the results will be reported in future publications. The microstructures of the Bi_2Te_3 films have been characterized using SEM (scanning electron microscope - Quanta 450) and the Rigaku MiniFlex 600 XRD was used to determine the changes in

the phases and crystal structures of the green and sintered films. The chemical composition was measured using EDX (Energy-dispersive X-ray spectroscopy) of SEM. To evaluate the thermoelectric properties of the deposited films, an MMR Seebeck Measurement System (SB1000 and K2000) has been used to measure the in-plane Seebeck coefficient of the films, at a temperature range of 300-500K, with a rate of 5k/min. The films were separated from the Cu substrate before measuring its Seebeck coefficients to eliminate the Cu substrate effect on the Seebeck coefficients of the deposited films. A large number of samples was prepared and SEM, XRD, density and Seebeck coefficient measurement experiments were repeated at least 20 times on various samples. The reported data is an average amount.

Results and discussion

To confirm the stoichiometry of the green and sintered films, XRD analysis of the films was performed (Figure 1) and the existence of the *p*-type Bi_2Te_3 phase is confirmed. No other phases and no changes were identified because of the sintering process. All peaks could be assigned to the rhombohedral structure, as previously reported [24-26]. The peaks exactly correspond to the (006), (015), (1010), (0111), (0015) and (115) reflections of the $Bi_{0.5}Sb_{1.5}Te_3$ compound in the stable Bi_2Te_3 phase [24-26]. In addition, the chemical composition and weight percentages of *p*-type Bi_2Te_3 powder were measured using the EDX (Energy-dispersive X-ray spectroscopy) of SEM [22] and its chemical formula was calculated as $Bi_{0.5}Sb_{1.5}Te_3$.

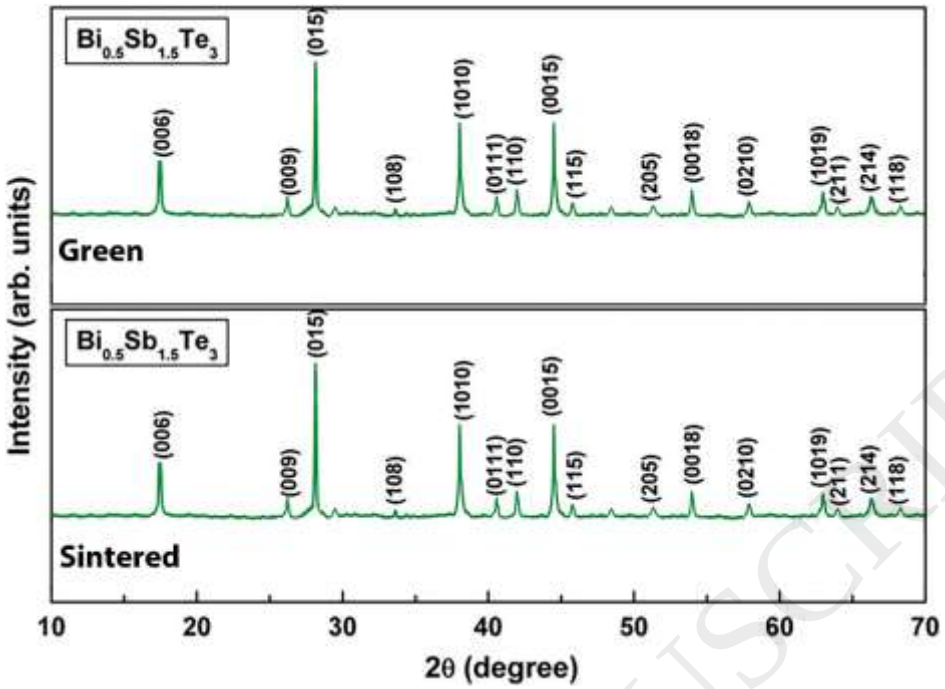

Figure 1. XRD results of (a) green and (b) sintered *n*-type Bi_2Te_3 films.

The film has a coherent, even and uniform density with no detectable cracks. Fig. 2 shows the microstructures of a high-quality green Bi_2Te_3 film deposited at 100V for 10 minutes at various magnifications. The film appeared smooth (Fig 2a) with powder particles deposited compactly and efficiently when examined at higher magnifications (Fig 2b, c, d), indicating the employment of appropriate EPD voltage and time.

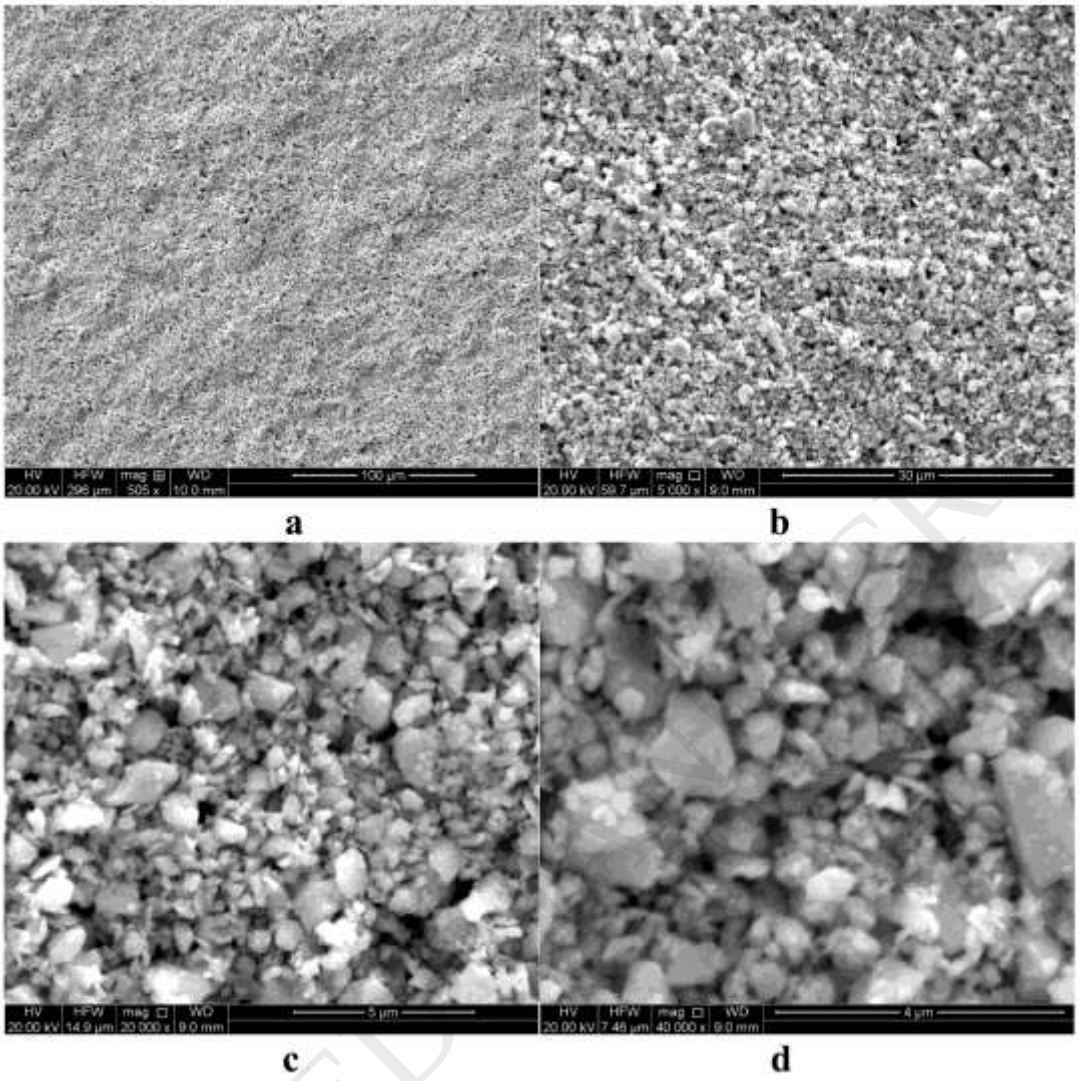

Fig. 2. SEM images of a typical Green Bi_2Te_3 film at various magnifications.

The sintering of the as-fabricated green films at 693K for 1 hour resulted in the formation of a crack-free and uniform microstructure, see Fig. 3a. Close observation of the sintered films (Fig. 3b, c, d) indicates the effectiveness of diffusion in closing the small porosities between the particles to render a coherent high-quality film produced by the EPD process.

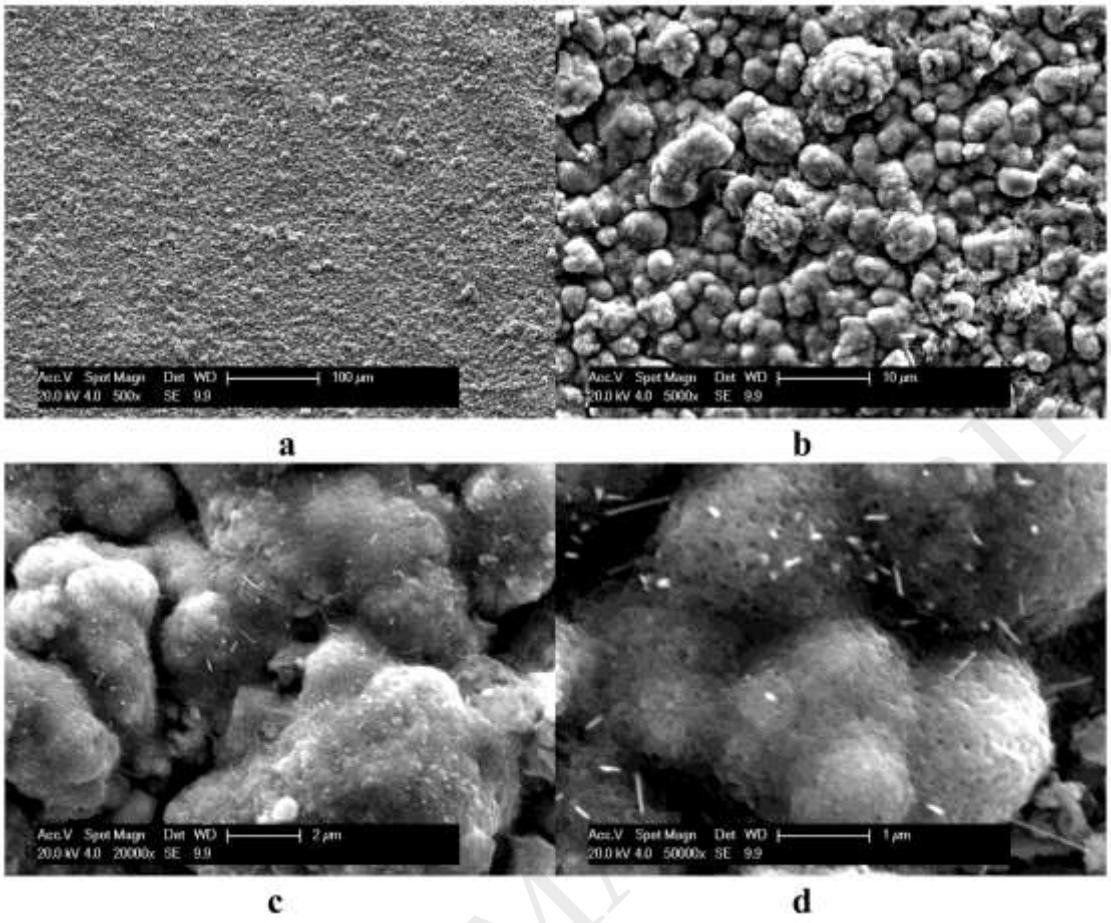

Fig. 3. SEM images of Sintered Bi_2Te_3 films at various magnifications.

In addition, the sintering process increases the density of the films. The density of the green and sintered films was increased from 5.6g/cm^3 to 7.17g/cm^3, respectively, which comprises approximately 72 and 92% of the theoretical density of Bi_2Te_3 powder (7.74 g/cm^3) [25]. The open porosity percentages of the films were also decreased by the sintering process to below 3% for the sintered films. In general, to achieve a high Seebeck coefficient and thermoelectric properties, a film with a density closer to the theoretical density is favourable [3, 5, 27, 28] because it can increase the diffusion of the charge carrier [3, 5, 7] and phonon drag [27, 29, 30] of a material.

Furthermore, the thickness of the green film is uniform, even, and approximately 25μm when investigated at higher magnification (Fig. 4a). The analysis of the cross-section of the sintered film confirms there is little or no porosity, suggesting the sintering temperature was suitable to achieve a dense microstructure, Fig. 4b. However, the coating has shrunk and the thickness of the sintered film decreased from around 25μm in the green state to approximately 16μm as a result of diffusion and closing down the pores [31, 32].

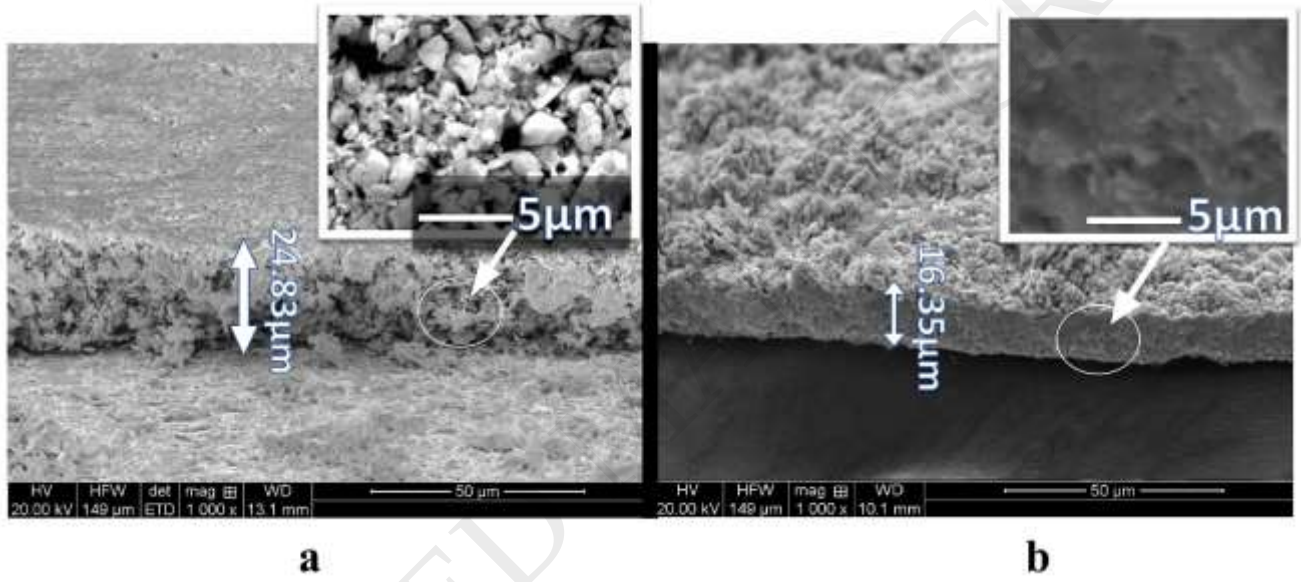

Fig. 4. SEM images of the thickness of the Bi_2Te_3 film. (a) Green film; (b) Sintered film.

The thermoelectric properties of the green and sintered deposited films were also investigated. The in-plane Seebeck coefficients of deposited films were measured at a temperature range of 300-500 K for both green and sintered films and the absolute values of the Seebeck coefficients are presented in Fig. 4. The results show that the Seebeck coefficients had a positive value, as expected, because the films were deposited from p-type thermoelectric materials.

It is clear that the values of the Seebeck coefficients of the sintered films are much higher than those of the green film. The Seebeck coefficient of the sintered film was around 10 times greater at room temperature and the difference increases even further to approximately 12 times greater when the test temperature increased to 500K. The results also reveal that the values of the Seebeck coefficients of the green films slightly increase with any increase in the test temperature; from 15μV/K at 300K to around 17μV/K at 500K (~15%). However, the rise in the values of the Seebeck coefficients of the sintered films is more significant; from 176μV/K at 300K to approximately 239μV/K at 500K (~50%).

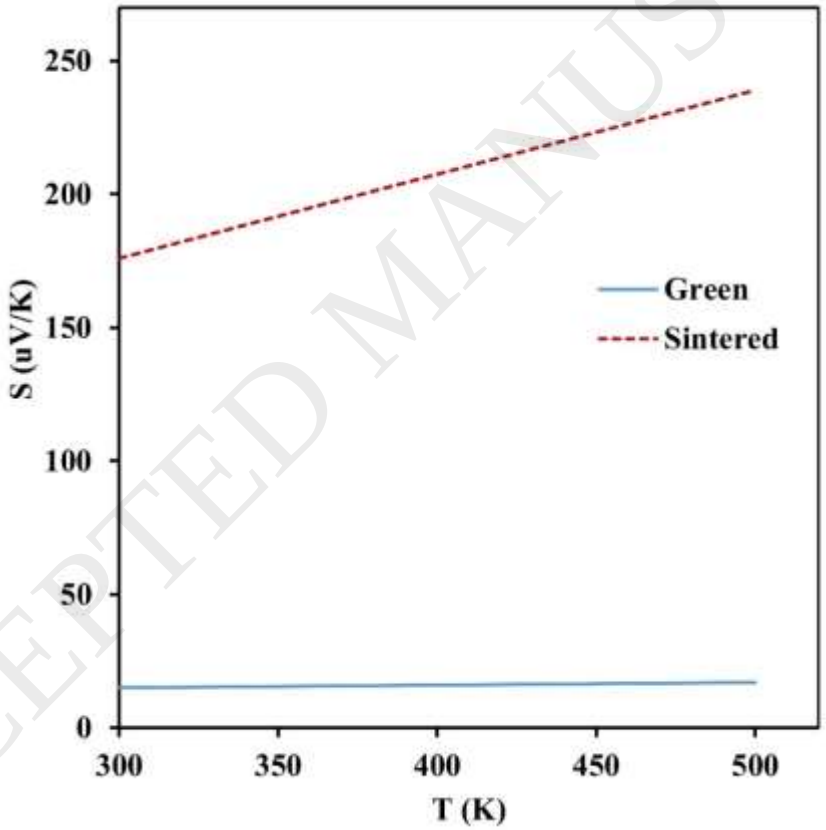

Fig. 5. Variations of the Seebeck coefficients of the green and sintered films with the test temperature.

The weak Seebeck coefficients of the green films may result from the weak van der Waals bonds between the particles of the green films, which can obstruct the electrical properties of the deposited films [30]. Conversely, for the sintered films, since the deposited particles were bonded together, the density of the film was increased and the porosity of the film was decreased. This can contribute to the diffusion of the charge carrier [3, 5, 7] and phonon drag [27, 29, 30] of a material and consequently an increase in the Seebeck coefficient and thermoelectric properties [3, 5, 27, 28].

Different values of Seebeck coefficients have been reported by researchers using various deposition method to prepare p-type Bi_2Te_3 film. A Seebeck coefficient of 142μV/K at 300K has been measured using an electrodeposition technique which is comparable to the EPD method [25, 33]. This suggests that the thermoelectric performance can be improved by decreasing the porosity of the deposited films, as well as omitting unwanted elements of the solutions from the films.

Furthermore, a Seebeck coefficient of 203μV/K at 300K has been measured when a co-sputtering method has been used to deposit a p-type Bi_2Te_3 film [34]. In comparison with the EPD method (176μV/K at 300K), a complex process and expensive equipment has been utilised to reach a relatively higher Seebeck coefficient. However, the process is slow (2μm per hour) and it needs a good vacuum pressure (6.0×10^{-4}Pa). During the EPD process, there is no need to have a vacuum chamber or any other expensive equipment and the deposition rate is much quicker (more than 2μm per minute, approximately 60 times faster). Although, the recorded Seebeck coefficient is around 25% lower, the finished cost is much lower which makes EPD more interesting for real TE applications. Beyond this, the Seebeck coefficient of the films deposited by EPD can be improved by various methods such as doping, which will be reported in future publications.

Conclusions

In conclusions, a crack-free *p*-type Bi_2Te_3 films were successfully deposited using a fast, cost-effective, electrophoretic deposition method for thermoelectric applications. Dense coatings were achieved after the sintering process at 693K. The SEM analysis was carried before and after the sintering process which showed uniform microstructures and even film thicknesses. In addition, the in-plane Seebeck coefficient of the green and sintered films were measured. The results showed a satisfactory thermoelectric performance for sintered films (239μV/K at 500K) which is comparable to other film deposition methods.

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References

1. Snyder, G.J. and E.S. Toberer, *Complex thermoelectric materials.* Nature Materials, 2008. **7**(2): p. 105-114.
2. Snyder, G., *Thermoelectric power generation: Efficiency and compatibility.* Thermoelectrics Handbook: Macro to Nano, 2006.
3. Alam, H. and S. Ramakrishna, *A review on the enhancement of figure of merit from bulk to nano-thermoelectric materials.* Nano Energy, 2013. **2**(2): p. 190-212.
4. Tritt, T.M., *Thermoelectric phenomena, materials, and applications.* Annual Review of Materials Research, 2011. **41**(1): p. 433-448.
5. Hamid Elsheikh, M., et al., *A review on thermoelectric renewable energy: Principle parameters that affect their performance.* Renewable and Sustainable Energy Reviews, 2014. **30**: p. 337-355.
6. Tritt, T.M. and M.A. Subramanian, *Thermoelectric materials, phenomena, and applications: A bird's eye view.* MRS Bulletin, 2006. **31**(03): p. 188-198.
7. Nolas, G.S., J. Poon, and M. Kanatzidis, *Recent developments in bulk thermoelectric materials.* MRS Bulletin, 2006. **31**(03): p. 199-205.
8. Majumdar, A., *Thermoelectricity in semiconductor nanostructures.* Science, 2004. **303**(5659): p. 777-778.

9. Aswal, D.K., R. Basu, and A. Singh, *Key issues in development of thermoelectric power generators: High figure-of-merit materials and their highly conducting interfaces with metallic interconnects.* Energy Conversion and Management, 2016. **114**: p. 50-67.
10. LeBlanc, S., et al., *Material and manufacturing cost considerations for thermoelectrics.* Renewable and Sustainable Energy Reviews, 2014. **32**: p. 313-327.
11. Böttner, H., G. Chen, and R. Venkatasubramanian, *Aspects of thin-film superlattice thermoelectric materials, devices, and applications.* MRS Bulletin, 2006. **31**(03): p. 211-217.
12. Gutierrez, C.P., J.R. Mosley, and T.C. Wallace, *Electrophoretic Deposition: A Versatile Coating Method.* Journal of The Electrochemical Society, 1962. **109**(10): p. 923-927.
13. Besra, L. and M. Liu, *A review on fundamentals and applications of electrophoretic deposition (EPD).* Progress in Materials Science, 2007. **52**(1): p. 1-61.
14. Corni, I., M.P. Ryan, and A.R. Boccaccini, *Electrophoretic deposition: From traditional ceramics to nanotechnology.* Journal of the European Ceramic Society, 2008. **28**(7): p. 1353-1367.
15. Ata, M.S. and I. Zhitomirsky, *Electrophoretic nanotechnology of ceramic films.* Advances in Applied Ceramics: Structural, Functional & Bioceramics, 2012. **111**(5/6): p. 345-350.
16. Ferrari, B. and R. Moreno, *EPD kinetics: A review.* Journal of the European Ceramic Society, 2010. **30**(5): p. 1069-1078.
17. Azarian Borojeni, I., et al., *Fabrication of Solid Oxide Fuel Cells (SOFCs) Electrolytes by Electrophoretic Deposition (EPD) and Optimizing the Process.* Key Engineering Materials, 2015. **654**: p. 83- 87.
18. Maiti, H.S., S. Datta, and R.N. Basu, *High-Tc Superconductor Coating on Metal Substrates by an Electrophoretic Technique.* Journal of the American Ceramic Society, 1989. **72**(9): p. 1733-1735.
19. Kishio, K., et al. *Electrophoretic Deposition under High Magnetic Field and Fabrication of Multi-layered Oxide pn Thermoelectric Modules*. in *Meeting Abstracts*. 2008. The Electrochemical Society.
20. Nozariasbmarz, A., et al., *Enhancement of thermoelectric power factor of silicon germanium films grown by electrophoresis deposition.* Scripta Materialia, 2013. **69**(7): p. 549-552.
21. Talebi, T., et al., *Electrophoretic Deposition of p-Type Bi2Te3 for Thermoelectric Applications.* International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering, 2017. **11**(4).
22. Talebi, T., et al., *Preparation of n-type Bi2Te3 Films by Electrophoretic Deposition.* International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering, 2017. **11**(4): p. 11 - 14.
23. Talebi, T., et al., *Fabrication of n-type Bi2Te3 film using electrophoretic deposition for thermoelectric applications.* Surface and Coatings Technology, 2017.
24. Yan, X., et al., *Experimental Studies on Anisotropic Thermoelectric Properties and Structures of n-Type Bi2Te2.7Se0.3.* Nano Letters, 2010. **10**(9): p. 3373-3378.
25. Goldsmid, H., *Bismuth telluride and its alloys as materials for thermoelectric generation.* Materials, 2014. **7**(4): p. 2577.
26. Jeon, S.-j., et al., *Microstructure evolution of sputtered BiSb–Te thermoelectric films during post-annealing and its effects on the thermoelectric properties.* Journal of Alloys and Compounds, 2013. **553**: p. 343-349.
27. Shakouri, A., *Recent developments in semiconductor thermoelectric physics and materials.* Annual Review of Materials Research, 2011. **41**(1): p. 399-431.
28. Schierning, G., *Silicon nanostructures for thermoelectric devices: A review of the current state of the art.* physica status solidi (a), 2014. **211**(6): p. 1235-1249.
29. Rao, A.M., X. Ji, and T.M. Tritt, *Properties of Nanostructured One-Dimensional and Composite Thermoelectric Materials.* MRS Bulletin, 2006. **31**(03): p. 218-223.
30. Liu, W., et al., *Recent advances in thermoelectric nanocomposites.* Nano Energy, 2012. **1**(1): p. 42-56.
31. Talebi, T., M. Haji, and B. Raissi, *Effect of sintering temperature on the microstructure, roughness and electrochemical impedance of electrophoretically deposited YSZ electrolyte for SOFCs.* International Journal of Hydrogen Energy, 2010. **35**(17): p. 9420-9426.

32. Van Tassel, J. and C.A. Randall, *Electrophoretic deposition and sintering of thin/Thick PZT films.* Journal of the European Ceramic Society, 1999. **19**(6–7): p. 955-958.
33. Wu, M., K. Binnemans, and J. Fransaer, *Electrodeposition of antimony from chloride-free ethylene glycol solutions and fabrication of thermoelectric Bi2Te3/(Bi1−xSbx)2Te3 multilayers using pulsed potential electrodeposition.* Electrochimica Acta, 2014. **147**: p. 451-459.
34. Cai, Z.-k., et al., *Thermoelectric properties and micro-structure characteristics of annealed N-type bismuth telluride thin film.* Applied Surface Science, 2013. **280**: p. 225-228.