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Fabrication of *n*-type Bi₂Te₃ film using electrophoretic deposition for thermoelectric applications

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Abstract

Fabrication of uniform, crack-free *n*-type Bi₂Te₃ films using a fast, cost-effective, electrophoretic deposition method for thermoelectric applications has been reported in this study. The sintering process has been done at 693K to achieve compact and dense coatings. The microstructures of the surface of the green and sintered films, as well as their thicknesses, have been investigated using SEM, which showed a uniform and even film has resulted using electrophoretic deposition (EPD). Furthermore, the Seebeck coefficients of the green and sintered films have been measured and in-plane Seebeck coefficients of 189 $\mu\text{V/K}$ have been recorded for the sintered film at 500 K.

Keywords—Electrophoretic deposition; Bi₂Te₃ Thick Films; Microstructure; Sintering; Seebeck coefficient; Thermoelectric materials.

Introduction

Thermoelectric (TE) materials are capable of generating potential differences when exposed to a temperature gradient [1]. The temperature difference can be provided by the enormous amount of

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waste heat (approximately 2/3 of the total energy production in the world [2, 3]) released every day into the atmosphere from different sources such as industrial processes, almost all of the energy production methods, cars, planes, computers and even stovetops [4]. Converting 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 [5, 6].

However, because of some serious challenges, such as the low specific power factor [7] of thermoelectric materials and the high production cost of thermoelectric generators [4], they have found limited applications. The main applications are for specific cases where a named characteristic like zero vibration is needed, such as for deep-space satellites [8]. The objective of this research is to provide some solutions for the important issues by fabricating high-quality thermoelectric film using a fast cost-effective film fabrication method called Electrophoretic deposition (EPD) [9].

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 [10, 11]. A high quality and crack-free film can be fabricated with a uniform microstructure requiring simple equipment [12]. In addition, EPD presents a number of advantages, which is especially important for TE applications. For instance, EPD can increase the grain boundaries of the microstructure and therefore enhance the TE properties [13]. Furthermore, 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 [10].

The EPD method has been used for research in countless areas such as solid oxide fuel cells [14], superconductors [15], etc.; it has also been utilized for various medical and industrial applications, such as corrosion protection, for many years [10]. However, a very limited amount of research has been reported on various TE materials such as Bi_2Te_3 , which is the focus component of this investigation [16-19].

This article reports on fabrication of crack-free uniform microstructures of n -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 has been measured.

Methodology

To prepare Bi_2Te_3 films, the time and voltage of the EPD process were 100V and 10 minutes, respectively. The details of the starting powder, the EPD process and film preparations have been reported elsewhere [18, 19]. 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 process 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 coefficients measurement experiments were repeated at least 20 times on various samples. The reported data is an average amount.

Results and discussion

Figure 1 shows the microstructures of a uniform green Bi_2Te_3 film deposited at 100V for 10 minutes at various magnifications. The film has a coherent, even and uniform density with no detectable cracks. It covered the entire submerged area of the substrate in the suspension well. The film appeared smooth (Figure 1a) with powder particles deposited compactly and efficiently when examined at higher magnifications (Figure 1b, c), indicating the employment of appropriate EPD voltage and time. The thickness of the green film is uniform, even, and approximately $25\mu\text{m}$ (Figure 3a).

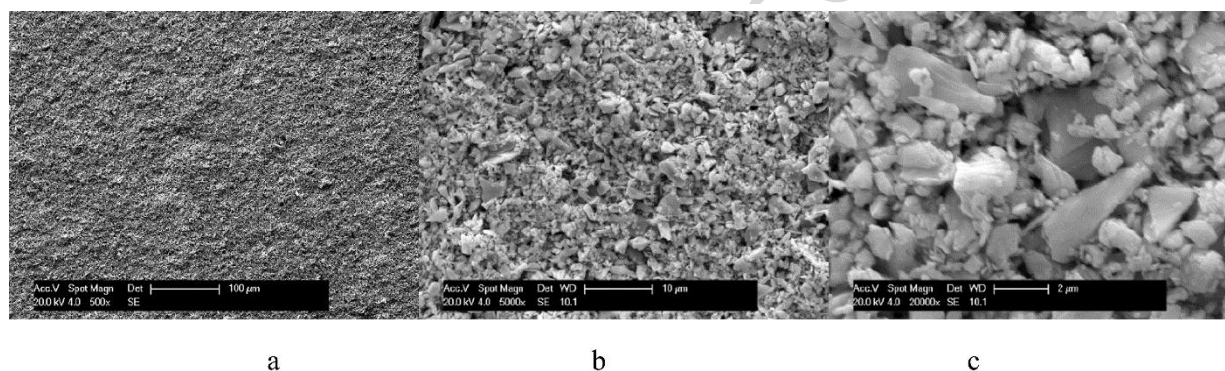


Figure 1. SEM images of a typical Green Bi_2Te_3 film.

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 Figure 2. Close observation of the sintered films (Figures 2b and c) indicate the effectiveness of diffusion in closing the small porosities between the particles to render a coherent film produced by the EPD process. In addition, the sintering process increases the density of the films. The density of the green and sintered films was increased from $5.6\text{g}/\text{cm}^3$ to $7.17\text{g}/\text{cm}^3$, respectively, which are approximately 72 and 92% of the theoretical density of Bi_2Te_3 powder ($7.74\text{g}/\text{cm}^3$) [20]. 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 [2, 4, 21, 22] because it can increase the diffusion of the charge carrier [2, 4, 5] and phonon drag [21, 23, 24] of a material.

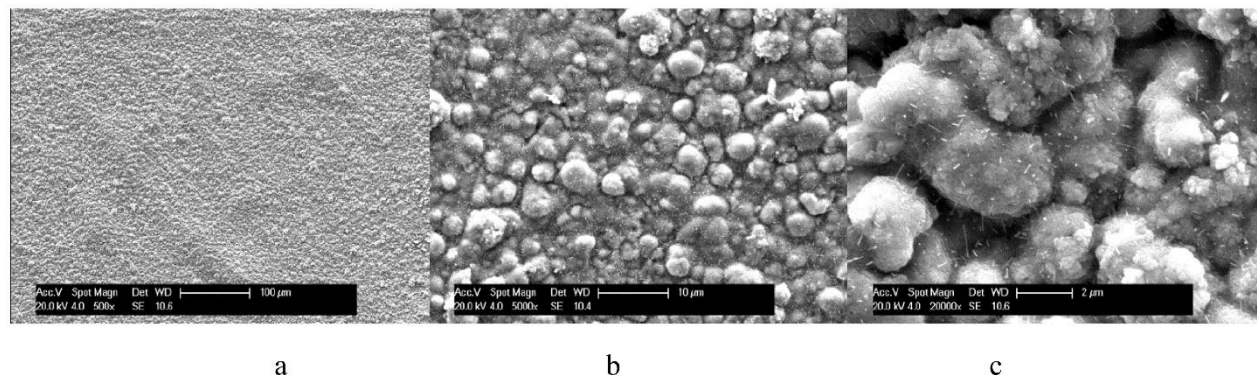


Figure 2. SEM images of Sintered Bi_2Te_3 films.

Furthermore, the analysis of the thickness measurement of the sintered film confirms there is little or no porosity, suggesting the sintering temperature was suitable to achieve a dense microstructure, Figure 3b. However, the coating has shrunk and the thickness of the sintered film decreased from around 25 μm in the green state to approximately 16 μm , as a result of diffusion and closing down the pores [25, 26].

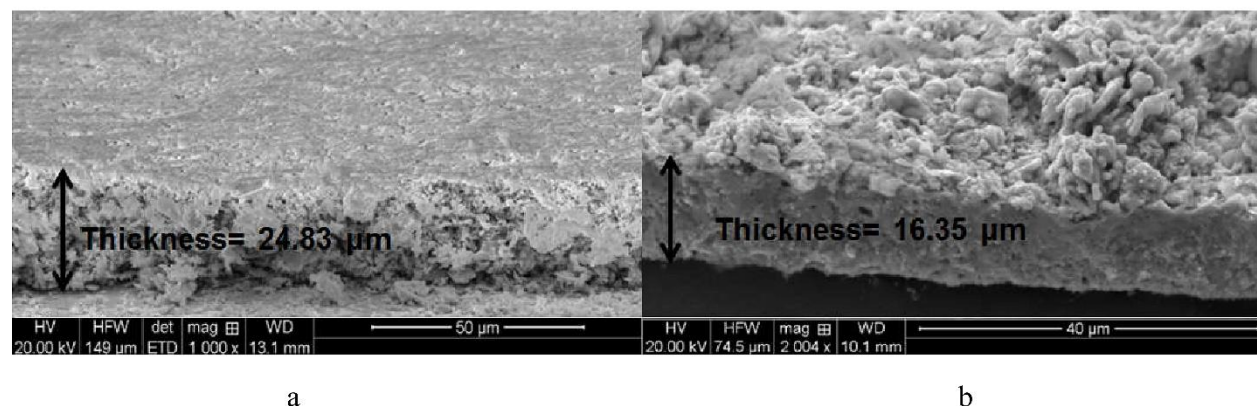


Figure 3. SEM images of the thickness of the Bi_2Te_3 film. (a) Green film; (b) Sintered film

To confirm the stoichiometry of the green and sintered films, XRD analysis of the films was performed (Figure 4) and the existence of the *n*-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 [20, 27, 28]. The peaks exactly correspond to the (006), (015), (1010), (0111), (0015) and (115) reflections of the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ compound in the stable Bi_2Te_3 phase [20, 27, 28]. In addition, the chemical composition and weight percentages of *n*-type Bi_2Te_3 powder were measured using the EDX (Energy-dispersive X-ray spectroscopy) of SEM [19] and its chemical formula was calculated as $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

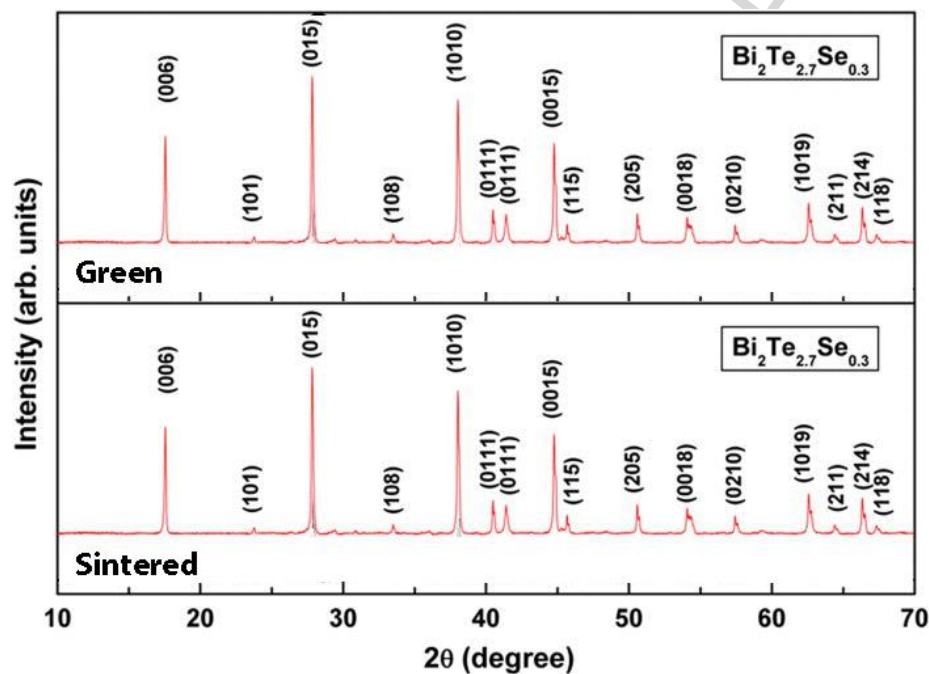


Figure 4. XRD results of (a) green and (b) sintered *n*-type Bi_2Te_3 films.

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 300-500K for both green and sintered films and the absolute values of the Seebeck coefficients are presented in Figure 5. The results show that the Seebeck coefficients had a negative value, as expected, because the films were deposited from *n*-type thermoelectric materials.

It is clear that the absolute 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 absolute values of the Seebeck coefficients of the green films slightly increase with any increase in the test temperature; from $13\mu\text{V/K}$ at 300K to around $15\mu\text{V/K}$ at 500K ($\sim 15\%$). However, the rise in the absolute values of the Seebeck coefficients of the sintered films is more significant; from $126\mu\text{V/K}$ at 300K to approximately $189\mu\text{V/K}$ at 500K ($\sim 50\%$).

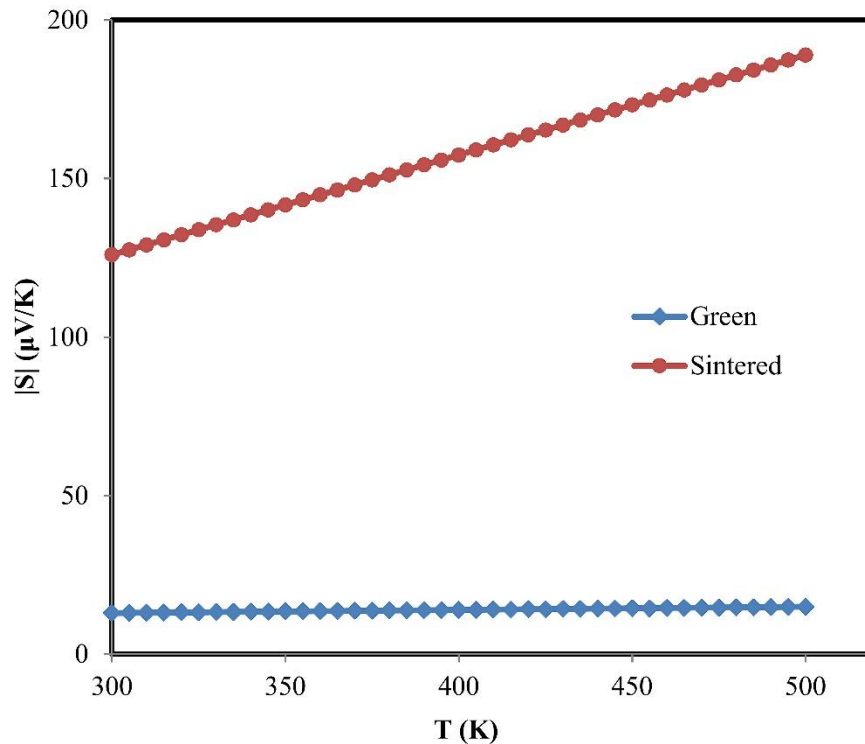


Figure 5. Variations of the Seebeck coefficients of the green and sintered films with the test temperature.

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 [24]. 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 [2, 4, 5] and phonon drag [21, 23, 24] of a material and consequently an increase in the Seebeck coefficient and thermoelectric properties [2, 4, 21, 22].

Different values of Seebeck coefficients have been reported by researchers using various deposition methods to prepare *n*-type Bi₂Te₃ film. A Seebeck coefficient of -80 μ V/K at 300K has been measured using an electrodeposition technique, which is comparable to the EPD method [29]. 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 160 μ V/K at 300K has been measured when a co-sputtering method has been used to deposit a Bi₂Te₃ film [30]. In comparison with the EPD method (126 μ V/K at 300K), a complex process and expensive equipment has been utilised to reach a relatively higher Seebeck coefficient. However, the process is slow (2 μ m 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 2 μ m 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 summary, a coherent, crack-free and uniform *n*-type Bi₂Te₃ film has been successfully deposited by a cost-effective electrophoretic deposition method for thermoelectric applications for the first

time. The SEM analysis showed that the films have uniform and even structures before and after the sintering process. Further investigations of the film thicknesses also showed a dense microstructure has been achieved by sintering the film at 693K. In addition, the Seebeck coefficient measurements indicated that films deposited by EPD had an acceptable thermoelectric performance after sintering at an appropriate temperature, which can lead to lowering the cost of TE devices for various applications.

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Highlights

In this paper, coherent uniform high-quality and crack-free n-type Bi_2Te_3 films has been fabricated using a fast, cost-effective, electrophoretic deposition method for the first time. After sintering process at 420 °C, a compact and dense coatings has been achieved.

It also has been reported that the thermoelectric properties of the sintered films produced by the cost-effective EPD method is comparable to other expensive methods.