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Effect of Annealing on Virgin and Recycled Carbon Fibre Electrochemically-Deposited with N-type Bismuth Telluride

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N-type thermoelectric bismuth telluride (Bi_2Te_3) was deposited on virgin carbon fibre (VCF) and recycled carbon fibre (RCF) substrates by electro-deposition. The effects of annealing on the surface morphology and the Seebeck coefficient of the Bi_2Te_3 films were investigated. A nearly stoichiometric N-type Bi_2Te_3 was obtained from an electrolyte of 8 mM of $Bi(NO_3)_3.5H_2O$ and 10mM of TeO_2, which exhibited the highest Seebeck coefficient of -20.1 µV/K and -13.0 µV/K for VCF and RCF individually. The effect of varying annealing temperature (548.15 K and 623.15 K) and annealing time (2 and 3 h) was carried out only on nearly stoichiometric N-type Bi_2Te_3 that revealed improvement in Seebeck coefficient up to 1.51 times and 1.24 times for VCF and RCF at 623.15 K for 2 h.

1. Introduction

The increasing usage of carbon fibre in the aerospace, automotive and sports goods industries since the late 20th century has led to an end of life concern for the carbon fibre composites with an estimated 3,000 t of carbon fibre scrap being generated annually (McConnell, 2010). The disposal of carbon fibre through incineration or landfill has been deemed not optimal and there have been environmental regulations that have imposed a ban on this material, as it is non-biodegradable (Pico et al., 2014). In 1999, the European Union has enforced the Landfill Directive (1999/31/EC) that restricts the disposal of carbon fibre as a chemical waste. Therefore, there is a need for recycling these carbon composites that would not only save disposal cost, but also provide an avenue for the reuse of this material (Pang et al., 2012).Different routes to utilise recycled carbon fibre are being explored to close the recycling loop. Amongst them, RCF has a great potential to be used in the field of thermoelectricity due to its natural electrically conductive nature. The primary parameter that determines the optimal performance of a thermoelectric module is the figure of merit (ZT) given by Eq (1). Where α is the Seebeck coefficient; T is the temperature; ρ is the electrical resistivity and κ is the thermal conductivity. Carbon fibre has a low electrical resistivity which makes it easier to tamper with its Seebeck coefficient, therefore recycled carbon fibre with a layer of thermoelectric coating will be an ideal flexible thermoelectric module (Pang et al., 2012). Seebeck coefficient is given due attention in this study, as it has the largest contribution to the ZT value as shown in Eq (1). The Seebeck coefficient is defined by Eq (2), where ΔV is the potential difference generated from an induced temperature difference, ΔT.

$$ZT = \frac{T\alpha^2}{\rho\kappa} \quad (1)$$

$$\alpha = \frac{\Delta V}{\Delta T} = \frac{V_H - V_C}{T_H - T_C} \quad (2)$$

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The chosen technique for the synthesis of Bi_2Te_3 is electro-deposition, as it has a low operating and capital cost, near room temperature operation, and relative ease to control the films composition compared to other techniques (Xiao et al., 2008).
According to Pang et al., (2012), some preliminary work has been done to deposit Bi_2Te_3 on recycled carbon fibre using a nitric acid bath that showed a significant improvement in the Seebeck coefficient of RCF. This study will look into thermal annealing to further enhance Seebeck coefficients of RCF. This study will be replicated for both VCF and RCF in order to determine the difference in Seebeck coefficient that arises from its fibre properties. Lastly, this work also investigates the effect of annealing temperature and time on the Seebeck coefficient of RCF and VCF.

2. Methodology

2.1 Carbon Fibres

The carbon fibres used in this experiment are virgin carbon fibres manufactured by Yoho Tenax Co. Ltd with model HTS-406K and T-800s PAN based recycled carbon fibres provided by Recycled Carbon Fibre Limited (RCF) Coseley, United Kingdom.

2.2 Preparation of Electrolyte

The electrolytes were used to deposit Bi_2Te_3 films on both virgin and recycled carbon fibres. The Bi_2Te_3 films were deposited from 1 M of 65 % aqueous nitric acid bath with three different compositions of $Bi(NO_3)_3.5H_2O$ (>98%, Sigma Aldrich) and TeO_2 (>98 %, Sigma Aldrich) as shown in Table 1 (Yoo et al., 2005).

Table 1: Different Compositions of Bismuth Telluride

Batch Number	Batch Composition	
	$Bi(NO_3)_3.5H_2O$ (mM)	TeO_2 (mM)
A	8	10
B	1	10
C	8	11

2.3 Electrochemical Deposition

Electro-deposition is carried out using a potentiostat (VersaStat-3, Princeton Applied Research) at room temperature. The potentiostat was used with a standard three cell electrode configuration whereby the working electrode is the virgin/recycled carbon fibre sheet with dimension of 8 cm x 0.5 cm, the reference electrode is a silver/silver chloride (Ag/AgCl) in 1 M of potassium chloride (KCl) and the counter electrode is a platinum rod.
Cyclic voltammetry is carried out at a scan rate of 0.01 V/s from -1 V to 1 V vs Ag/AgCl (Pang et al., 2012). In the potentiostatic mode, constant agitation is provided at 300 rpm to the electrolyte at a constant deposition potential for 1 h.

2.4 Measurement of Seebeck Coefficient

The Seebeck coefficient is measured using an in house Seebeck measurement set up using the K-type thermocouple and Peltier element. Seebeck coefficient is calculated using the formula in Eq (2) by taking an average of six readings. Where ΔV in microvolts is the potential difference generated between V_H, the potential at hot side and V_C, the potential at cold side, ΔT in Kelvin is the temperature induced between the T_H, temperature on hot side and Tc, temperature on cold side. The improvement in Seebeck after annealing is given by the Seebeck Increment Factor (SIF), which is the ratio of the Seebeck coefficient measured after annealing to that of before annealing.

2.5 Annealing

The carbon fibre strips were placed in a tubular furnace connected to a gas cylinder containing 5 % hydrogen in argon gas. The flow controller was adjusted to a flow rate of 0.006 m^3/h. The tubular furnace was programmed to have a ramping of 4.72 K/s to attain the target temperature of 548.15 K and 623.15 K, as well as annealing time that was varied for 2 and 3 h individually for each annealing temperature.

3. Results and Discussion

3.1 Deposition of N-type Bismuth Telluride and Seebeck Coefficient

Bismuth telluride films with different compositions of Bi and Te were deposited on RCF and VCF with the same electro-deposition parameters. Bi_2Te_3 is a well-known efficient thermoelectric material at room temperature, but a very large part of its efficiency is dependent on the composition of the semiconductor. The thermoelectric properties of Bi_2Te_3 are directly linked to the stoichiometry of the Bi_2Te_3 films formed; hence it is important to determine the atomic percentage of Bi and Te present in this film (Cai et al., 2013). This is because bismuth telluride films with stoichiometric composition of Bi_2Te_3 have a [110] preferred orientation, which is an ideal thermoelectric device configuration as cleavage planes are perpendicular to the surface (Szymczak et al., 2014). In this study, bismuth telluride was deposited on both VCF and RCF from three different batches of electrolytes that have different composition of Bi^{3+} and $HTeO^{2+}$ ions which produced different stoichiometric formulas of Bi_2Te_3 as shown in Figure 1. Figure 1 exhibits various stoichiometric ratios as it has been deposited from electrolytes containing different ratios of Bi^{3+} to $HTeO^{2+}$ ions as shown in Table 1, the purpose is to deposit a bismuth telluride compound which has a stoichiometric ratio close to Bi:Te of 2:3.

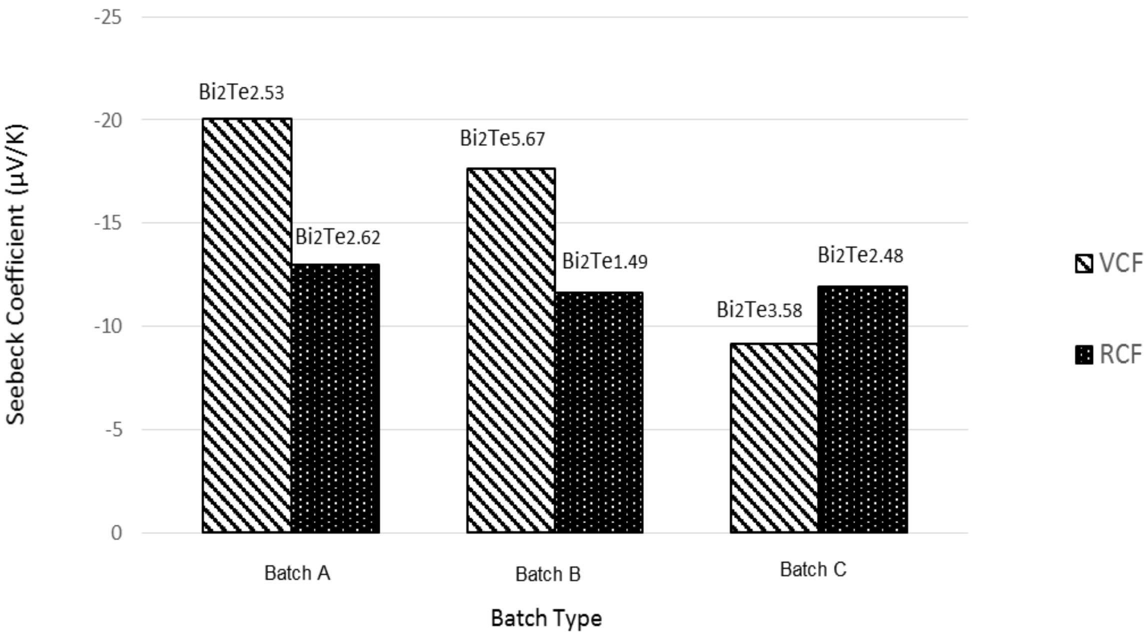

Figure 1: Seebeck Coefficient for Batch A, B and C of bismuth telluride

Based on Figure 1, Batch A produces Bi_2Te_3 films closest to stoichiometric composition for both RCF and VCF. It is also noteworthy that stoichiometric films have relatively larger power factors as compared to others which is a key factor that measures the efficiency of a thermoelectric module (Kim and Lee, 2006). From Figure 1, it can be observed that films closer to stoichiometric ratio show a higher Seebeck coefficient, which could probably be attributed to the arrangement of Bi and Te atoms in the films that impact the crystal structure, orientation and subsequently the carrier concentrations. Referring to the SEM images in Figure 2, it can be clearly observed from the SEM images that the fibre strands of RCF (2d) are of random orientation as compared to the orderly orientation of VCF (2a). For the deposition of Bi_2Te_3, the RCF has a less uniform coating on its strands as compared to that of VCF, resulting in a lower Seebeck coefficient.

3.2 Effect of Annealing on Seebeck coefficient of N-type Bismuth Telluride

Seebeck coefficient is one of the thermoelectric factors that are highly influenced by the chemical composition of the material. According to Huang et al., (2009), annealing accelerates the diffusion and agglomeration of atoms and improves the film crystallization of Bi_2Te_3. Annealing for all batches was carried out at a temperature of 623.15 K because tellurium elements tend to easily evaporate at a high temperature range about 673.15 K, due to its low melting point at 723.15 K and high evaporation pressure

(Lee et al., 2012). Annealing was also carried out for Bi_2Te_3 in an environment with 5 % hydrogen in argon gas to prevent the oxidation of the elements; argon also reduces the partial pressure of oxygen in the furnace (Li et al., 2008).

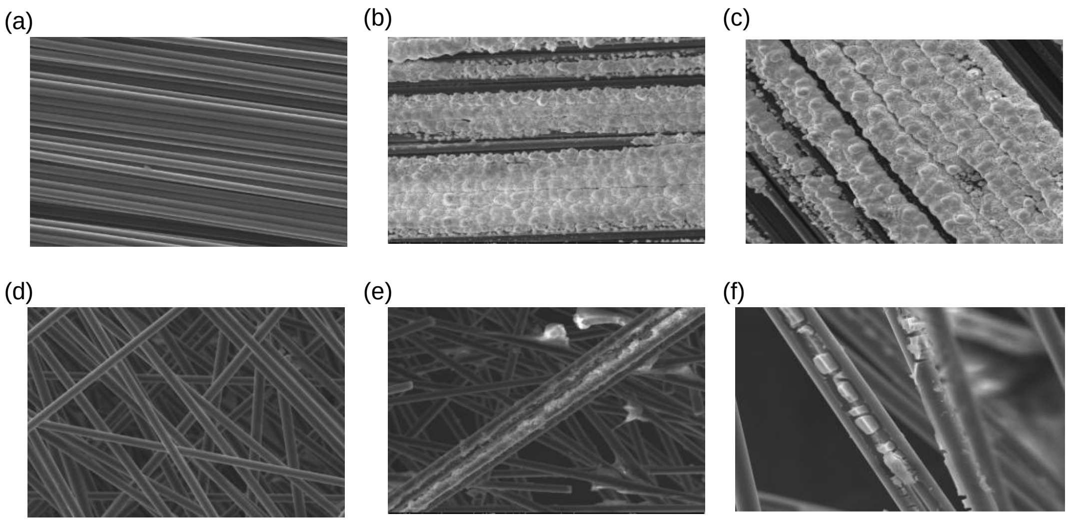

Figure 2: (a) Uncoated VCF (b) VCF deposited with Bi_2Te_3 (c) Annealed VCF deposited with Bi_2Te_3 (d)Uncoated RCF (e) RCF deposited with Bi_2Te_3 (f) Annealed RCF deposited with Bi_2Te_3

Further justifications to the use of 623.15 K are supported by Lee et al., (2012), in which a stable Bi_2Te_3 phase was formed at 623.15 K with no detected evaporation of Te. The Seebeck coefficient is found to be the highest at 623.15 K and further increase beyond 623.15 K resulted in a decrease of Seebeck coefficient. In addition, a similar phenomenon was also observed by Wang et al., (2013) at annealing temperature of 623.15 K with no structure destabilisation of Bi_2Te_3.

Referring to Table 2, it is noteworthy that all batches of bismuth telluride showed a significant improvement in Seebeck coefficient after annealing. This enhancement could be attributed to the fact that annealing helps increase grain size, which results in reduced grain boundaries as observed in Figure 2(c) and 2(f), thus improving carrier mobility (Rashid et al., 2013). Since the Seebeck coefficients obtained are of negative sign, it indicates the formation of N-type semiconductors in which the dominant carrier is electrons (Lin et al., 2013).

The results also show that bismuth telluride films that are closer to the stoichiometry of Bi_2Te_3 for both VCF and RCF show a much higher improvement in Seebeck coefficient. A similar phenomena was also observed with close to stoichiometric bismuth telluride films grown by co-sputtering (Kim and Lee, 2006). This increase in Seebeck coefficient is due to the decrease in carrier concentrations and subsequent improvement in carrier mobility in stoichiometric specimens.

Table 2: Seebeck Increment Factors (SIF) for Batch A, B and C at 623.15 K for 2 h

Batch Number	Seebeck Coefficient of VCF		Seebeck Increment Factor (SIF)	Seebeck Coefficient of RCF		Seebeck Increment Factor (SIF)
	Before Annealing (μV/K)	After Annealing (μV/K)		Before Annealing (μV/K)	After Annealing (μV/K)	
A	-20.055	-30.263	1.509	-12.997	-16.116	1.240
B	-17.652	-19.882	1.126	-11.652	-12.719	1.092
C	-9.128	-11.611	1.272	-11.915	-13.149	1.104

3.3 Effect of varying annealing temperature and time on Seebeck coefficient

As the Bi_2Te_3 film from Batch A showed the highest increment in Seebeck coefficient for both VCF and RCF, which in turn indicates a promising composition for thermoelectric film; a preliminary study on the effect of temperature and time of annealing on Seebeck coefficient was focused on Batch A.

Despite variations in the annealing parameters, all conditions displayed an increment in Seebeck coefficient as shown in Figure 3. It can be observed that annealing at 623.15 K for 2 h resulted in the largest improvements for both VCF and RCF. On the other hand, Bi_2Te_3 films annealed at 548.15 K for 2 h showed a much lower SIF which could be attributed to the fact that lower annealing temperatures may not be able to provide adequate energy to complete crystallisation of the films and reduce the defect concentrations (Wang et al., 2013).

While increasing annealing temperature improved the Seebeck coefficient, the same scenario was not observed with increasing annealing time. Referring to Figure 3, it can be observed for both VCF and RCF that prolonging annealing time resulted in the least improvement in SIF, which is consistent with observations reported by Li et al., (2008) as it decreases the homogeneity of the films.

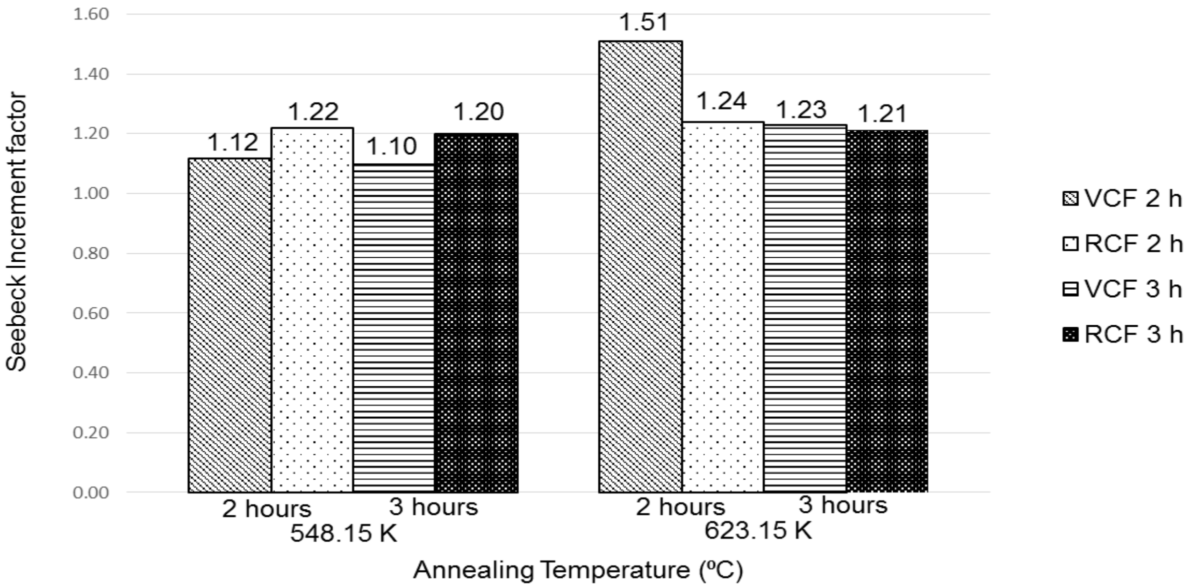

Figure 3: Seebeck Increment Factor for different annealing temperature and time

4. Conclusions

Bismuth telluride films were successfully deposited on both VCF and RCF at room temperature using the electro-deposition technique. Effects of annealing Bi_2Te_3 thermoelectric films on the surface morphology and Seebeck coefficient were investigated. Nearly stoichiometric N-type Bi_2Te_3 was obtained from an electrolyte with 8 mM of Bi $(NO_3)_3.5H_2O$ and 10 mM of TeO_2, with the highest Seebeck coefficient, which proves that stoichiometric specimens have higher figure of merit. The SEM images proved that there is an increase in grain size, which results in an increased Seebeck coefficient for annealed samples. Annealing for longer durations did not help to improve Seebeck coefficient; however, annealing at higher temperature helps improve Seebeck within a range of 1.21 to 1.54 times. The optimum annealing temperature and time is 623.15 K and 2 h for nearly stoichiometric N-type bismuth telluride.

References

Cai Z., Fan P., Zheng Z., Liu P., Chen T., Cai X., Luo J., Liang G., Zhang D., 2013, Thermoelectric properties and micro-structure characteristics of annealed N-type bismuth telluride thin film, Applied Surface Science, 280, 225–228.

Kim D.-H., Lee, G.-H., 2006, Effect of rapid thermal annealing on thermoelectric properties of bismuth telluride films grown by co-sputtering, Materials Science and Engineering: B, 131(1-3), 106–110.

Lee J., Kim J., Moon W., Berger A., Lee J., 2012, Enhanced Seebeck Coefficients of Thermoelectric Bi_2 Te_3 Nanowires as a Result of an Optimized Annealing Process, Journal of Physical Chemistry, 116, 19512–19516.

Li S., Soliman H.M.A., Zhou J., Toprak M.S., Muhammed M., Platzek D., Ziolkowski P., Müller E., 2008, Effects of Annealing and Doping on Nanostructured Bismuth Telluride Thick Films, Chemistry of Materials, 20(13), 4403–4410.

Lin J., Chen Y., Lin C., 2013. Annealing Effect on the Thermoelectric Properties of Bi_2Te_3 Thin Films Prepared by Thermal Evaporation Method. Journal of nanomaterials, 2013, 1-6, DOI: 10.1155/2013/201017.

McConnell V.P., 2010. Launching the carbon fibre recycling industry, Reinforced Plastics, 54(2), 33–37.

Pang E.J.X., Pickering S.J., Chan A., Wong K.H., Lau P.L., 2012, N-type thermoelectric recycled carbon fibre sheet with electrochemically deposited Bi_2Te_3, Journal of Solid State Chemistry, 193, 147–153.

Pico D., Seide G., Gries T., 2014, Thermo Chemical Processes : Potential Improvement of the Wind Blades Life Cycle, Chemical Engineering Transactions, 36, 211–216.

Rashid M.M., Cho K.H., Chung G.-S., 2013, Rapid thermal annealing effects on the microstructure and the thermoelectric properties of electrodeposited Bi_2Te_3 film, Applied Surface Science, 279, 23–30.

Szymczak J., Legeai S., Michel S., Diliberto S., Stein N., Boulanger C., 2014. Electrodeposition of stoichiometric bismuth telluride Bi_2Te_3 using a piperidinium ionic liquid binary mixture, Electrochimica Acta, 137, 586–594.

Wang X., He H., Wang N., Miao L., 2013, Effects of annealing temperature on thermoelectric properties of Bi_2Te_3 films prepared by co-sputtering, Applied Surface Science, 276, 539–542.

Xiao F., Hangarter C., Yoo B., Rheem Y., Lee K.-H., Myung N.V., 2008, Recent progress in electrodeposition of thermoelectric thin films and nanostructures, Electrochimica Acta, 53(28), 8103–8117.

Yoo B.Y., Huang C.-K., Lim J.R., Herman J., Ryan M.A., Fleurial J.-P., Myung N.V., 2005. Electrochemically deposited thermoelectric n-type Bi_2Te_3 thin films, Electrochimica Acta, 50(22), 4371–4377.