Thermoelectric properties of bismuth telluride thin films electrodeposited from a non-aqueous solution.

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ABSTRACT

We report the thermoelectric properties of Bi$_2$Te$_3$ thin films electrodeposited from the weakly coordinating solvent dichloromethane (CH$_2$Cl$_2$). It was found that the oxidation of porous films is significant, causing the degradation of its thermoelectric properties. We show that the morphology of the film can be improved drastically by applying a short initial nucleation pulse, which generates a large number of nuclei, and then growing the nuclei by pulsed electrodeposition at much lower overpotential. This significantly reduces the oxidation of the films as smooth films have smaller surface-to-volume ratio and are less prone to oxidation. X-ray photo-electron spectroscopy (XPS) shows that those films with Te(O) termination show complete absence of oxygen below the surface layer.

A thin film transfer process was developed using polystyrene as a carrier polymer to transfer the films from the conductive TiN to an insulating layer for thermo-electrical characterisation.
Temperature dependent Seebeck measurements revealed a room temperature coefficient of -51.7 μV/K growing to nearly -100 μV/K at 520 °C. The corresponding power factor reaches a value of 88.2 μW/mK² at that temperature.

**KEYWORDS:** Thermoelectric materials, bismuth telluride, non-aqueous electrodeposition, thin film transfer

**INTRODUCTION**

There is growing awareness and concern over the negative effect of greenhouse gases on the environment, yet fossil fuel combustion still accounts for the majority of energy conversion ¹. Moreover, more than 60% of energy worldwide is lost mostly in the form of waste heat ². Thermoelectric generators could be employed to extract the waste heat and convert it into electricity, thus enabling a better use of existing energy conversion technologies ³⁻⁵ or possibly thermal sensing ⁶.

Bismuth telluride is the most efficient and most widely used thermoelectric material for low temperature applications (up to 200 °C) ⁷. Currently, there are a range of fabrication techniques being used for thin film fabrication, such as sputtering, chemical vapour deposition (CVD), pulse laser deposition (PLD), molecular beam epitaxy (MBE), evaporation and electrodeposition. In comparison to other methods for thin film fabrication, electrodeposition of such films has advantages of being relatively cost-effective as it does not require high vacuum or elevated temperatures, offers easier control over thickness and composition, and can be used for the
deposition of films with thicknesses ranging from nanometres to hundreds of micrometres over a large area. Electrodeposition is also particularly well suited to deposition on complex geometries 8–10. Electrodeposition of Bi$_2$Te$_3$ thin films has mainly been investigated in aqueous acidic solutions, such as nitric, sulphuric or hydrochloric acid 11–17. Several electrochemical methods have been employed for electrodeposition of Bi$_2$Te$_3$ thin films, including potentiostatic electrodeposition 11–14,16, galvanostatic electrodeposition 15,17, and pulsed electrodeposition 18–22. Non-aqueous electrolytes have a wider electrochemical window than water allowing the investigation of more negative overpotentials and Bi$_2$Te$_3$ thin films have also been successfully electrodeposited from these without concomitant reduction of the solvent. Organic solvents also provide improved solubility of Bi(III) and Te(IV) salts which are only moderately soluble in aqueous acidic media limiting the deposition rate. The use of non-aqueous solvents also widens the range of precursor salts that can be employed compared with aqueous media. The electrodeposition of Bi$_2$Te$_3$ thin films from non-aqueous solvents, such as DMSO 22, ethylene glycol 23, chloride-free ethylene glycol 24 and a 1-ethyl-1-octyl-piperidinium TFSI/ 1-ethyl-1-octyl-piperidinium bromide mixture 25 have been reported in the literature.

We recently reported potentiostatic electrodeposition of Bi$_2$Te$_3$ thin films from dichloromethane 26. Although we were successful in controlling the composition of those films by varying the deposition potential, the films were highly porous and made up of small crystallites. In this work, we show that using nucleation pulses and pulsed electrodeposition allows significant improvement of the film morphology, and consequently the thermoelectric properties. In addition, a thin film transfer process was successfully developed allowing thermo-electric characterisation of these films for the first time. The films were transferred from the TiN electrodes onto an insulating substrate (SiO$_2$) for subsequent electrical characterisation using polystyrene as a carrier polymer.
Unlike commonly used poly(methyl methacrylate)\textsuperscript{27}, polystyrene has advantages of easier removal after the transfer, and does not form wrinkles on the transferred films resulting in a complete transfer of the deposited film\textsuperscript{28}. Electrodeposited bismuth telluride thin films reported in literature have so far been transferred by epoxy resin for thermoelectric measurements\textsuperscript{29–31}. However the epoxy method leaves cracks in the transferred films visible through microscopy and the delamination from original substrate is not complete. Here we show that electrodeposited bismuth telluride thin films can be completely lifted from its original substrate and transferred to an insulating substrate without cracks visible by optical microscope nor electron microscopy.

**RESULTS AND DISCUSSION**

In order to improve the film morphology of the Bi\textsubscript{2}Te\textsubscript{3} films electrodeposited using potentiostatic conditions in our previous work\textsuperscript{26}, nucleation of the film has been optimised. The Bi\textsubscript{2}Te\textsubscript{3} films were grown by introducing a short initial nucleation pulse at a high overpotential which generates a large number of nuclei, and then growing them potentiostatically or by pulsed deposition at lower overpotential. Firstly, the early stage of film growth was investigated by applying a short nucleation pulse at high overpotentials after which the nuclei were grown potentiostatically at -0.6 V vs. Ag/AgCl with a passed charge of -0.26 C, which would correspond to 200 nm thickness assuming a uniform distribution over the whole electrode area (Supporting Information, Section 3). Figure 1 shows a schematic, SEM images and histograms of the size distribution of the resulting deposited particles. The deposits were grown by applying an initial nucleation pulse of -1.0 V, -1.2 V, and -1.4 V vs. Ag/AgCl for 1, 3, or 5 s. As can been seen from the figure, by increasing the length of the nucleation pulse, increased coverage of the substrate surface was achieved with
smaller and more uniform particles. In addition, by applying a higher initial overpotential for the same amount of time the same effect of generating smaller, denser and more uniform nuclei was achieved. This indicates progressive nucleation meaning that the nucleation process is slow and new nuclei continue to form during the deposition while those already formed continue to grow. Hence, by applying a potential of -1.4 V for 5 s and then growing the nuclei at -0.6 V vs. Ag/AgCl, almost full coverage of uniform, densely packed particles was obtained. ImageJ \textsuperscript{32} was used to extract the number and the areal size of the electrodeposited crystallites plotted as histograms. The deposits formed with nucleation potentials of -1.0 V for 5 s and -1.4 V for 5 s show particle counts of at least a factor of 10 higher than the deposited formed with shorter pulses at lower potential. This corresponds to a volume particle size reduction of the same factor. These nucleation pulse values were therefore selected for further investigation and optimisation of bismuth telluride thin film growth.
Figure 1. SEM images and histograms of electrodeposited bismuth telluride deposits grown at $E_{\text{dep}}=-0.6$ V, preceded by nucleation pulses of $E_{\text{nuc}}=-1.0$ V (a-e), -1.2 V (f-j) and -1.4 V vs. Ag/AgCl (k-o) with nucleation pulse times $t_{\text{nuc}}=1$ s (red: b,g,l), 3 s (blue: c,h,m), and 5 s (green d,i,n).

Figure 2 shows SEM images of films grown potentiostatically (2b,c,d), by pulsed electrodeposition (2f,g,h), potentiostatically preceded by a nucleation pulse (2j,k), and by pulsed deposition preceded
by a nucleation pulse (2m,n). Growing films by pulsed electrodeposition yields somewhat smoother films with improved composition repeatability compared to those grown potentiostatically. For the pulsed deposition during the off-time, when no current passes, the concentrations of Bi and Te species at the electrode surface replenish by diffusion. As a result, under pulsed conditions the composition of the films can be better controlled due to the replenishment of the reactants in each cycle \(^{19}\). The duration of on- and off-pulses during pulsed electrodeposition was optimised to 5 s on-time and 10 s off-time. As can be seen from Fig. 2, the films grown potentiostatically and by pulsed electrodeposition at potentials of \(-1.0\) V (2b,f) and \(-0.8\) V (2c,g) vs. Ag/AgCl both exhibit similar porous but continuous morphologies. The thickness of the films is estimated to be 1 µm from the total charge passed of \(-1.3\) C for potentiostatically grown films. For the films grown by pulsed deposition, the estimated thickness is 950 nm from the charge passed of \(-1.2\) C and 1.4 µm from the charge passed of \(-1.8\) C for films grown at \(-1.0\) and \(-0.8\) V vs. Ag/AgCl, respectively. However, when growing films potentiostatically and by pulsed electrodeposition at a lower potential of \(-0.6\) V vs. Ag/AgCl, a significant change in morphology was observed (2d,h). The resulting deposits in this case are not films but rather comprise discontinuous islands. Furthermore, the deposits obtained by pulsed electrodeposition are smoother, slightly larger and more uniform in size than the deposits obtained potentiostatically. The calculated thickness of the uniform film over the given area grown potentiostatically is 1 µm, and 1.8 µm from a charge of \(-2.3\) C for the film grown by pulsed deposition at \(-0.6\) V vs. Ag/AgCl. Table 1 gives the average and standard deviation of Bi to Te ratios and atomic percentage of oxygen measured by EDX elemental analysis on three different areas of the films. The presence of Bi and Te confirms the deposition of bismuth telluride, with slight variation of average Bi to Te ratios from stoichiometric composition (0.7) when applying different potentials and deposition
methods. Furthermore, the small standard deviation (≤0.05) in Bi to Te ratios obtained in all films proves excellent composition uniformity regardless of the method. The O signal most probably indicates oxidation of the bismuth telluride films.

![Figure 2. Schematics and SEM images of potentiostatic (a-d), pulsed (e-h), potentiostatic preceded by nucleation pulse (i-k), and pulsed preceded by nucleation pulse (l-n) bismuth telluride deposition for potentials of -1.0 V (b,f), -0.8 V (c,g), -0.6 V (d,h), -0.6 V preceded by nucleation pulse of -1.4 V (j,m) and -1.0 V (k,n) vs. Ag/AgCl. $t_{\text{on}}=5$ s and $t_{\text{off}}=10$ s for all pulsed electrodepositions.](image-url)
Table 1. Elemental composition showing Bi to Te atomic ratios and atomic percentage of O measured on three different areas of the film showing average values and standard deviation. All films are electrodeposited from an electrolyte containing 2.25 mM [N\textsuperscript{Bu}_4][BiCl\textsubscript{4}], 3 mM [N\textsuperscript{Bu}_4]_2[TeCl\textsubscript{6}] and 0.1 M [N\textsuperscript{Bu}_4]Cl by different methods. $t_{on}=5$ s and $t_{off}=10$ s for all pulsed depositions.

| Method | Potential vs. Ag/AgCl / V | Bi:Te ± stdev | % atomic O ± stdev |
|--------|---------------------------|---------------|--------------------|
| Potentiostatic | $E_{dep}=-1.0$ | 0.5 ± 0.01 | 32.4 ± 1.08 |
| Potentiostatic | $E_{dep}=-0.8$ | 0.5 ± 0.01 | 38.0 ± 0.25 |
| Potentiostatic | $E_{dep}=-0.6$ | 0.8 ± 0.03 | 13.1 ± 0.46 |
| Pulsed | $E_{dep}=-1.0$ | 0.7 ± 0.03 | 33.8 ± 1.83 |
| Pulsed | $E_{dep}=-0.8$ | 0.6 ± 0.02 | 17.8 ± 4.41 |
| Pulsed | $E_{dep}=-0.6$ | 0.8 ± 0.05 | 13.8 ± 3.73 |
| Potentiostatic with nucleation pulse | $E_{dep}=-0.6, E_{nuc}=-1.4$ | 0.6 ± 0.04 | 4.4 ± 0.26 |
| Potentiostatic with nucleation pulse | $E_{dep}=-0.6, E_{nuc}=-1.0$ | 0.9 ± 0.01 | 26.0 ± 1.44 |
| Pulsed with nucleation pulse | $E_{dep}=-0.6, E_{nuc}=-1.4$ | 0.5 ± 0.02 | 0.3 ± 0.50 |
| Pulsed with nucleation pulse | $E_{dep}=-0.6, E_{nuc}=-1.0$ | 0.7 ± 0.01 | 6.5 ± 0.95 |

Comparing, the films were grown potentiostatically and by pulsed electrodeposition preceded by a nucleation pulse. As can be seen in Figure 2, considerable change in morphology is noticeable between films grown potentiostatically (2j,k) and by pulsed electrodeposition (2m,n) after introducing an initial nucleation pulse at higher potential. The films grown by pulsed electrodeposition are compact, continuous and smooth, while those grown potentiostatically are discontinuous. The calculated thickness of the deposits electrodeposited potentiostatically is 1 µm. For the films grown by pulsed electrodeposition, the calculated thickness from the passed charge of -0.6 C is 500 nm and 1.4 µm for charge of -1.8 C for nucleation potentials of -1.0 and -1.4 V vs.
Ag/AgCl, respectively. Cross section SEM images of the films electrodeposited by pulsed electrodeposition preceded by a nucleation pulse reveals the actual thicknesses of 675 nm and 2 µm for nucleation pulses of -1.0 and -1.4 V vs. Ag/AgCl, respectively. The 35% discrepancy between the calculated and measured value is possibly due to the residual porosity in the films. On the other hand, the calculated thickness of the porous film electrodeposited potentiostatically at -1 V vs. Ag/AgCl is 1 µm, while the cross-sectional SEM reveals a thickness of 4.5 µm. This large factor of 4 discrepancy between theoretical and measured value is definitely due to the porosity of the film. Furthermore, as shown in Table 2, the oxygen content is significantly lower in films grown by pulsed deposition preceded by a nucleation pulse compared to films obtained by other methods. This is probably due to the compact and smooth surface morphology of these films which have a smaller exposed surface area than the porous films, and are therefore less prone to atmospheric oxidation.

**Crystal structure of electrodedeposited bismuth telluride films**

Figure 3 shows the diffraction patterns of bismuth telluride films electrodeposited onto TiN electrodes; there are peaks at 2θ angles of 23.64°, 27.71°, 38.31°, 40.97°, 45.10° and 50.05°. The X-ray diffraction analysis of bismuth telluride thin films electrodeposited by different methods shows that the diffraction patterns are very similar regardless of the method. The peaks can be attributed to trigonal Bi₂Te₃, although the presence of elemental Te cannot be completely discounted as they share many reflection positions. The results were fitted against the literature pattern 33 and show good agreement. The 015 reflection at 27.7° is of the highest intensity for all the films, and its width indicates crystallite size with the broadest indicating the smallest and the
narrowest indicating the biggest crystallite size. This relationship between the peak width and the crystallite size is given by the Scherrer equation: \( \tau = \frac{K\lambda}{\beta \cos \theta} \).

Crystallite sizes of bismuth telluride films electrodeposited by different methods were obtained using the PDXL package and are shown in Table 2. The smallest crystallite size was obtained for films electrodeposited potentiostatically at -1 V vs. Ag/AgCl, which corresponds to the highest nucleation rate. The films obtained by pulsed electrodeposition at the same potential exhibit bigger crystallite size. Growing films at an even lower overpotential of -0.6 V vs. Ag/AgCl by pulsed electrodeposition gave much bigger crystallite size due to the lower nucleation rate at the lower overpotential. The films electrodeposited by pulsed electrodeposition at the lower overpotential of -0.6 V vs. Ag/AgCl preceded by a nucleation pulse also possess a larger crystallite size, comparable to those grown without a nucleation pulse. Thus, it is possible to alter the crystallite sizes of bismuth telluride films which, in turn, could have a beneficial effect on the electrical conductivity and therefore the thermoelectric properties of the films.
Figure 3. XRD patterns collected on bismuth telluride films electrodeposited potentiostatically at -1.0 V (a), by pulsed deposition at -1.0 V (b), by pulsed deposition at -0.6 V without an initial nucleation pulse (c) and by pulsed deposition at -0.6 V with an initial nucleation pulse at -1.0 V (d) and -1.4 V (e) vs. Ag/AgCl. $t_{on}=5$ s and $t_{off}=10$ s for all pulsed depositions.
Table 2. Lattice parameters and crystallite sizes for different bismuth telluride films from X-ray diffraction data obtained using the PDXL programme.

| Method                                      | Potential               | a (Å)     | c(Å)     | Crystallite size (Å) |
|---------------------------------------------|-------------------------|-----------|----------|----------------------|
| Potentiostatic                              | \(E_{\text{dep}}=-1.0\) V | 4.16(10)  | 30(3)    | 18                   |
| Pulsed                                      | \(E_{\text{dep}}=-1.0\) V | 4.1(4)    | 30.0(19) | 27                   |
| Pulsed                                      | \(E_{\text{dep}}=-0.6\) V | 4.48(6)   | 28.8(5)  | 35                   |
| Pulsed with an initial nucleation pulse     | \(E_{\text{dep}}=-0.6\) V, \(E_{\text{nuc}}=-1.0\) V | 4.35(8)   | 29.2(5)  | 41                   |
| Pulsed with an initial nucleation pulse     | \(E_{\text{dep}}=-0.6\) V, \(E_{\text{nuc}}=-1.4\) V | 4.33(4)   | 30.0(5)  | 36                   |

Oxidation of bismuth telluride films

Surface oxidation of electrodeposited bismuth telluride films was investigated by X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out on films electrodeposited by pulsed electrodeposition either with or without an initial nucleation pulse as shown in Fig. 4. The samples were taken out of the solution after the deposition and transferred onto an insulating substrate within a couple of days before the measurements were taken. The scans show the Bi 4f and Te 3d doublets. For each sample, the first measurement was taken at the surface layer followed by four cycles of etching with Ar ions for 60 s in order to expose deeper layers in the bulk of the material. The etching rate is approximately 0.5 nm/s, meaning that after each etching cycle measurements were taken 30 nm deeper in the bulk of the material. The reference for XPS spectra analysis is the C 1s peak at a binding energy of 284.8 eV. The Bi 4f\(/2\) peak is composed of two contributions at 157.4±0.3 and 158.6±0.4 eV corresponding to Bi in Bi\(_2\)Te\(_3\) and Bi in Bi\(_2\)O\(_3\), respectively with the associated Bi 4f\(/2\) peaks at 162.8±0.3 and 163.9±0.5 eV.\(^{34-37}\) The two peaks for Bi-Te and Bi-O are observed due to spin orbital splitting of the f-orbital into f\(/2\) and f\(/2\) components with area ratio of 3/4. In our cases, the free fitted area ratio is 0.79 for both Bi-Te and
Bi-O. The Te has contributions of $3d_{5/2}$ at $572.1 \pm 0.4$ and $575.8 \pm 0.5$ eV correspond to Bi$_2$Te$_3$ and TeO$_2$, respectively. The contributions of $3d_{3/2}$ are at $582.6 \pm 0.4$ eV and $586.2 \pm 0.5$ eV$^{34-37}$. The free fitted area ratio of the $d_{5/2}$ and $d_{3/2}$ doublet is 0.69, close to the theoretical value of 2/3.

The Bi peaks in films electrodeposited by pulsed electrodeposition show that the Bi$_2$O$_3$ peaks have higher intensities than Bi$_2$Te$_3$ even in deeper layers of the material, although the Bi$_2$Te$_3$ peak intensities increase slightly as deeper layers are exposed (Fig. 4a). The more compact and smoother film electrodeposited by pulsed electrodeposition with an initial nucleation pulse at -1.0 V shows a similar trend (Fig. 4c). For both films, the Te on the surface is mainly in the form of TeO$_2$, while after exposure of the deeper layers Te in the form of Bi$_2$Te$_3$ is more prominent although a significant contribution from TeO$_2$ is still present (Fig. 4b and d).

In contrast, in the case of the film electrodeposited with an initial nucleation pulse at -1.4 V, there is no Bi at all in the surface layer, and the deeper layers are composed of Bi$_2$Te$_3$ with an almost negligible amounts of Bi$_2$O$_3$ (Fig. 4e). The Te spectra confirm the Bi spectra observation for this film. Here, the surface layer is predominantly Te in the form of TeO$_2$ with a significant amount of Bi$_2$Te$_3$, and the deeper layers are in the form of Bi$_2$Te$_3$ with a negligible amount of oxidised Te (Fig. 4f). The film possesses Te termination which is mainly oxidised and prevents further oxidation of the underlying film. These data are in full agreement with the EDX data which showed 33.8% and 6.5% of oxygen for the former two films, and 0.3% for the film with the initial nucleation pulse at -1.4 V followed by the pulsed electrodeposition at -0.6 V. Music et al.$^{38}$ also observed that Te termination of bismuth telluride slows down the oxidation of Bi$_2$Te$_3$. After the last etching cycle, the measurements were taken about 120 nm into the bulk of the material still revealing at least some oxidation in the bulk as a result of oxygen diffusion. Although it was reported that Bi$_2$Te$_3$ thin films grown by molecular beam epitaxy are stable and surface oxidation
occurs on the time scale of months \(^9\), in the case of porous films the oxidation is significant and can be reduced by decreasing the surface-to-volume ratio and more importantly, by obtaining Te termination on the surface.
Figure 4. The Bi 4f (left) and Te 3d (right) regions of the XPS spectra for bismuth telluride films electrodeposited: by pulsed electrodeposition at -1.0 V (a, b), pulsed electrodeposition at -0.6 V preceded by a nucleation pulse at -1.0 V (c, d), a nucleation pulse at -1.4 V (e, f). Blue: surface prior to etching, orange: after 60 s of etching, yellow: after 120 s of etching, purple: after 180 s of etching, and green: after 240 s of etching.
**Thin film transfer**

**Figure 5.** Schematic of the polystyrene-based process used to transfer Bi$_2$Te$_3$ films electrodeposited on TiN to an insulating SiO$_2$ substrate.

The separation of the bismuth telluride film was achieved in KOH solution, as KOH is acting on the interface between the substrate and lifting the film. The separation then gradually spreads due to capillary wetting. Fig. 6a and b show images taken under the optical microscope of a bismuth telluride film electrodeposited onto a TiN electrode and a bismuth telluride film transferred to the SiO$_2$ substrate, respectively. Although polystyrene residues are visible on the film after the transfer, the transfer process is complete and the transferred films are uniform without wrinkles or cracks (Fig 6b). Fig. 6c and d show SEM images of the bismuth telluride film before and after transfer, they also show that there are no cracks in the film after transfer demonstrating the integrity of the transfer process.
Figure 6. Optical images of a bismuth telluride film electrodeposited on a TiN electrode: a) before the transfer, and b) after transfer to the SiO₂ substrate. SEM images of a bismuth telluride film c) before and d) after the transfer.

THERMOELECTRIC CHARACTERISATION

Thermoelectric characterisation was conducted on the film electrodeposited by pulse electrodeposition at -0.6 V vs. Ag/AgCl for on-time 5 s and off-time 10 s with an initial nucleation pulse of -1.0 V vs. Ag/AgCl for 5 s. The electrodeposited film is n-type with a charge carrier concentration of \((2.8 \pm 1.2) \times 10^{20} \text{ cm}^{-3}\) and resistivity of 15.9 mΩ cm at room temperature obtained from Hall measurements. The resistivity decreases with increasing temperature (Fig. 7a), meaning that the electrodeposited bismuth telluride film exhibits semiconducting behaviour with further thermal activation at higher temperature. The film exhibits a Seebeck coefficient of \(-51.7 \mu \text{V/K}\) at
300 K, which increases with temperature reaching a value of -96.6 μV/K at 520 K (Fig 7a). The decrease in Seebeck coefficient after 520 K is due to the bipolar effect. At the temperature of ~500 K electrons from the valence band are elevated into the conduction band. This gives rise to minority carriers (in this case holes), travelling in the opposite direction. The two types of carriers have opposite signs of Seebeck coefficient cancelling each other, and therefore decreasing the material’s Seebeck coefficient with further temperature increase. The power factor is defined as $S^2\sigma$ meaning that it depends only on the Seebeck coefficient and the electrical conductivity of the material. Fig. 7b shows the power factor of the thin film as a function of temperature, showing that the power factor increases with increasing temperature reaching a value of 88.2 μW/m K$^2$ at 520 K, in accordance with the increase in Seebeck coefficient. The porous films obtained potentiostatically or by pulsed electrodeposition are insulating probably due to oxidation of the films as a result of high surface-to-volume ratio, and no Seebeck or resistivity data could be extracted. There is a range of values for Seebeck coefficient and resistivity of electrodeposited bismuth telluride thin films reported in literature. However, we compare our data to that from the Martin-Gonzalez group $^{19,21,40}$ who have carried out an extensive study on electrodeposition of bismuth telluride thin films from an aqueous solution. The obtained carrier concentration and the Seebeck coefficient values of our electrodeposited bismuth telluride films are close to the reported data, however the resistivity value is higher than the reported ones. Manzano et al. $^{21}$ reported carrier concentration of $3.2 \times 10^{20}$ cm$^{-3}$ and Seebeck coefficient of -58 μV/K, which correspond to our measured values of $(2.8 \pm 1.2) \times 10^{20}$ cm$^{-3}$ for carrier concentration and -51.7 μV/K for Seebeck coefficient. The reported resistivity is 1.5 mΩ cm, lower than our measured value of 15.9 mΩ cm.
Figure 7. Dependence of a) resistivity and Seebeck coefficient, and b) power factor with temperature for bismuth telluride film electrodeposited by pulsed electrodeposition at -0.6 V vs. Ag/AgCl for on-time 5 s and off-time 10 s with an initial nucleation pulse to -1 V vs. Ag/AgCl for 5 s. Error bars are based on tool manufacturers information. Lines are guides to the eye.

CONCLUSION

Bismuth telluride films were fabricated by potentiostatic and pulsed electrodeposition with or without a preceding nucleation pulse from dichloromethane using \([\text{N}^n\text{Bu}_4][\text{BiCl}_4]\) and \([\text{N}^n\text{Bu}_4]_2[\text{TeCl}_6]\) as the Bi and Te precursors. The composition repeatability between replicate samples was significantly improved in films produced by pulsed electrodeposition compared to those obtained potentiostatically. In addition, somewhat smoother films were obtained by pulsed electrodeposition, however, both methods yield either porous or discontinuous films which are unsuitable for thermoelectric applications. Nucleation of the films was optimised by applying an initial nucleation pulse at high overpotential followed by growth of the films either potentiostatically or by pulsed electrodeposition at lower overpotential. The films grown potentiostatically preceded by a nucleation pulse are discontinuous while those grown by pulsed
electrodeposition preceded by a nucleation pulse are continuous, compact and smooth. XPS measurements reveal that the porous films are prone to oxidation possibly due to their high surface to volume ratio, while the smooth and compact films are significantly less oxidised. Moreover, it was found that if the smooth and compact film were Te terminated the oxidation was suppressed. The effect of oxidation was also observed in EDX compositional analysis, where the oxygen content dropped considerably for smooth films obtained by pulsed electrodeposition preceded by a nucleation pulse as compared to the porous films. The XRD measurements show that films grown at the lower overpotential have larger crystallite sizes, and the films grown at low overpotential either with or without a preceding nucleation pulse exhibit similar crystallite sizes. In order to perform electrical measurements the films were transferred using polystyrene as a carrier polymer. The transfer process was complete and the films had no wrinkles or cracks after transfer. The porous films produced by potentiostatic and pulsed electrodeposition were found to be insulating most probably due to their high surface area prone to oxidation, which degrades thermoelectric properties of these films. The compact and smooth film produced by pulsed electrodeposition at -0.6 V preceded by a nucleation pulse at -1.0 V vs. Ag/AgCl exhibits semiconducting behaviour with the resistivity of the film decreasing with increasing temperature. The temperature dependent Seebeck coefficient measurements show a Seebeck coefficient of -51.7 μV/K at room temperature, reaching -96.6 μV/K at 520 K. The power factor reaches value of 88.2 μW/ m K² at 520 K.
MATERIALS AND METHODS

Electrodeposition

Electrolytes were prepared in anhydrous CH₂Cl₂ (Sigma-Aldrich, 95 %), dried by refluxing with CaH₂ (followed by distillation and then stored in the glovebox, the water content in dried CH₂Cl₂ was ca. 18 ppm) with addition of 0.1 M [N₄Bu₄]Cl (Sigma-Aldrich, ≥99.0%, as-received) as the supporting electrolyte. The Bi and Te precursors ([N₄Bu₄][BiCl₄] and [N₄Bu₄][TeCl₆]) were synthesized as described in the literature 41.

The cyclic voltammetry (Supporting Information, Section 1) and electrodeposition experiments were carried out in a recirculating glovebox (Belle Technology, UK) using an Autolab potentiostat (µAUT70706). The experiments were carried out in electrolyte containing 2.25 mM [N₄Bu₄][BiCl₄], 3 mM [N₄Bu₄][TeCl₆] and 0.1 M [N₄Bu₄]Cl in anhydrous CH₂Cl₂ using a three-electrode system with a 1 cm diameter Pt coin as the counter electrode, and an Ag/AgCl (0.1 M [N₄Bu₄]Cl in anhydrous CH₂Cl₂) reference electrode. As the working electrode, either a 3 mm diameter glass sealed glassy carbon (GC, Sigradur G, HTW, Germany) or 7×11 mm titanium nitride (TiN) electrode was used. The glass sealed GC electrode was used for precursor characterisation experiments. It was cleaned by polishing with alumina powder (1 µm and 0.05 µm diameter in sequence, micropolish, Buehler, Germany) on a water saturated polishing pad (Microcloth, Buehler). The fabrication of 7×11 mm TiN working electrodes is described in our previous work 41.

Thin film characterisation

Scanning electron microscopy (SEM) was performed using a Zeiss EVO LS 25 with an accelerating voltage of 10 kV, and energy-dispersive X-ray (EDX) data were obtained with an
Oxford INCAx-act X-ray detector. EDX calibration was carried out using a Bi$_2$Te$_3$ powder standard (Strem Chemicals, 99.99%). High resolution SEM measurements were carried out with a field emission SEM (Jeol JSM 7500F) at an accelerating voltage of 2 kV. X-ray diffraction (XRD) measurements were carried out using a Rigaku Smartlab diffractometer either in symmetric or grazing incidence mode ($\theta_1=1^\circ$) with a 9 kW Cu-K$\alpha$ ($\lambda = 1.5418$ Å) source, parallel line focus incident beam and a Hypix detector. Phase matching and lattice parameter refinement were carried out using the PDXL2 software package and diffraction patterns from the Inorganic Crystal Structure Database (ICSD)\textsuperscript{33}. X-ray photoelectron spectroscopy (XPS) data were obtained using a ThermoScientific Theta Probe System with Al–K$\alpha$ radiation (photon energy= 1486.6 eV). XPS depth profiling was performed by using an Ar ion gun at a beam voltage of 3 kV on a 2×2 mm raster area.

The in-plane electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) were simultaneously measured on a commercial JouleYacht Thin-film Thermoelectric Parameter Test System (MRS-3L). The system was calibrated using a nickel foil reference standard and the measurement accuracy was found to be within 5% for resistivity, and 7% for Seebeck measurements. The Hall coefficient ($R_H$) was determined at 300 K on a Nanometrics HL5500PC instrument using a van de Pauw configuration. The carrier concentration ($n$) and in-plane mobility ($\mu$) were calculated according to $1/n=eR$ and $\mu=\sigma R$, respectively.

**Thin film transfer**

1×1 cm target substrates with 50 nm thick SiO$_2$ were fabricated by dry thermal oxidation of a Si wafer in a Tempress Furnace tube. 20 g of polystyrene (Sigma Aldrich, Mw~280,000 by GPC) was dissolved in 100 mL toluene (Fisher Chemical) to prepare 20 W/V% solution. The solution was spin-coated on the Bi$_2$Te$_3$ thin films at 500 rpm for 10 s followed by 1000 rpm for 50 s. The
samples were then baked at 85 °C for 30 min to dry the polymer. A cut was made on the samples to allow solution to penetrate between the Bi₂Te₃ films coated with PS and the TiN substrates. The samples were then dipped into AZ 400K (Merck, 2% KOH) solution which enables exfoliation of the Bi₂Te₃ films. Afterwards, the films coated with polymer were transferred onto SiO₂ substrates and left to dry in air for 3 days to allow adhesion of the bismuth telluride films to the SiO₂ substrates. Prior to the film transfer, the SiO₂ substrates were activated by O₂ plasma for 5 min in a Plasmalab 80 Plus (RIE) to improve adhesion of the transferred films. Finally, the carrier polymer was dissolved from Bi₂Te₃ films by dipping the samples in chloroform (Sigma Aldrich, ≥99 %). The films were then dipped into acetone and isopropanol to remove the solvent (a schematic diagram of the transfer process can be found in Fig. 5).

Optical microscopy (Nikon Eclipse LV150) and high resolution SEM (field emission SEM, Jeol JSM 7500F, accelerating voltage of 2 kV) were used to characterise the films before and after the transfer.
ASSOCIATED CONTENT

Supporting Information

Cyclic voltammetry in an electrolyte containing 2.25 mM [N\textsuperscript{4}Bu\textsubscript{4}][BiCl\textsubscript{4}] and 3 mM [N\textsuperscript{4}Bu\textsubscript{4}]\textsubscript{2}[TeCl\textsubscript{6}] (Section 1), image of a substrate with the electrodeposited bismuth telluride film (Section 2), and film thickness calculation (Section 3).

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