Bismuth-telluride-based alloys are currently the best commercially available thermoelectric materials for applications at room temperatures. Up to 150 micron thick layers of bismuth antimony telluride (Bi$_{0.5}$Sb$_{1.5}$Te$_3$) were directly deposited onto nickel by either potentiostatic or potentiodynamic electrodeposition. Cyclic voltammetry was employed to identify the optimal deposition potential. The films were characterized by scanning electron microscopy, energy dispersive X-rays and X-ray diffraction. The p-type films were found to be well adherent, uniform and stoichiometric with a high power factor of $2.3 \times 10^{-4}$ W m$^{-1}$ K$^{-2}$ at film growth rates of up to 40 $\mu$m h$^{-1}$.

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Experimental

Film fabrication.—Electrolytes were composed of 5 mM Ammonium bismuth citrate (Bi(NH$_4$)$_3$Cit, Sigma-Aldrich, ≥99.0%), 20 mM potassium antimonyl tartrate trihydrate (K$_5$Sb$_7$Tar, Sigma-Aldrich, ≥99.0%), 30 mM tellurium dioxide (TeO$_2$, Alfa Aesar, 99.99%), in 1 M nitric acid (HNO$_3$, Fisher 70%) with 100 to 300 mM sodium citrate (Na$_3$Cit, Sigma-Aldrich ≥99.0%). Ethylenediaminetetraacetic acid disodium (Na-EDTA, Sigma-Aldrich, ≥99.0%) was added at concentrations of 5 to 30 mM. Water from a Purite Select Fusion 160 (Ondeo) water purification system (resistivity 18.2 MΩ cm) was used to prepare all electrolyte solutions. To complex Te$^{3+}$ TeO$_2$ powder is first dissolved in a small volume of concentrated NaOH solution, and then neutralized with citric acid (H$_3$Cit, Sigma-Aldrich, 99 + %).

A conventional three-electrode electrochemical cell connected to an Ivium Technology potentiostat/galvanostat was used for performing all electrochemical deposition experiments with a large-area platinum grid counter electrode and a Saturated calomel electrode (SCE) reference electrode. A 1 cm$^2$ Ni foil (Alfa Aesar, 0.127 mm thick, 99 + %) served as the working electrode. This was etched in concentrated HCl for 1 min, followed by etching in 1 M HNO$_3$ solution at a potential of +0.15 V vs SCE for 30 seconds to remove any surface oxide to enable better adhesion of the Bi-Te-Sb deposits to the Ni surface. The Ni working electrodes were then thoroughly rinsed in deionized water. Electrodeposition was carried out by potentiostatic as well as potentiodynamic (pulsed) deposition. Potentiostatic electrodeposition was performed at potentials of $-0.22 \text{ V}, -0.25 \text{ V}, -0.28 \text{ V}, -0.31 \text{ V}, -0.35 \text{ V}$ vs SCE. The potentiodynamic (pulsed) electrodeposition employed zero current resting pulses for 4s, followed by deposition pulses of 10 ms at either $-0.20 \text{ V}$ or $-0.25 \text{ V}$ vs. SCE.

Characterization.—The electrodeposited Bi-Te-Sb films were imaged by scanning electron microscope (SEM, JSM 5910) equipped with Energy dispersive X-ray (EDX, Oxford Inca 300) for compositional analysis.

The Seebeck coefficient, $S$, was measured with a custom-built measurement unit that was calibrated against a polycrystalline bismuth foil reference standard with an accuracy of 5%. A commercial Hall effect measurement unit (HMS 300 from Ecopia) was employed for determining the Hall mobility, electrical conductivity and carrier concentration of the deposited films in-plane by the van der Pauw technique (direct current (dc) of 19 mA and a permanent magnetic field of 0.37 T at room temperature). All electrodeposited films were delaminated from the underlying Ni substrate prior to Hall effect measurements by embedding them in an epoxy layer to ascertain that there was no interference from the Ni substrate.
Results and Discussion

Cyclic voltammetry (CV) was employed to identify the optimum deposition potential for the formation of stoichiometric layers of Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} on Ni. Figure 1 shows representative cyclic voltammograms recorded at a 1 cm\textsuperscript{2} Ni working electrode immersed in electrolyte solutions of 5 mM Bi(NH\textsubscript{4})\textsubscript{3}Cit, 20 mM K\textsubscript{2}Sb\textsubscript{2}Tar, 30 mM TeO\textsubscript{2}, 200 mM Na\textsubscript{3}Cit in 1 M HNO\textsubscript{3}. Na-EDTA at concentrations of 5 mM, 10 mM and 30 mM was added to the electrolyte as well. The Ni working electrode potential was scanned from +0.0 V to −0.6 V vs. SCE. At small concentrations of Na-EDTA, three reduction peaks can be identified (cf. Fig. 1) which have been labeled as D1-D3. Peak D1 corresponds to bismuth (Bi) deposition, D2 to tellurium (Te) deposition, and D3 to antimony (Sb) deposition. As the concentration of Na-EDTA is increased to 10 mM and above, the D1 and D2 reduction peaks combine to form one reduction feature, corresponding to Bi\textsubscript{2}Te\textsubscript{3} deposition which can be attributed to a mutually induced co-deposition mechanism. In order to produce stoichiometric Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} a deposition potential in the region of −0.2 and −0.35 V vs. SCE was chosen based on these results.

Figure 2 shows a sequence of SEM images obtained from a 2 \(\mu\)m Ni electrode surface following potentiostatic electrodeposition at deposition potentials of −0.22 V, −0.25 V, −0.28 V, −0.31 V, −0.35 V vs. SCE respectively. The composition of the Bi-Sb-Te electrodeposits at each deposition potential was analyzed by EDX as shown in Figure 2. A small degree of surface roughness is evident in the SEM images whilst the composition of the electrodeposits was found to be stoichiometric for deposition potentials over the range −0.25 V to −0.35V vs SCE. This was then compared to results (as shown in Figure 3) in which pulsed (potentiodynamic) electrodeposition was applied to produce smoother deposits with better thermoelectric properties.
Pulsed electrochemical deposition was then carried out by employing zero current resting pulses for 4s and deposition pulses of 10 ms at −0.2V or −0.25V vs. SCE respectively.

Figures 3a, 3b shows SEM images and EDX data of a 150 μm thick Bi-Sb-Te deposit produced by potentiodynamic electrodeposition at potentials of −0.25 and −0.20 V vs. SCE respectively. The composition across the film thickness as analyzed by EDX is also shown and reveals that at a potential of −0.25 V, the composition across the film is close to being constant and stoichiometric, whereas at a potential of −0.20 V the films are tellurium rich. As established

Figure 3. Cross-sectional SEM images and corresponding compositional analysis by EDX. The BiSbTe was deposited at −0.25 V (top), or −0.20 V (bottom).

Figure 4. XRD pattern of stoichiometric Bi$_{0.5}$Sb$_{1.5}$Te$_3$ film deposited by potentiostatic electrodeposition (a) and potentiodynamic (pulsed) electrodeposition (b), obtained on a Rigaku SmartLab diffractometer using Cu-Kα radiation (λ = 1.5406 Å).
from the results presented in Figure 1 −0.20 V vs. SCE represents the lowest potential for producing stoichiometric Bi-Sb-Te deposit and the actual composition may vary which has been confirmed here by EDX analysis.

As the deposition progresses beyond a film thickness of 150 microns, a dendritic structure forms at a potential of −0.25 V vs. SCE which may be attributable to the depletion of the electrolyte of the respective ions.

Figure 4 shows typical XRD patterns recorded for potentiostatic (Fig. 4a) and potentiodyamic (Fig. 4b) electrodeposited Bi0.5Sb1.5Te3 films respectively. All XRD peaks can be indexed to the rhombohedral Bi0.5Sb1.5Te3 crystal structure according to the standard ICDD card (PDF-2-release 2012 RDB) with a space group of R3m. In both cases the (015) peak is the most prominent XRD peak, indicating that the preferred growth direction is along the (015) plane, which is in line with results in the literature. The average grain size of the films is calculated to be 17.0 nm based on the Scherrer equation.

Hall effect measurements of the Bi-Sb-Te films resulted in p-type semiconducting behavior with a Hall mobility of up to ~200 cm²/(V·s), carrier concentration of 2.0 × 10²⁰ cm⁻³, electrical conductivity up to ~100 S cm⁻¹ whilst measurement of the Seebeck coefficient yielded values +150 μV/K which results in a high power factor of 2.3 × 10⁻⁴ W m⁻¹ K⁻² in case of the potentiodynamic electrodeposited bismuth antimony films. This is the highest power factor reported in the literature to-date for electrodeposited Bi0.5Sb1.5Te3.

Transport property measurements for potentiostatically electrodeposited Bi-Sb-Te films yielded Hall mobilities of up to 90 cm²/(V·s), a carrier concentration of 1.30 × 10¹⁹ cm⁻³, electrical conductivity up to ~86 S cm⁻¹ whilst Seebeck measurements resulted in a Seebeck coefficient of +112 μV/K resulting in a power factor of 1.1 × 10⁻⁴ W m⁻¹ K⁻².

Conclusions
Stoichiometric and uniform p-type Bi0.5Sb1.5Te3 films with thicknesses of up to 150 μm were electrodeposited onto Ni by potentiodynamic electrodeposition at high growth rates of up to 40 μm/hour. These yielded a high power factor of 2.3 × 10⁻⁴ W m⁻¹ K⁻² and were found to exhibit better thermoelectric properties than potentiostatically deposited Bi0.5Sb1.5Te3 films. This makes them promising materials for the fabrication of p-type legs in commercial TE devices.

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