Electrochemically Copper doped Bismuth Tellurium Selenide Thin Films

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Abstract

We report the first results of a study on electrochemically doped copper bismuth tellurium selenide thin films electrodeposited from aqueous nitric acid electrolytes containing up to 2 mM of $Cu(NO_3)_2$. The effect of $Cu(NO_3)_2$ concentration on the composition, structure and thermoelectric properties of the bismuth tellurium selenide films is investigated by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and Seebeck and Hall effect measurements. A $Cu(NO_3)_2$ concentration of 1.5 mM is found to offer a Seebeck coefficient of up to -390 μV K^{-1} at room temperature which is the highest reported to date for an electrodeposited bismuth tellurium compound.

1. Introduction

Thermoelectric generators offer an attractive route for renewable energy generation by exploiting the Seebeck effect to convert waste heat into useful electrical energy. They are of considerable interest due to the need to move away from diminishing fossil fuel supplies and to meet greenhouse gas emission targets. At present the best materials for room temperature operation (both power generation and refrigeration) of commercial thermoelectric devices are based on bulk alloys of bismuth telluride and antimony telluride [1,2]. Thermoelectric devices have many advantages such as solid-state operation with no moving parts, zero-emission, silent operation, vast scalability and high reliability with no maintenance and long operating lifetimes [1,2]. Despite these merits however barriers exist to the widespread adoption of thermoelectric technology due to the low efficiency of current thermoelectric materials. The efficiency of thermoelectric materials is related to the unitless figure of merit ZT of a thermoelectric material which can be defined as

$$ZT = \frac{S^2\sigma}{\kappa} \quad ,$$

where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the total thermal conductivity. The power factor is defined as $S^2\sigma$.

Theoretical calculations of low dimensional structures demonstrate that nanostructuring of thermoelectric materials offers an opportunity to engineer materials with significantly enhanced thermoelectric properties by enhancing the density of states (DOS) near the Fermi level via quantum confinement and a reduction in lattice thermal conductivity [3, 4]. Other approaches for enhancing thermoelectric properties include band structure engineering of materials through doping [5]. There is evidence that substitution of bismuth with group IB elements such as copper (Cu) is an effective way to achieve higher thermoelectric performance [6]. Due to their small atomic radius of 135 pm [7], Cu atoms can be interstitially incorporated into the Bi-Se-Te layered structure to produce lattice distortion and causing a reduction of lattice and electronic thermal conductivity leading to enhanced thermoelectric properties. Studies investigating the effect of doping on the thermoelectric properties of bismuth telluride systems are comparatively rare and most studies employ high temperature vacuum based approaches for inducing doping which are costly and require specialized equipment [6]. In addition whilst the electrodeposition of bismuth telluride has been extensively reported [8-14] there are comparatively few reports on the electrodeposition of bismuth tellurium selenide [15-17]. To the best of our knowledge there have been no reports to date by other groups, that show the electrochemical doping of copper into bismuth telluride based compounds. Our group has previously conducted preliminary studies on the electrochemical copper doping of bismuth tellurium selenide [18]. We are only aware of one paper which has been devoted to investigating the doping of copper and studying its effects on the thermoelectric properties of bismuth tellurium selenide. This is based in on a study by Cui et al. [6] who prepared n-type $(Bi_2Te_3)_{0.9}$-$(Bi_{2-x}Cu_xSe_3)_{0.1}$(x = 0-0.2) bulk layers by spark plasma sintering. It was found that the introduction of a small amount of Cu significantly improved the thermoelectric properties by improving the electrical conductivity (750 S m^{-1} to 800 S m^{-1} at 312.5 K) and the Seebeck coefficient (-135 μV K^{-1} to -150 μV K^{-1} at 312.5 K) and reducing the thermal lattice conductivity.

In the present study we have demonstrated for the first time that it is feasible to use electrochemical deposition for the fabrication of high quality copper-doped n-type bismuth tellurium selenide thin films that displayed an enhanced Seebeck coefficient.

2. Experimental

2.1. Materials

All solutions were prepared using water from a Merck Millipore Milli-Q gradient A10 Ultrapure water purification system with a resistivity of 18.2 MΩ cm. Bi powder (Alfa Aesar, 99.999%), TeO_2 powder (Sigma Aldrich, 99.9995%), SeO_2 (Across Organics 99.999%) and HNO_3 (Fisher, 70% analytical grade) were used as received. The electrolyte solution consists of 8 mM Bi, 9 mM TeO_2 and 1 mM SeO_2 dissolved in 1 M HNO_3 with $Cu(NO_3)_2$ concentrations (Sigma-Aldrich 99.999%) varying between 0 and 2 mM.

2.2. Film fabrication by electrodeposition

All electrochemical experiments were performed using a standard three-electrode configuration, where a large-area platinum grid and saturated calomel electrodes (SCEs) were used as counter and reference electrodes, respectively. The working electrode for cyclic voltammetry studies was a 2 mm gold disc electrode encapsulated in Kel-F (CH101, CH Instruments Inc.) which was polished using 3 grades of alumina powder on microcloth (Buehler 407218). The gold working electrode was washed in deionized water and then connected to a computer-controlled Autolab PGSTAT12 potentiostat/galvanostat. For all other studies the working electrode consisted of a Si Wafer, sputtered with a 20 mn Ti adhesion layer, followed by a 200 nm Au layer. The working area of 1 cm^2 was defined with polyimide tape and Cu tape was used to make contact.

The morphology and chemical composition of the deposited films was analyzed by scanning electron microscopy (Zeiss Evo LS25 ESEM) equipped with an Oxford Instruments energy dispersive X-ray (EDX, Oxford Inca 300) detector with an accuracy of 5%. X-ray diffraction (XRD) data were obtained using a Rigaku SmartLab SmartLab diffractometer with Cu Kα radiation (λ = 1.5406Å). Seebeck measurements were conducted on a custom made Seebeck measurement unit which was calibrated against a polycrystalline Bi foil reference standard with an accuracy of 5%. For Seebeck, electrical and Hall effect measurements, samples were set into epoxy on glass. The epoxy was allowed to set for a minimum of 12 h, after which time the glass and Au substrate were separated by mechanical force, leaving the electrodeposited films intact on glass. For electrical and Hall measurements4 contacts were made to the extremities of the corners of the samples using conductive epoxy (Circuit Works) in which 0.2 mm diameter copper wire was embedded. The opposite end of the Cu wire was then soldered onto a sample board. The measurements were conducted on commercial Ecopia HMS-3000 Hall Effect measurement system.

3. Results and discussion

Figure 1 shows representative cyclic voltammograms (CVs) for the electrolytes of bismuth telluride selenide in the presence of copper nitrate $Cu(NO_3)_2$ at concentrations varying between 0 to 2 mM. The electrolyte solutions contained 8 mM Bi, 9 mM TeO_2 and 1 mM SeO_2 dissolved in 1 M HNO_3. The potential scan was started at + 0.50 V vs. SCE and then swept between the limits +1.00 V vs. SCE and -0.50 V vs. SCE at a scan rate of 20 mV s^{-1}. The reduction peak observed at -0.05 V vs. SCE can be attributed to the formation of $Bi_2Te_{3-x}Se_x$ whilst the oxidation peaks at +0.43 V and +0.46 V vs. SCE are attributable to the oxidation of $Bi_2Te_{3-x}Se_x$ and Bi respectively in agreement with the literature [9-11]. Whilst the CVs are generally similar in shape with increasing quantities of $Cu(NO_3)_2$ being added to the electrolyte, the formation of a pronounced oxidation peak however can be observed at +0.20 V vs. SCE which has been magnified in the inset in Figure 1. This peak can be attributed to the oxidation of copper to Cu^{2+} as verified by CVs (cf. Figure 1S in supplementary information) obtained in an electrolyte comprising only 1 mM $Cu(NO_3)_2$ dissolved in 1 M HNO_3. On the basis of these voltammetric studies a potential of +0.05 V vs SCE was selected for the deposition of bismuth tellurium selenide thin films from different Cu^{2+} containing electrolytes with a maximum concentration of up to 2 mM. The deposition time in each case was 2 hours and the films had an average thickness of 6 microns as determined from the charge passed, surface profilometry and cross-sectional SEM analysis. The composition of the bismuth tellurium selenide thin films was then determined by EDX and is summarised in Figure 2.

In the absence of Cu^{2+} the composition of the bismuth telluride selenide films was found to be in the average ratio of Bi:Te:Se 1.89:2.76:0.37 which is very close to the ideal stoichiometry of (2:2.7:0.30) bismuth tellurium selenide [9]. It is evident that Cu incorporation into bismuth telluride selenide increases with increasing Cu^{2+} concentrations prevalent in the electrolyte resulting in a maximum of 15 at% Cu incorporation at a $Cu(NO_3)_2$ concentration of 2 mM. The atomic percentage of Bi, Te and Se present in the films varies in the following manner: the fraction of Se appears to remain nearly constant throughout, whilst the at% of Te is lowered by approximately 3% at maximum Cu content and the Bi content is lowered by 13% at the maximum $Cu(NO_3)_2$ concentration. These observations are consistent with the hypothesis that Cu is being incorporated into the bismuth telluride selenide lattice by replacing Bi. This is consistent with the observations made by other studies on Cu doping in bismuth tellurium selenide based on other fabrication methods [6].

To verify our hypothesis of Cu being incorporated into the bismuth tellurium selenide films we performed XRD (cf, Figure 3). The XRD patterns reveal a prominent peak in the (0 1 5) direction hence indicating a preferential growth orientation in the (0 1 5) direction. The crystal structure of the bismuth tellurium selenide films can be indexed to a rhombohedral R3m space group as fitted by the PDXL software file No: 00-051-0643 for bismuth tellurium selenide. Another prominent feature is the increase in the signal to noise ratio that can be observed in the XRD patterns with increasing $Cu(NO_3)_2$ concentrations. At the highest copper nitrate concentration of 2 mM the (015) peak has broadened significantly and no other diffraction peaks can be observed. These results would suggest that the incorporation of copper into the crystal structure reduces the grain size and induces a degree of lattice disorder as has also been inferred from other studies [6].

Subsequently we investigated the effect of copper doping on the thermoelectric properties of the bismuth tellurium selenide thin films and the results are summarised in Figure 4. The electrical conductivity decays exponentially with increasing $Cu(NO_3)_2$ concentrations (cf. Figure 4a) in the electrolyte, whilst the Seebeck coefficient increases to a value as high as -390 μV/K at a $Cu(NO_3)_2$ concentration of 1.5 mM as can be appreciated from Figure 4b. To the best of our knowledge this is the highest reported Seebeck coefficient for an electrodeposited n-type bismuth telluride based material. The measured power factor as a function of $Cu(NO_3)_2$ concentration is displayed in Figure 4c and the overall trend is a decrease from an initial value of 0.18 mW $m^{-1}K^{-2}$ to a value close to zero. As stated in the introduction using doping as a strategy to enhance the thermopower of a material without depressing the electronic conductivity is challenging as the thermoelectric power and electrical conductivity change in opposite directions [5] and in reality, a compromised set of values must be achieved. This trend can be clearly observed here as well in terms of the electrical conductivity, Seebeck coefficient and power factor for Cu doped bismuth tellurium selenide thin films.

CONCLUSIONS

We have clearly demonstrated for the first time that Cu doping is feasible in electrodeposited bismuth tellurium selenide films and that this induces a lattice disorder as evidenced by an increase in the XRD signal to noise ratio. During incorporation copper replaces the bismuth which is in agreement with previous studies. Copper doping was seen to increase the Seebeck coefficient achieving a maximum value of -390 $\mu V\ K^{-1}$ at a $Cu(NO_3)_2$ concentration of 1.5 mM, which is so far the highest ever reported value for an n-type electrodeposited bismuth tellurium based compound. However, the electrical conductivity as well as the power factor were observed to decrease with increasing copper content and clearly a compromise needs to be reached in terms of the optimum copper doping levels to achieve the best thermoelectric performance.

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Figure 1. Cyclic voltammograms of a 2 mm diameter gold disk electrode immersed in an electrolyte solution containing 8 mM Bi, 9 mM TeO_2 and 1 mM SeO_2 dissolved in 1 M HNO_3 in the presence $Cu(NO_3)_2$ at concentrations varying between 0 to 2 mM. The scan rate was 20 mV s^{-1}.

Figure 2. Compositional EDX analysis of 2 hour electrodeposited bismuth tellurium selenide films from solutions containing 8 mM Bi, 9 mM TeO_2 and 1 mM SeO_2 dissolved in 1 M HNO_3 in the presence $Cu(NO_3)_2$ at concentrations of 0 to 2 mM.

Figure 3: $2\theta/\theta$ XRD diffractograms of 2 hour electrodeposited bismuth tellurium selenide films electrodeposited from solutions containing 8 mM Bi, 9 mM TeO_2 and 1 mM SeO_2 dissolved in 1 M HNO_3 in the presence $Cu(NO_3)_2$ at concentrations varying between 0 to 2 mM.

Figure 4. Dependence of electrical conductivity, Seebeck coefficient and power factor on increasing $Cu(NO_3)_2$ concentration in electrolyte.

FIGURES

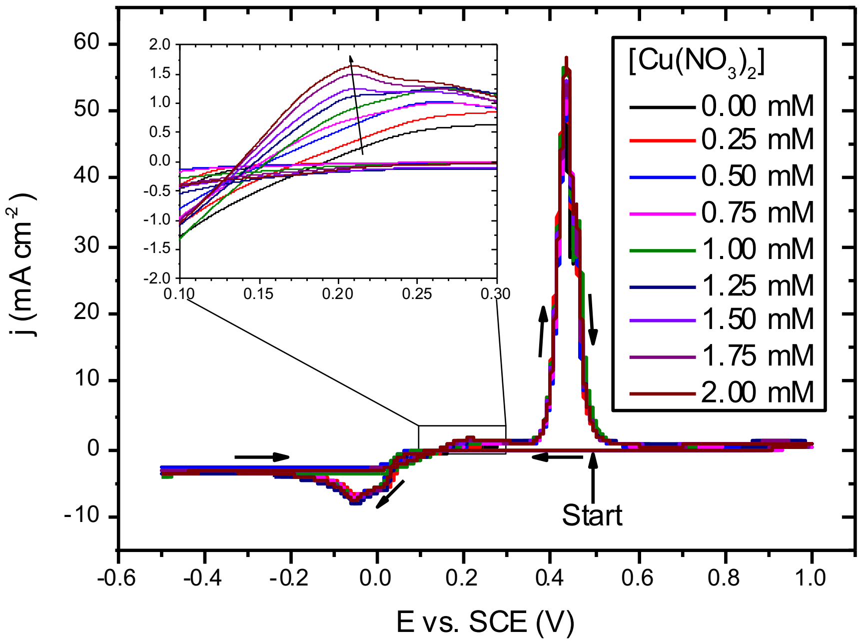


Figure 1

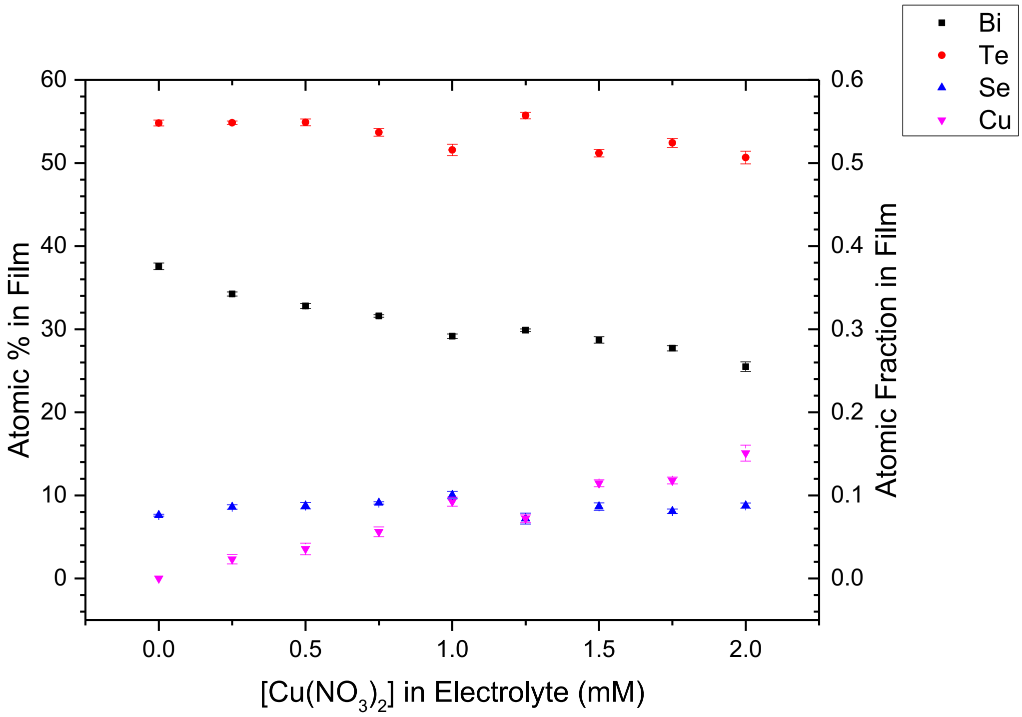


Figure 2

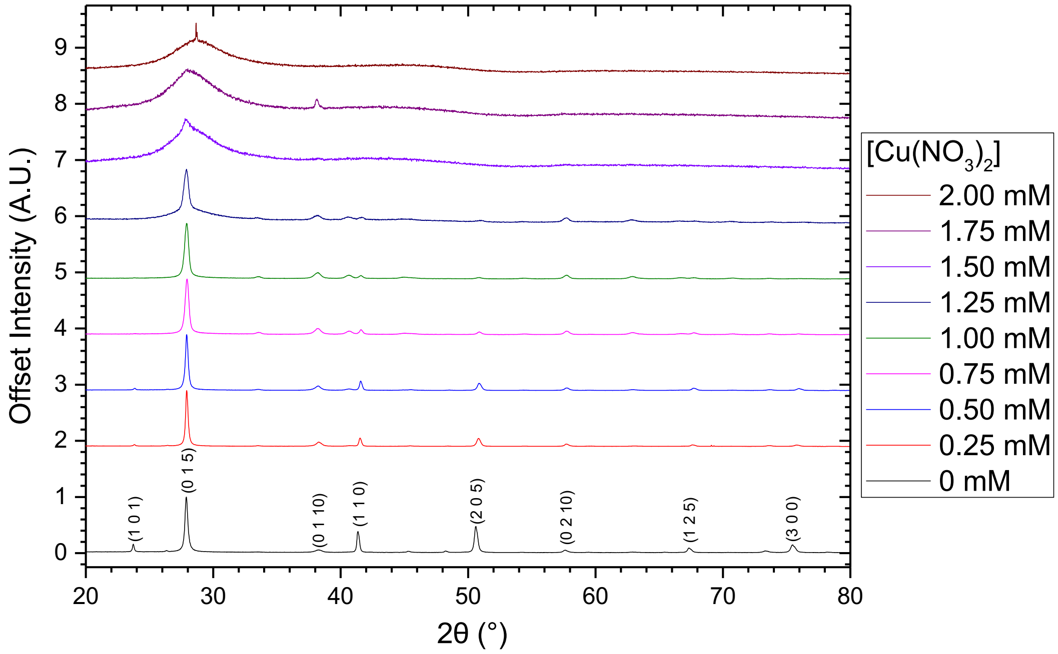
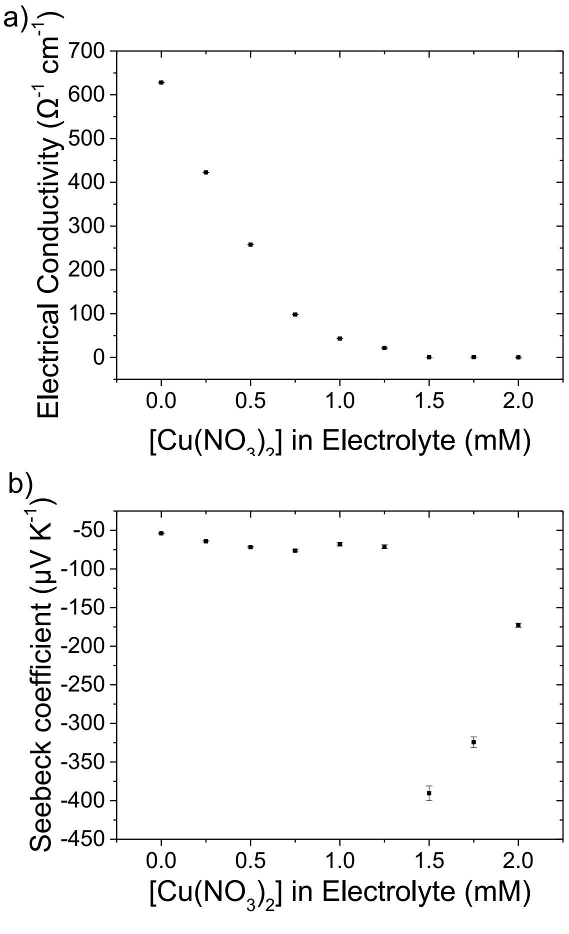

Offset Intensity (A.U.)
2θ (°)
0
1
2
3
4
5
6
7
8
9
20
30
40
50
60
70
80
(1 0 1)
(0 1 5)
(0 1 10)
(1 1 0)
(2 0 5)
(0 2 10)
(1 2 5)
(3 0 0)
[Cu(NO3)2]
2.00 mM
1.75 mM
1.50 mM
1.25 mM
1.00 mM
0.75 mM
0.50 mM
0.25 mM
0 mM

Figure 3


a)
Electrical Conductivity (Ω-1 cm-1)
0
100
200
300
400
500
600
700
0.0
0.5
1.0
1.5
2.0
[Cu(NO3)2] in Electrolyte (mM)
b)
Seebeck coefficient (μV K-1)
-50
-100
-150
-200
-250
-300
-350
-400
-450
0.0
0.5
1.0
1.5
2.0
[Cu(NO3)2] in Electrolyte (mM)

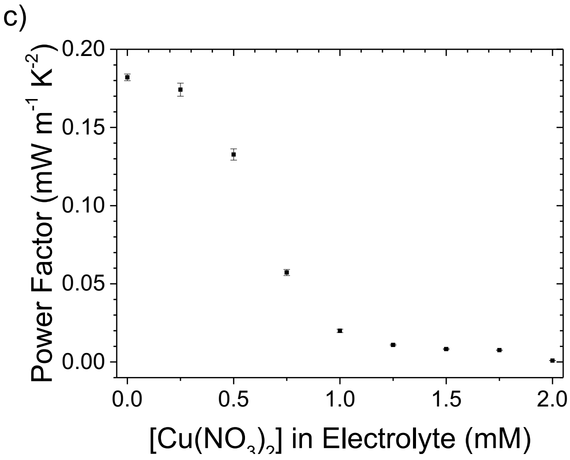

c)
Power Factor (mW m-1 K-2)
0.00
0.05
0.10
0.15
0.20
0.0
0.5
1.0
1.5
2.0
[Cu(NO3)2] in Electrolyte (mM)

Figure 4