

Investigation of the Properties of Electrochemically Deposited Semiconductor Materials for Thermoelectric Applications

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Abstract

At JPL, it is our desire to fabricate thermoelectric micro-devices for power generation and cooling applications using an electrochemical deposition (ECD) technique. We believe that the performance of our current micro-device developed is limited by the properties of the ECD materials. Therefore, the objective of this study is to develop ECD methods for obtaining n-type Bi_2Te_3 and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ thermoelectric materials with near bulk properties, as well as optimizing morphology and transport properties. The films of Bi_2Te_3 and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ were initially obtained under various ECD conditions. Seebeck coefficients and transport properties were then measured along the direction parallel to the substrates before and after annealing at 250°C for 2hrs. From the data obtained, ECD n- Bi_2Te_3 material can achieve a high Seebeck coefficient ($-189 \mu\text{V/K}$) when it is deposited at -200 mV vs. SCE . The in-plane resistivity, in-plane mobility, and carrier concentration are 3.0 mohm-cm , $31 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, and $6.79 \times 10^{19} \text{ cm}^{-3}$, respectively. As for the p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$, it is possible to achieve a high Seebeck coefficient ($+295 \mu\text{V/K}$) when it is deposited at 0.3 mA/cm^2 . The in-plane resistivity, in-plane mobility, and carrier concentration are 9.8374 mohm-cm , $66.58 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, and $9.54 \times 10^{18} \text{ cm}^{-3}$, respectively. From the results of our preliminary study, we have found the conditions for depositing high quality Bi_2Te_3 and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ materials with thermoelectric properties comparable to those of their state-of-the-art bulk samples.

Introduction

Advances in the microelectronics industry have made it possible to miniaturize components and devices. With the miniaturization of electronic devices, there has also been a tremendous focus on developing miniaturized power conversion and thermal management systems [1,2]. For example, in the optoelectronics industry, thermal management is a significant factor in optimizing device performance. Thermoelectric devices make use of the Seebeck effect for power generation and can also utilize the Peltier effect for active cooling [3]. A thermoelectric module generally consists of several n- and p-type leg elements connected in series electrically and in parallel thermally. Thermoelectric microdevices can convert rejected or waste heat into usable electric power, at moderate ($200\text{-}500\text{K}$) temperatures and often with small temperature differentials. For the temperature range of $200\text{-}500\text{K}$, alloys based on n-type Bi_2Te_3 and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ are the best materials for numerous applications. These materials can also be used as the basic materials for electronic and sensor building of nanowires and nanotubes.

At the Jet Propulsion Laboratory (JPL), we are currently studying the properties of nano-wire made from the above mentioned materials. We have also fabricated thermoelectric microdevices using a combination of integrated circuit (IC) processing techniques and electrochemical deposition (ECD) of compound semiconductors ($\text{Bi}_2\text{Te}_3/\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$) [4-6]. This technique is also called thermoelectric microdevice fabrication by a MEMS-like electrochemical process. Successive layers of photoresist were patterned and electrochemically filled with compound semiconductor materials or metal interconnectors (Au or Ni). In ECD, dissolved species are deposited as a film by reduction on a conducting surface. A non-conducting mould is used to guide the deposition onto only select areas. This allows the fabrication of tall structures having high aspect ratios from a variety of electrically conducting materials without deep etching. ECD has many advantages over other deposition technologies: precisely controlled room temperature operation open to the atmosphere, low energy requirements, fast deposition rates, and inexpensive material cost [7].

Our generation I thermoelectric microdevice was built on either a glass or oxidized silicon substrate containing 63 couples (63 n-legs/63 p-legs) at approximately 20 microns in structure height and 60 microns in diameter (Figure 1) with a device area close to $1.7 \text{ mm} \times 1.7 \text{ mm}$. The measurements and calculations for the fabricated devices indicate that the resistivity of the device is low, close to the desired value. The fabricated microdevices were tested and evaluated for power generation and effective cooling performance. To measure cooling, we evaluated device performance using an IR camera with differential thermal imaging software. We were able to detect a maximum cooling effect of about 2K . To measure power generation, a 75 watt light source was illuminated directly above the device while the current generated was measured. For both glass and silicon substrate devices, about 1mV/string was produced. This translated to a ΔT of approximately 1.25K . The low power can be attributed to a small temperature gradient and non-optimal materials properties (primarily low Seebeck). Our study demonstrated the feasibility of the device fabrication and function, and our next step is to improve the

performance of the devices. We believe that the performance of the current micro-device developed is limited by the properties of the ECD materials. Therefore, the objective of our study is to develop ECD methods for obtaining n-type Bi_2Te_3 and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ thermoelectric materials with near bulk properties and optimized morphology and transport properties.

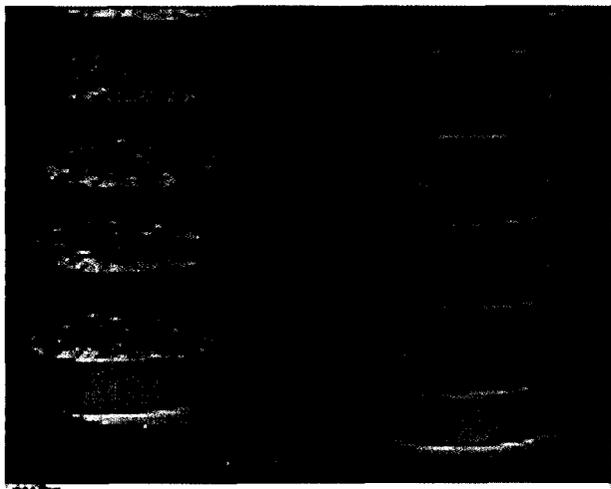


Figure 1. SEM of ECD p- $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and n- Bi_2Te_3 leg elements.

Experimental

In our experiments, the substrates used for ECD are SiO_2/Si wafers sputtered on top with either $1\mu\text{m}$ Bi_2Te_3 or $1\mu\text{m}$ $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. Films of n-type Bi_2Te_3 and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ compounds were deposited at room temperature by either a constant potential or constant current density method (using EG&G PAR 273A potentiostat) in a standard three electrode configuration. These three electrode cells had a Pt counter electrode and a saturated calomel electrode (SCE) reference. For n-type Bi_2Te_3 material, films were electrodeposited from nitric baths (1 M HNO_3 , pH=0). The thermoelectric properties of these films were compared to bulk n-type Bi_2Te_3 materials after annealing at 250°C for two hours. As for the p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ material, films were ECD from nitric baths containing ethylene diamine tetraacetate (EDTA) and citric acid as complexing agents. The thermoelectric properties of these films were also compared to bulk p-type Bi-Sb-Te materials after annealing at 250°C for two hours. Specifically, the electrolyte composition for n-type Bi_2Te_3 ECD is $[\text{Bi}]=8\text{ mM}$, $[\text{Te}]=10\text{ mM}$ and $[\text{HNO}_3]=1.0\text{ M}$. The electrolyte composition for the p-type solution is $[\text{Bi}]=0.5\text{ mM}$, $[\text{Sb}]=32.0\text{ mM}$, $[\text{Te}]=2.0\text{ mM}$, $[\text{Citric Acid}]=0.2\text{ M}$, $[\text{EDTA}]=30.0\text{ mM}$, $[\text{HNO}_3]=1.0\text{ M}$. Solutions containing Sb use chelating agents such as citrate and EDTA to allow higher concentrations of the less soluble element at pH 0. Seebeck coefficients and transport properties were then measured along the direction parallel to the substrates before and after annealing at 250°C for 2hrs. The electrical resistivity, the carrier concentration, and the carrier mobility were obtained by conducting the Hall effect measurements. For Seebeck coefficients, which were measured by using a new setup, a temperature gradient was created along the film and the corresponding temperature and voltage drops were recorded. The microstructure and composition of the films were investigated by using X-ray diffractometry (XRD) and Scanning Electron Microscope (SEM).

Results and Discussions

The objective of this study is to synthesize thin films of Bi_2Te_3 -based materials with thermoelectric properties comparable to state-of-the-art bulk samples, using a promising ECD process. Because of its superior properties, Bi_2Te_3 -based alloys are the thermoelectric materials of choice for our applications at room temperature. In the ECD process, the desired elements are deposited on an electrode using an aqueous solution of anions or anionic compounds. Depending on the current density used in deposition, the deposition rate can be varied widely. Film several tens of microns thick can be made in a few hours using ECD. It is also simple to scale up the film size with easily maintained equipment. Also, slight variations in the deposition potential or solution concentration may be used to induce off-stoichiometric films, thus providing doping to p- or n-type through stoichiometric deviation.

The electrolytes for the ECD is prepared by dissolving bismuth and tellurium metals in HNO_3 to make the oxide anions BiO^+ and HTeO_2^+ . Bi_2Te_3 is insoluble in dilute HNO_3 , so reduction of HTeO_2^+ to Te^{2-} and BiO^+ to Bi^0 on a conductive substrate will result in the deposition of Bi_2Te_3 on the substrate surface. The overall reaction for the process is:



JPL's studies have shown that variation in grain size and composition may be introduced by changing the potential at which the deposition is carried out, as well as by changing the concentration of the ions in solution.

Previous studies have also shown that the Bi_2Te_3 material electrodeposited on a stainless steel electrode grows with an orientation perpendicular to the c axis of the Bi_2Te_3 hexagonal cell. This is an important finding because of the anisotropic properties of Bi_2Te_3 . The maximum thermoelectric figure of merit is obtained when the transport properties are measured along the direction perpendicular to the c axis. The primary disadvantage of using ECD for semiconducting films is that the film must be deposited on a conductive substrate. This condition makes it difficult to precisely measure the electrical properties of the film without removing the film from the substrate. However, it is very difficult to remove the film without damage. Past studies on the anisotropy of the Bi-Te material have shown that the actual performance of the film, measured parallel to its growth, is better than its performance parallel to the substrate. Thus, we examined the film parallel to the c axis with the knowledge that the actual results would be better than what the data shows.

(a) ECD of n-type Bi_2Te_3

N-type Bi_2Te_3 films were deposited on the $\text{Bi}_2\text{Te}_3/\text{SiO}_2/\text{Si}$ substrates electrochemically either by applying constant potential or constant current (density). Afterwards, samples were annealed at 250 °C for 2 hours. The electrical properties of the films were measured in a direction perpendicular to the film growth axis. The electrical resistivity, the carrier concentration, and the carrier mobility were obtained by conducting Hall effect measurements. The Seebeck coefficients were measured in a direction parallel to the film surface. These data are shown in Table I and II. From the data obtained, ECD n- Bi_2Te_3 material can achieve a high Seebeck coefficient (-189 $\mu\text{V}/\text{K}$) when it is deposited at -200 mV vs. SCE. The in-plane resistivity, in-plane mobility, and carrier concentration are 3.0 mohm-cm, 31 $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$, and $6.79 \times 10^{19} \text{cm}^{-3}$, respectively. This is close to the maximum values obtained for bulk materials with similar composition. For n-type Bi_2Te_3 , constant current ECD does not result in films with good electrical properties. These films are susceptible to flaking off of the substrate, but the cause is unclear. The microstructure and composition of the films were investigated by XRD and SEM. Bi_2Te_3 films deposited in this manner exhibited heavily doped n-type behavior with dense growth. Electron Dispersive Spectroscopy (EDX) analysis confirmed near Bi_2Te_3 stoichiometry. Figure 2 shows the Te composition for various films deposited at different potentials. It shows that film deposited at -200 mV (vs. SCE) has a relatively low Te composition, however, it is higher than that of the film deposited at -10 mV. Figure 3 shows the micrographs of the films of Bi_2Te_3 which were deposited on the Si substrates. The films are dense with very small grain size. Two types of microstructural morphology were observed. One has needle-like morphology and the other has plate-type morphology. The film deposited at -200 mV, which gives a better electrical properties, has the needle-like morphology. Its composition as determined by EDS is Te rich Bi_2Te_3 . For the time being, then, it is suggested that potentiostatically controlled growth should be used for the n-type Bi_2Te_3 deposition for micro-device fabrication. Further studies of the potential and solution concentrations at which optimum electrical properties can be obtained will be continued.

Table I. Properties of the n-type Bi_2Te_3 films deposited galvanostatically.

Potential (mV)	Thickness (micron)	Resistivity (m ohm cm)	Hall Coefficient cm ⁻³ .coul ⁻¹	Mobility (cm ² v ⁻¹ s ⁻¹)	Carrier Concentration (cm ⁻³)	Seebeck number ($\mu\text{V}/\text{K}$)
1	4	1.5199	0.00731	4.81	8.55E+20	
4	4	1.2808	0.0169	13.19	3.70E+20	
7	4.5	1.3396	0.0217	16.22	2.88E+20	
10	5	4.364	0.091	20.86	6.87E+19	-27.3
15	4	0.9209	0.0215	23.39	2.9E+20	-60
20	7	1.1507	0.0222	19.32	2.81E+20	-68

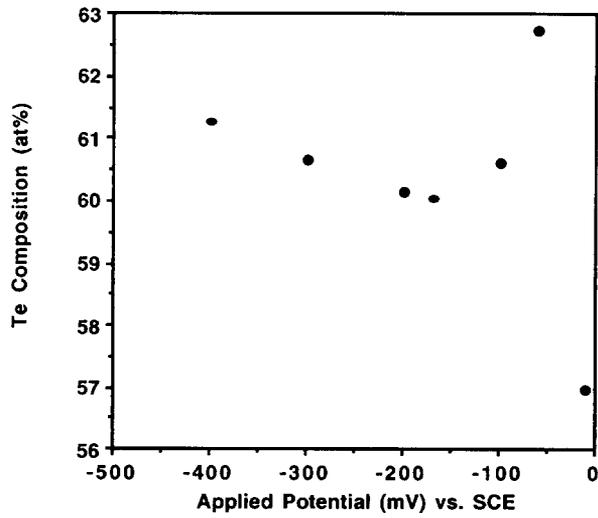


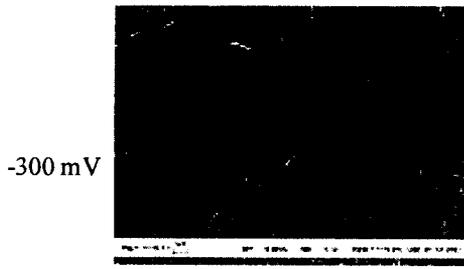
Figure 2. Te composition of the n-type Bi_2Te_3 films deposited at various potentials.



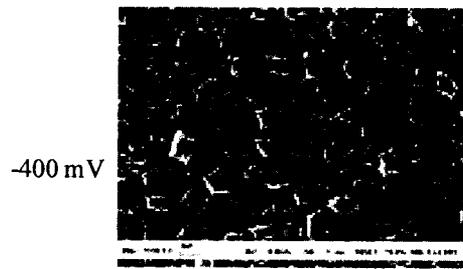
-60 mV

-100 mV

-200mV

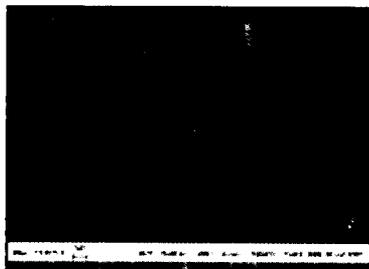


-300 mV

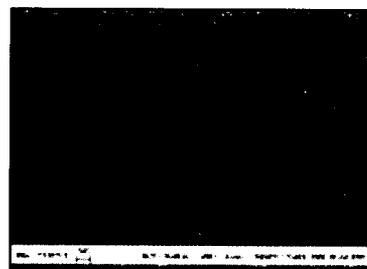


-400 mV

(1) Te-rich Bi_2Te_3 films



-10 mV



-170 mV

(2) Bi-rich Bi_2Te_3 films

Figure 3. Micrographs of n-type Bi₂Te₃ films deposited on Si substrates.

Table II. Properties of the n-type Bi₂Te₃ films deposited potentiostatically.

Potential (mV)	Thickness (micron)	Resistivity (m ohm cm)	Hall Coefficient cm ⁻³ .coul ⁻¹	Mobility (cm ² v ⁻¹ s ⁻¹)	Carrier Concentration (cm ⁻³)	Seebeck number (uV/K)
sputtered	1	1.4887	0.00445	2.989	1.40E+21	
-10	4	1.6177	0.0753	46.57	8.30E+19	-79
-30	6	1.7019	0.0457	26.85	1.37E+20	
-60	2.5	11.6128	0.139	11.96	4.50E+19	-132
-100	6.2					-176
-160	4					-151
-170	13	1.8921	0.0624	32.99	1.00E+20	-103
-180	9					-116
-190	7					-93.6
-200	8	2.9487	0.092	31.21	6.79E+19	-188.5
-300	9	5.52	0.032	5.79	1.96E+20	-76
-400	4.5	4.5867	0.218	47.5	2.87E+19	-40.7

(b) ECD of p-type Bi_{2-x}Sb_xTe₃

P-type Bi_{2-x}Sb_xTe₃ films were deposited on the Bi_{2-x}Sb_xTe₃/SiO₂/Si substrates electrochemically by either applying constant potential or constant current (density). The as received samples after deposition were annealed at 250 °C for 2 hours. The electrical properties of the films were measured in a direction perpendicular to the film growth axis. In general, films deposited by constant current densities showed better electrical properties than those deposited at fixed potentials. It was found that film is able to achieve a high Seebeck coefficient (+295 μV/K) when it is deposited at 0.3 mA/cm². The in-plane resistivity, in-plane mobility, and carrier concentration are 9.8374 mohm-cm, 66.58 cm² V⁻¹ S⁻¹, and 9.54 x 10¹⁸ cm⁻³, respectively. These data are shown in the Table III and IV. For p-type Bi_{2-x}Sb_xTe₃, the constant current electrochemical deposition produces films with good bonding strength with substrates, which is different from films obtained for n-type material. The microstructure and composition of the films were also investigated by using XRD and SEM. EDX analysis confirmed that the composition consists of mainly Sb and Te, with very small amounts of Bi. Figure 4 and 5 show the film compositions for various films deposited at different potentials and current densities, respectively. Figure 6 shows the micrographs of the p-type Bi_{2-x}Sb_xTe₃ films deposited at different current densities. The film morphology is very different when films were deposited at different current densities. The film deposited at 0.3 mA/cm², which shows a higher Seebeck coefficient, has a very small grain size. From our results, it is suggested that the galvanostatically controlled growth will be used for the p-type Bi_{2-x}Sb_xTe₃ material deposition for the micro-device fabrication. In our studies, it was found that p-Bi_{2-x}Sb_xTe₃ material composition is very sensitive to initial electrolyte concentrations. Upon increasing Bi content, both film and leg elements resulted in unfavorable dendritic/columnar growth. It is difficult to fabricate complete devices if the tops of the electrodeposited legs are too rough. Further study of the effect of initial electrolyte concentration on the film morphology will be continued.

Table III. Properties of the p-type Bi_{2-x}Sb_xTe₃ films deposited potentiostatically.

Potential (mV)	Thickness (micron)	Resistivity (m ohm cm)	Hall Coefficient cm ⁻³ .coul ⁻¹	Mobility (cm ² v ⁻¹ s ⁻¹)	Carrier Concentration (cm ⁻³)	Seebeck number (uV/K)
sputtered	1	3.1811	0.119	37.39	5.25E+19	
-110	2	5.8539	0.246	42.04	2.54E+19	144.5
-120	8	6.2288	0.411	65.99	1.52E+19	107
-140	6	2.6911	0.141	52.4	4.43E+19	166
-160	10	4.3064	0.658	152.76	9.5E+18	146

Table IV. Properties of the p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ films deposited galvanostatically.

Current (mA/cm ²)	Thickness (micron)	Resistivity (m ohm cm)	Hall Coefficient cm ³ .coul ⁻¹	Mobility (cm ² v ⁻¹ s ⁻¹)	Carrier Concentration (cm ⁻³)	Seebeck number (uV/K)
0.1	3.8	7.9144	0.478	60.36	1.31E+19	184
0.2	3	3.6627	0.249	68.11	2.51E+19	192
0.3	5	9.8374	0.655	66.58	9.54E+18	295
0.5	5.5	73.8515	0.849	11.49	7.36E+18	275
0.7	2.4	3.8658	0.0696	18.01	8.98E+19	50
1	6	2.7849	0.357	128.07	1.75E+19	93
4	4.5	1.7915	0.0147	8.23	4.24E+20	21
7	4	1.4203	0.0339	23.89	1.84E+20	3
8.4	6.5	1.2932	0.0479	37.08	1.30E+20	110
10	2	1.4414	0.056	38.83	1.12E+20	90

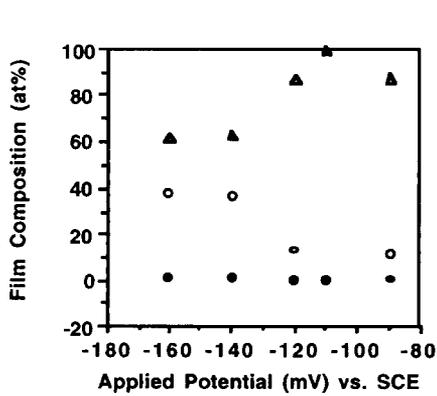


Figure 4. Compositions of the p-type films deposited at various potentials.

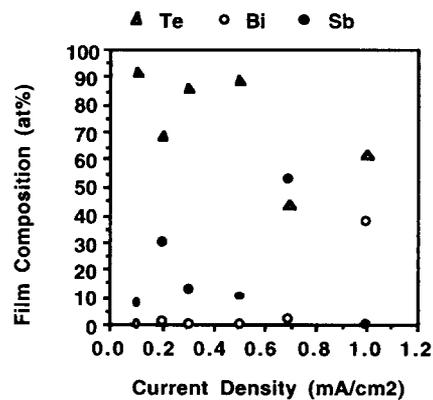


Figure 5. Compositions of p-type films deposited under various current densities.

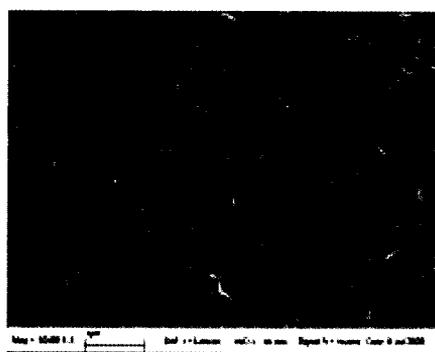
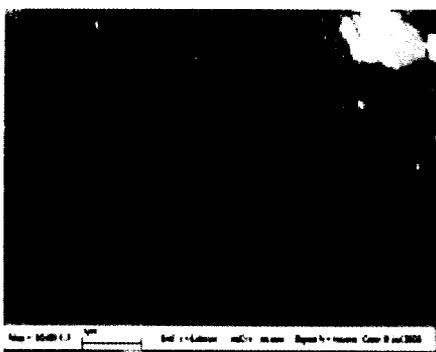
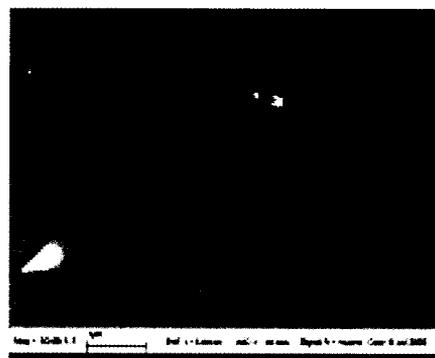
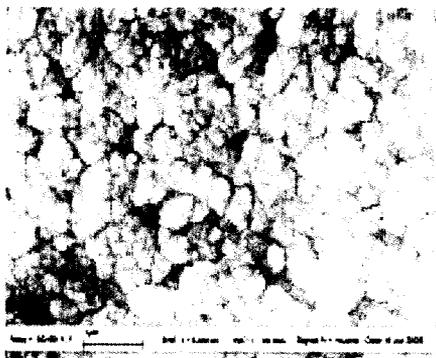


Figure 6. Micrographs of the p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ films deposited at various current densities. From upper left to right, the current densities used are 0.1 mA/cm^2 , 0.2 mA/cm^2 , 0.3 mA/cm^2 and 0.7 mA/cm^2 , respectively.

Conclusion

At JPL, we have developed a process to fabricate thermoelectric microdevices using a combination of IC techniques and ECD methods. We believe that the performance of our current microdevice developed is limited by the properties of the ECD materials. Therefore, the objective of this study is to develop ECD methods for obtaining thermoelectric materials with near bulk properties, as well as optimizing morphology and transport properties. In this study, the films of Bi_2Te_3 and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ were initially obtained under various deposition conditions. Seebeck coefficients and transport properties were then measured along the direction parallel to the substrates before and after annealing at 250°C for 2hrs. From the data obtained, ECD n-type Bi_2Te_3 material can achieve a high Seebeck coefficient ($-189 \mu\text{V/K}$) when it is deposited at -200 mV vs. SCE. The in-plane resistivity, in-plane mobility, and carrier concentration are 3.0 mohm-cm , $31 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, and $6.79 \times 10^{19} \text{ cm}^{-3}$, respectively. As for the p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$, it is possible to achieve a high Seebeck coefficient ($+295 \mu\text{V/K}$) when it is deposited at 0.3 mA/cm^2 . The in-plane resistivity, in-plane mobility, and carrier concentration are 9.8374 mohm-cm , $66.58 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, and $9.54 \times 10^{18} \text{ cm}^{-3}$, respectively. From the results of our preliminary study, we have found the best conditions for depositing high quality Bi_2Te_3 and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ materials with thermoelectric properties comparable to those of their state-of-the-art bulk samples.

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