

Electrochemical Deposition of $(\text{Bi,Sb})_2\text{Te}_3$ for Thermoelectric Microdevices

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ABSTRACT

New experimental methods have been developed to electrochemically deposit p-type Sb-rich $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$, Pb-doped and Bi-doped Bi_2Te_3 , and PbTe thick films. Some of the deposited films were dense and had a smooth surface morphology. These films were deposited potentiostatically at room temperature in an acidic aqueous electrolyte. Experimental deposition of Bi_2Te_3 alloys into various thick nanoporous templates made out of anodized alumina has also been achieved. Miniaturized thermoelements for microdevices (25 μm tall, 60 μm diameter) were grown by plating through thick photoresist templates. The experimental techniques developed, as well as the transport properties of some of the films and filled templates, will be presented.

INTRODUCTION

Electrochemical deposition (ECD) is a promising alternative technique to bulk synthesis for fabrication of thermoelectric microdevices. It is a simple, inexpensive, fast and safe technique, in which compounds are deposited on a substrate using an electrolyte and controlled current or potential. Deposition parameters determine the film composition, growth rate and morphology. Electrochemical deposition is a well-known technique for growth of metals, but is a relatively new method for growth of semiconductors [1]; nevertheless, it holds great promise for the fabrication of miniaturized thermoelectric elements and devices [2].

Our interests focus on n-type and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ materials as well as other known compounds such as PbTe, Zn_4Sb_3 and CoSb_3 . We have previously reported the successful development of ECD techniques for the growth of n-type Bi_2Te_3 and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ [3]. However, p-type films with thickness higher than 5 μm typically possess a rough morphology unsuitable for application to devices. This paper briefly reports progress in optimizing ECD experimental conditions to grow smooth p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ films, the growth of microelements and nanostructures using templates, and the fabrication of complete thermoelectric devices using a combination of electrochemical deposition and integrated circuit techniques.

ELECTRODEPOSITION OF $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ THERMOELECTRIC FILMS

Experimental Method

All experiments were run in a three electrode configuration (Pt counter electrode, Pt or Au working electrode and a SCE reference) using an EG&G Princeton Potentiostat/Galvanostat 273A. The standard electrolytes contained millimolar amounts of oxidized high purity elements, salts or chelating agents in aqueous 1 M HNO_3 (pH 0). Film thickness was measured using a

Dektak profilometer. The atomic composition was obtained using a Siemens D-500 x-ray diffractometer or with an Ion Coupled Plasma technique. The crystallographic orientation of the films were studied with a JEOL JXA-733 electron superprobe. The Seebeck coefficient was measured in a cross-plane direction using a simple differential thermocouple setup.

N-type Bi₂Te₃ Films

We have previously reported our capability of producing good quality n-type Bi₂Te₃ films and thermoelectric elements (legs) [3, 4]. Since that time, we have run a matrix of experiments to optimize our experimental parameters for the n-type material. This matrix followed the Robust Design "Taguchi" approach, a mathematical model that allows one to evaluate a matrix of experimental parameters without having to perform every possible experimental combination [5]. This method allowed us to perform only 18 experiments (twice) instead of 4374 of them. Experimental parameters included in the study were deposition potential, temperature, metal concentrations, solution pH, stirring rate, Ar de-aeration and substrate quality. Results to date indicate that a combination of slightly elevated temperature (45°C), slow solution stirring rate and low voltage (-2mV vs. SCE) worked best for depositing smooth, uniform stoichiometric films. De-aerating the electrolyte with Argon or small changes in solution pH (0 to 1.0) did not have any significant impact on film morphology or properties. Pulse deposition techniques, alternating potential between deposition and short etch-back sequences can decrease even further the surface roughness from about 1 μm to less than 0.2 μm.

However, post deposition heat treatments are still needed to anneal lattice defects, reduce electron concentration and optimize electrical properties. Figure 1(a) displays the morphology of n-type Bi₂Te₃ thermoelements electrodeposited under these conditions and then heat-treated at 250°C for 1 hour.

Excess Bi and Pb-doped Bi₂Te₃ Films

It is well known that for bulk Bi₂Te₃ p-type conductivity can be obtained by doping with excess Bi (stoichiometric deviation) or Pb [6]. We were able to successfully grow films with excess Bi or Pb doping, up to a few at.%. However, these films were still n-type, even after high temperature annealing. It appears that defects in the film as a result of electrochemical deposition overrides the effect of the doping. A detailed study of the type and concentration of defects in electrodeposited Bi₂Te₃ films is needed to understand the source of the high electron concentration in as-deposited films. Studies on thick films deposited by the hot-wall epitaxy method suggested that Te vacancies and not antisite defects (i.e. Te atom on Bi site) could be responsible [7].

As a result of these studies, we have focused on finding the optimal experimental conditions for electrodepositing p-type Sb-rich Bi_{2-x}Sb_xTe₃ films.

P-type BiSbTe₃ Alloy Films

Sb₂Te₃-rich Bi_{2-x}Sb_xTe₃ compositions are best for p-type thermoelements. Such alloys can be obtained in electrodeposited films by controlling the [Sb]/[Bi] and [Sb]/[Te] ratio in the electrolyte. However, The solubility of Sb into the pH=0 acidic electrolyte is very low (up to 0.0008 M) and relatively high deposition voltages (-120 mV and more negative values) must

typically be used [3], resulting in slow deposition rates and columnar, dendritic growth and highly porous films. At less negative voltages, Bi and especially Te deposition tend to dominate the process and off-stoichiometric films are obtained. Much higher [Sb] concentrations can be obtained by using chelating agents such as EDTA or tartaric acid (up to 0.03 M). However the reaction kinetics are also changed (slow release of chelated Sb for deposition). Using again a Robust Design “Taguchi” approach to cover a wide experimental space, conditions to work around these limitations and produce p-type legs with suitable composition and morphology have been identified. The p-type legs produced as a result of these changes are shown in Figure 1(b).

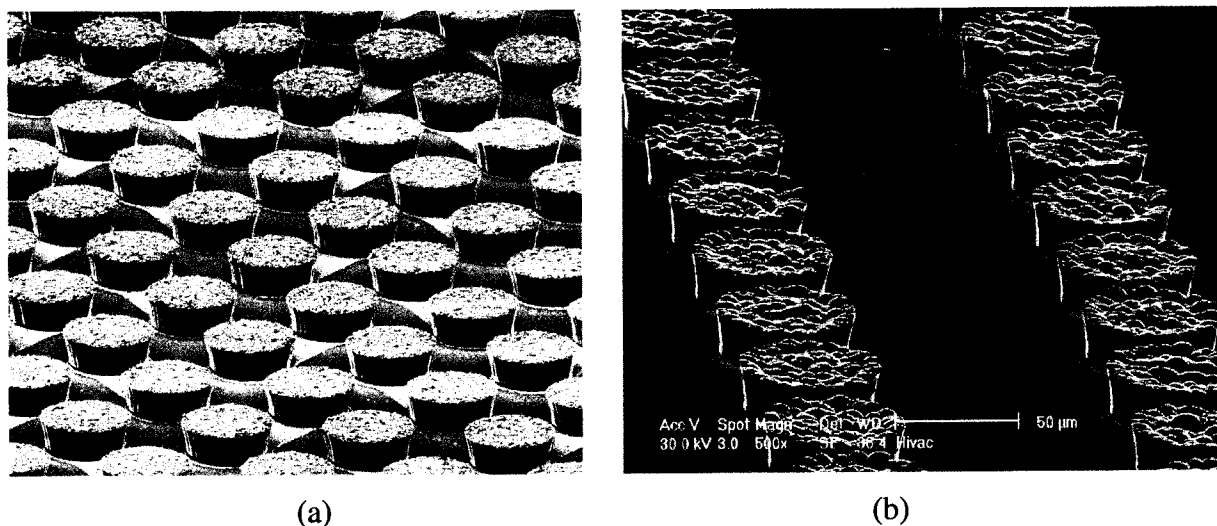


Figure 1. (a) Micrograph of electrodeposited n-type Bi_2Te_3 25 μm thick thermoelements subsequently heat-treated at 250°C for one hour in inert atmosphere; (b) Micrograph of electrodeposited p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ 25 μm thick thermoelements; notice the increased surface roughness compared to n-type deposits.

Further improvements in surface morphology can be obtained by using a pulse deposition technique (similarly to that for n-type deposition), albeit resulting in a slower deposition rate. In addition to completing optimization of deposition conditions in the pH=0 acidic electrolytes, recent studies on near neutral pH solutions (pH=6-7) with very high elemental solubility (0.01 to 0.1 M) could offer an attractive alternative [8]. Experimental details and deposition results will be reported later.

ELECTRODEPOSITION OF NEW MATERIALS AND STRUCTURES

PbTe and $\text{Bi}_x\text{Pb}_y\text{Te}_z$ Films

There is interest in investigating the electrochemical deposition of novel thermoelectric materials such as Zn_4Sb_3 and CoSb_3 -based skutterudites, materials that are already being studied at JPL in bulk form. Our recent work on Pb-doped Bi_2Te_3 films has led us to consider the deposition of a more traditional thermoelectric material, PbTe, as well as layered compounds based on both Bi_2Te_3 and PbTe, such as PbBi_4Te_7 .

The setup for the PbTe experiments was very similar to that of Bi₂Te₃: three electrode configuration, aqueous HNO₃-based (pH=1) electrolyte. In order to achieve a 50:50 atomic ratio of lead and tellurium in the film, it was found that close concentrations of [Pb] and [Te] were required, in a departure from earlier results [9]. Current experimental conditions are a 2:1 [Pb]:[Te] concentration ratio and deposition voltages in the -150 to -200mV range (vs. SCE). Figure 2(a) shows the voltammogram of [Pb]+[Te] in 0.1 M [HNO₃] aqueous solution. The electrolyte with a high [Pb] concentration (25:1) shows an anodic Pb⁰ oxidation peak near -0.4V (vs. SCE). Both solutions show the anodic oxidation of Te near +0.5V. Pb and Te codeposition into a near-stoichiometry PbTe polycrystalline film (Figure 2(b) micrograph) occur in the -0.1 to -0.3V potential range. Films with excess Pb or excess Te can be prepared, with the x-ray diffraction pattern of a stoichiometric film shown in Figure 2(b).

To date, deposited PbTe films were found to be n-type (Seebeck on average of -76 μV/K) single phase, face-centered cubic crystals (Figure 2). This result matches the bulk material well, however, the film's surface quality is not yet appropriate for use in a thermoelectric device. Future experiments will focus on improving the film morphology by slowing down the growth rate and varying the electrolyte, potentially using a chelating agent.

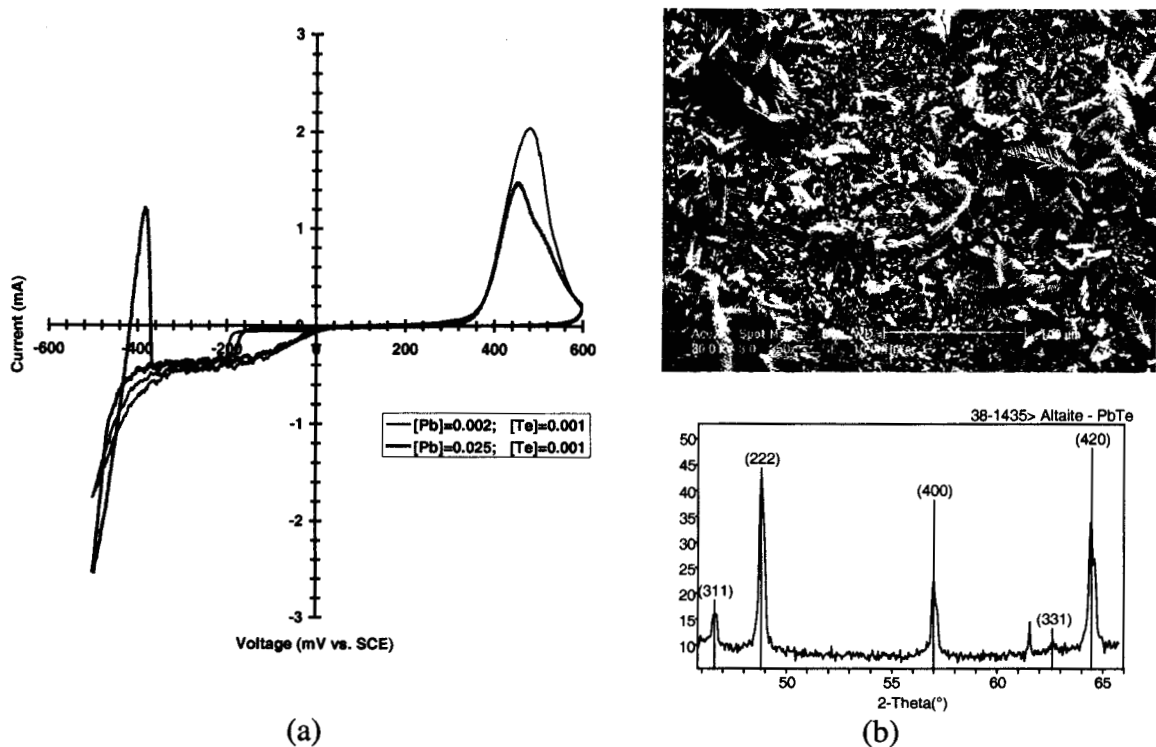


Figure 2. (a) Voltammogram of [Pb]+[Te] electrolytes in 0.1 M [HNO₃] aqueous solution. Only the 25:1 electrolyte with a high [Pb] concentration shows an anodic Pb⁰ oxidation peak near -0.4V (vs. SCE). (b) Micrograph of an as-deposited stoichiometric PbTe film and corresponding x-ray diffraction pattern, partially Bi₂Te₃- filled opal template. The small response at 61.5 degrees is believed to be from either an intermetallic associated with the substrate or a small amount of film oxide.

Finally, initial experiments on depositing $Pb_xBi_yTe_z$ films have shown that a number of crystalline compositions could be obtained with $PbBi_4Te_7$ and possibly $Pb_4Bi_2Te_7$ identified. Further study of this system with attractive bulk properties [10] through electrochemical deposition techniques is in progress.

Nanowires

Recent theoretical and experimental results [11,12] have shown the potential of low dimensional thermoelectric structures such as nanowires for altering electrical and thermal transport properties and potentially lead to significant improvements in the figure of merit. Using anodized alumina nanotube templates (Figure 3(a)) metallized on one side, Bi_2Te_3 nanowires with extremely high length over cross-section ratio can be grown, as shown on Figure 3(b). Nanowires as small as 8 nm in diameter were recently grown using custom-made templates. Initial Seebeck measurements on the 200nm diameter nanowires did not show any significant departure from values typical of as-deposited films, around $-50 \mu V/K$ at 300K.

This technique can be applied to other thermoelectric materials of interest, including Bi, and more experimental data will be reported later.

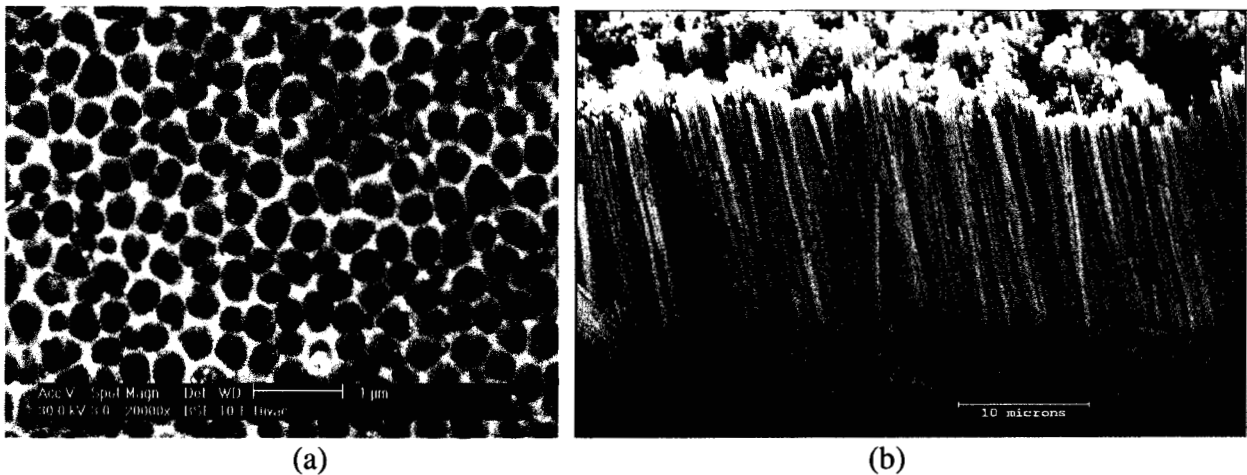


Figure 3. Micrographs of an empty nanotube alumina template (a) and side view of n-type Bi_2Te_3 nanowires (b), 200nm in diameter and 20 μm long, grown using such templates (the template has been removed by etching and the Pt bottom metallization can be seen).

ELECTRODEPOSITION OF COMPLETE THERMOELECTRIC MICRODEVICES

There is a growing interest in highly miniaturized multifunctional electronic and optoelectronic devices [4,13]. The high degree of integration sought for such devices requires novel approaches to thermal management, power generation, storage, management and distribution issues. Thermoelectrics can address some of these issues provided that high performance, miniaturized devices can be embedded into such multifunctional structures.

A key aspect of our research effort into thermoelectric microdevices is to develop techniques that are compatible with micromachining, integrated circuit and semiconductor technology. We have reported previously on our approach that combines electrochemical deposition of

thermoelectric thick films, advanced UV photolithography and standard vapor deposition of thin metal films [4]. This combination offers a high degree of flexibility in designing and fabricating thermoelectric microdevices. A single photolithography mask can usually combine all of the necessary patterns to completely fabricate one microdevice configuration. Several fully interconnected microdevice structures have recently been successfully synthesized, as shown in Figures 4(a) and 4(b). Even though various fabrication steps still need to be optimized, this picture demonstrates that complete thermoelectric microdevices can be successfully built on top of a silicon substrate without any soldering step. Efforts are now focusing on fabricating several operational devices and testing their electrical and thermal performance.

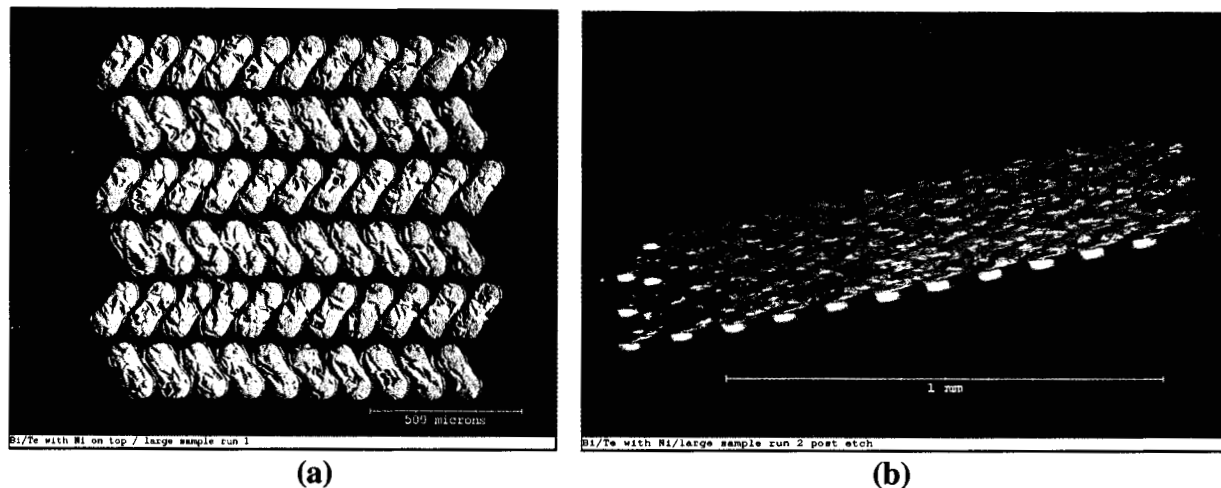


Figure 4. Micrographs of a complete Bi_2Te_3 -based thermoelectric microdevice structure (only *n*-type material was used here). Each leg is $25\ \mu\text{m}$ thick and $60\ \mu\text{m}$ in diameter. Bottom interconnects are sputtered Au films and top interconnects are electroplated Ni films. (a) after Ni deposition and (b) after photoresist removal.

CONCLUSION

We have discussed here several areas of electrochemical deposition research being carried out by the Thermoelectrics Group at the Jet Propulsion Laboratory. Recent advances in electrochemical deposition of *p*-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and PbTe films and nanostructures are promising. Complete microdevice fabrication is under development; a working device will soon be ready for testing of its thermoelectric properties. We will investigate novel thermoelectric materials such as Zn_4Sb_3 and CoSb_3 , as well as new methods to deposit $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ alloys in the next year. We expect that electrochemical deposition of this group of semiconductor alloys will become a standard manufacturing process, allowing further miniaturization of thermoelectric microdevices.

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