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Single Bath Electrochemical Deposition of Bi_2Te_3/Sb_2Te_3 Superlattices

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In recent years, there has been extensive discussion of the possibility of increasing the thermoelectric figure of merit in common thermoelectric materials to values substantially above their bulk values by engineering low dimensionality structures such as superlattices and nanowires. Several researchers have calculated the possible improvements in electrical and thermoelectric properties such as Seebeck coefficient and power factor. Bismuth nanowires have been made and measured, and improvements in electrical properties have been observed, but it has been found that the diameter of an alloy nanowire such as Bi_2Te_3 must be less than 10 nm in order for it to exhibit improved thermoelectric properties, as shown in Figure 1.

For the past 10 years, several researchers have been investigating approaches to making thermoelectric materials by electrochemical deposition [1, 4]. State-of-the-art fabrication and processing of semiconducting materials for thermoelectric elements have reached mechanical limits [5], and electrochemical deposition (ECD) makes it possible to fabricate devices components on the nanometer and micrometer scale [2]. At JPL, we have made thermoelectric micro-devices electrochemically and have begun work on nanodevices in the form of nanowires [6-8].

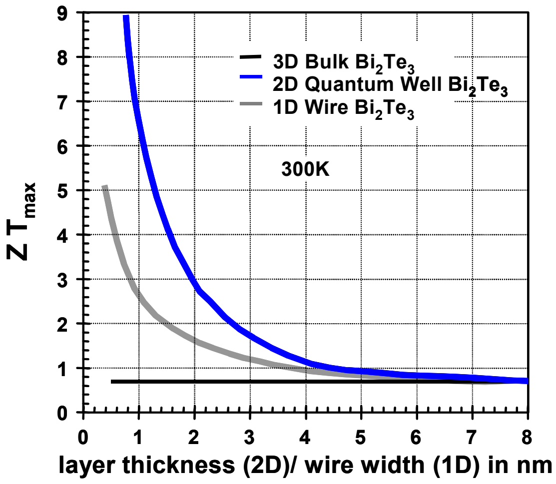
We have previously reported on microdevices and on nanowires made using electrochemical deposition [5-7]. In this paper we report on superlattices made in the Bi_2Te_3/Sb_2Te_3 system from a single deposition bath, and on the improved Seebeck coefficient measured on these superlattices.

We have grown nanowires in the Bi_2Te_3 system in alumina templates; and it has been difficult to measure both the electrical and thermal properties of these nanowires. The alumina template acts as a thermal shunt, effectively controlling the filled template thermal conductivity, in spite of the very high aspect ratio of the wires (100:1). Until methods for separating the thermal effect of the template from that of the nanowires are developed, it will not be possible to make reliable measurements of the thermoelectric properties of the nanowires. Therefore, in order to determine whether improved thermoelectric properties can indeed be achieved through electrochemically deposited materials which exhibit quantum effects, we have made superlattices of materials in the Bi_2Te_3/Sb_2Te_3 system and measured the Seebeck coefficient and thermal properties of the superlattices.

Depositions are made from a single bath by pulse deposition. The single bath is used to minimize the work involved in moving the sample between baths, to minimize the possibilities of reaction of the deposited material in air during the bath change and to ensure abrupt superlattice interfaces. Materials are deposited from an acidic, aqueous bath of Bi, Sb and Te at room temperature in a three-electrode configuration (Pt counter electrode, Pt or Au working electrode and a SCE reference). Layers are made by pulse deposition, where first a n-type, Bi-rich layer is deposited at –20 mV vs. SCE, and then a p-type Sb-rich layer is deposited at –120 mV vs. SCE. Each layer of 1-5 nm is deposited in a few seconds. The layers have been imaged using electron microscopy in order to estimate the layer thicknesses.

Thick layers of the same materials were studied by electron microscopy and electron dispersive spectroscopy. These studies have shown the surface roughness of the layers to be less than 1 nm and the interface regions significantly thinner than the superlattice layer thickness.

Layers 1-5 nm thick of n-type $Bi_{2-x}Sb_xTe_3$ (average x=0.2) were deposited alternating with layers of p-type $Sb_{2-y}Bi_yTe_3$ (avg. y=0.7) were deposited on a Pt foil substrate. The Seebeck coefficient measured for 800 pairs of 1-5 nm thick layers is 3.5 times greater than the Seebeck coefficient measured for layers 500 nm thick. Thermoelectric measurements were made to determine whether the increased Seebeck coefficient is caused by increases in electron density of states at the Fermi level or by an absolute change in charge carrier concentration brought by the pulsed deposition conditions and a different defect type or concentration in the grown superlattice.



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