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# Thermoelectric properties of $Bi_{0.5}Sb_{1.5}Te_3$ thin films grown by pulsed laser deposition

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ABSTRACT

We report on the pulsed laser deposition of p-type $Bi_{0.5}Sb_{1.5}Te_3$ thin films onto fused silica substrates by ablation of dense targets of $Bi_{0.5}Sb_{1.5}Te_3$ with an excess of 1 wt% Te. We investigated the effect of film thickness, substrate temperature and post-annealing duration on the thermoelectric properties of the films. Our results show that the best power factor (2780 $\mu W/K^2m$ at 300 K) is obtained for films grown at room temperature and then post-annealed in vacuum at 300 °C for 16 h. This is among the highest power factor values reported for $Bi_{0.5}Sb_{1.5}Te_3$ films grown on fused silica substrates.



## 1. Introduction

Thermoelectric devices are of interest for applications as power generators and heat pumps, which interconvert heat and electricity via the Seebeck and the Peltier effect, respectively. The performance of these solid state thermoelectric energy converters depends on the dimensionless thermoelectric figure of merit ($ZT$) of the materials, given by $ZT = S^2T/\rho\kappa_t$, where $S$, $\rho$, $\kappa_t$, and $T$ are the Seebeck coefficient, electrical resistivity, total thermal conductivity, and absolute temperature, respectively. A good thermoelectric material must combine a large Seebeck coefficient S with low electrical resistivity $\rho$ and low thermal conductivity $\kappa_t$. Another crucial criterion to characterize thermoelectric materials is the power factor, defined as $PF = S^2/\rho$ [1].

Bulk $Bi_{0.5}Sb_{1.5}Te_3$ (BST) is considered as a state-of-the-art p-type thermoelectric material in the temperature range 273–473 K because it exhibits high power factor and low thermal conductivity over this temperature range. For example, Caillat et al. [2] have reported that single crystals of BST exhibit a power factor of 4800 $\mu W/K^2m$ and a thermal conductivity of 1.51 W/mK at 300 K. In addition, Kitagawa et al. [3] have recently reported that BST pellets fabricated by mechanical alloying and hot pressing exhibit a power factor of 3600 $\mu W/K^2m$ at 300 K.

The development of thermoelectric thin films has brought a new perspective to the integration of thermoelectric cooling devices into microelectronic systems for thermal management purposes. Several techniques have been employed to deposit BST thin films on a variety of substrates including flash evaporation [4], radio-frequency sputtering [5,6], direct current magnetron sputtering [7,8], and pulsed laser deposition (PLD) [9,10]. In these studies, it has been shown that the thermoelectric properties of BST films depend on several parameters including type of substrate, substrate temperature, film thickness and post-annealing treatment. Nevertheless, the deposition of BST thin films with bulk-like thermoelectric properties remains a challenge because of issues related to stoichiometry and antisite defects.

PLD is considered to be a good method to obtain stoichiometric transfer of material from target to a film on a substrate even in the case of a multicomponent compound [11]. As there are not many works on the growth of BST films by PLD, we have carried out a systematic investigation on this topic using targets with excess of Te to compensate for possible Te volatilization losses due to its high vapor pressure [12]. We used PLD to deposit BST thin films by laser ablating dense targets of $Bi_{0.5}Sb_{1.5}Te_3$ with an excess of 1 wt% Te. The films were deposited on fused silica substrates at various temperatures between room temperature and 350 °C. We

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investigated the effect of substrate temperature, film thickness and post-annealing duration on the thermoelectric properties of the films.

## 2. Experiment

### 2.1. Film deposition

A KrF* excimer laser (wavelength 248 nm, pulse width 25 ns) operating at 10 Hz was used to ablate home-made BST targets with excess of Te. The PLD targets (BST + 1 wt% Te) were made by mixing high purity metals of Bi, Sb and Te in the desired amounts and melting them at 850 °C in an evacuated sealed quartz tube. The obtained ingots were ground using an agate mortar and pestle. The resulting fine powder was cold pressed at 4 kbars into 15 mm diameter disks. The films were deposited on low thermal conductivity fused silica substrates. Prior to deposition the substrate was cleaned thoroughly in an ultrasonic bath and then was mounted in a vacuum chamber, opposite to the target at a distance of 4 cm. The chamber was evacuated to a base pressure of $\sim 4 \times 10^{-6}$ mbar prior introducing ~0.13 mbar of high purity Ar gas. The laser beam was incident on the target at 45° and the laser ablation fluence was 2 J/cm$^2$. The target was continuously rotated and rastered to avoid local heating of the target and achieve stoichiometric films. We deposited BST films at various substrate temperatures between room temperature and 350 °C in order to obtain the optimum growth conditions, which result in the best power factor (PF). Films with different thicknesses were produced in order to investigate the effect of thickness on PF. Also, BST films were grown at room temperature and then were subjected to a post-annealing process. Based on published reports, we selected to perform the annealing process at 300 °C in argon atmosphere and vacuum for different times: (Ar – 5 h, 10 h and 16 h; vacuum – 16 h) [7].

### 2.2. Film characterization

The structure, morphology and chemical stoichiometry of the BST thin films were characterized using techniques such as grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively. EDX spectra were collected under the same conditions (accelerating voltage, beam current, magnification, and acquisition time) from at least three different regions of each sample. Quantitative analysis of the different elements (atomic percent concentration) was performed by standard-less analysis with 3% accuracy. The thickness of the films was measured using an optical profilometer.

The temperature dependence of electrical resistivity and Seebeck coefficient as well as the Hall coefficient at 300 K were measured using a commercial physical properties measurement system (PPMS, Quantum Design). The Seebeck coefficient was measured using the steady state technique with thermal gradients of 1% of the measurement temperature and miniature Cernox temperature sensors. The distance between the voltage leads and the temperature sensors was about 1 mm. The electrical resistivity was measured using the four-probe ac method. Electrical resistivity and Seebeck coefficient were measured simultaneously on samples with width of 5 mm and length of 10 mm using the Thermal Transport Option (TTO) of PPMS. A picture of a typical sample is shown in Fig. 1. The Hall coefficient was measured using the Van der Pauw under a magnetic field of 2 T. The total relative errors in the measurements of electrical resistivity, thermopower and carrier density are about 5%, 7% and 5%, respectively.

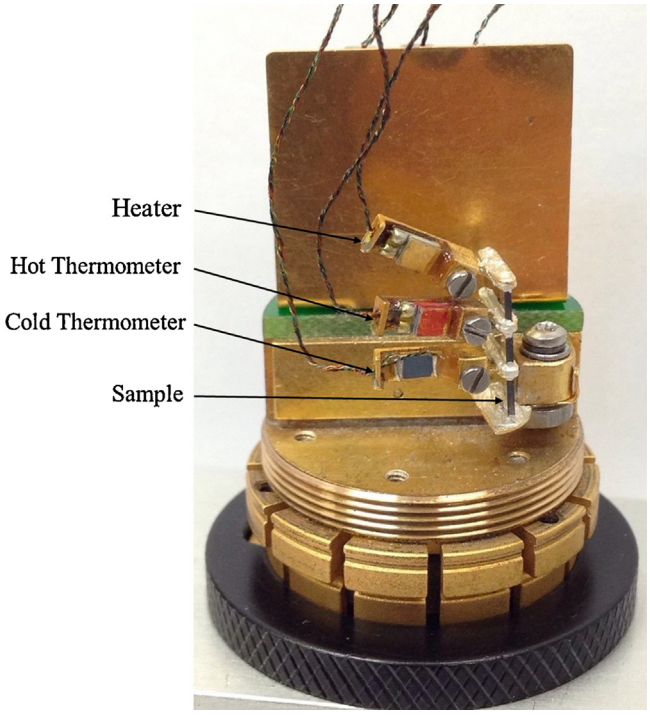


**Fig. 1.** Picture of a typical sample for resistivity and Seebeck coefficient measurements using the thermal transport option (TTO PPMS, Quantum Design).

## 3. Results and discussion

### 3.1. Effect of thin film thickness

In order to investigate the influence of film thickness on the thermoelectric properties of BST films, a series of samples were grown at 350 °C by varying the number of laser pulses and keeping the rest of the deposition conditions identical. The thickness of the as-grown films varied between 100 nm and 480 nm and was found to be a crucial parameter for their thermoelectric properties. All samples exhibit similar XRD patterns (not shown); i.e., they are all fully oriented and the observed (0 0 l) reflections indicate preferential growth along the *c*-axis.

Films thicker than 280 nm have microcracks and the coalescence of these cracks leads to exfoliation. This effect is attributed to the large difference in the thermal expansion coefficient between the fused silica substrate ($1 \times 10^{-6}$/K) and the BST films ($\sim 20 \times 10^{-6}$/K). Specifically, the large thermal expansion coefficient mismatch generates cracks in the films due to the large tensile thermal strains induced upon cooling down to room temperature following the deposition of the films.

On the other hand, BST films thinner than 180 nm are dense with smooth surfaces. As shown in Table 1, the best power factor at 300 K is obtained for 180 nm-thick films, i.e., PF = 2150 μW/K$^2$m, because of its lower resistivity than the other samples. Given that all samples are fully oriented along *c*-axis, we expect the effect of anisotropy to be weak, and hence, we propose that the lower resistivity value of the 180 nm-thick sample is a thickness effect; i.e.,

**Table 1**
Room-temperature thermoelectric properties of BST films with different thicknesses.

| Thickness (nm) | $\rho$ (Ω m) | $S$ (μV/K) | PF (μW/K$^2$m) |
|---|---|---|---|
| 120 | $9.3 \times 10^{-6}$ | 128 | 1756 |
| 180 | $8 \times 10^{-6}$ | 135 | 2150 |
| 280 | $1 \times 10^{-5}$ | 120 | 1398 |

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