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Thermal conductivity of thermoelectric thick films prepared by electrodeposition

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HIGHLIGHTS

- A novel technique was used to measure the thermal conductivities of thermoelectric thick films.
- The thick films are of Bi–Te and Sb–Te compositions and were prepared by electrodeposition.
- We used a particular method to prepare a measurable sample.
- We compared the thermal conductivities of the films made by different aqueous solutions.

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ABSTRACT

Because of a lack of appropriate methods and the difficulties of sample preparation, few direct measurements of the thermal conductivity of thermoelectric materials in thin films have been reported. We prepared thermoelectric thin films of four types containing Bi–Te and Sb–Te by electrodeposition from aqueous solutions with and without added surfactant, and evaluated their intrinsic thermal conductivity with a modified parallel-strip technique. Three thermoelectric materials showed values 0.2–0.5 W m^{-1} K^{-1} of intrinsic thermal conductivity; for the other type problems of sample preparation precluded measurement. According to observations with a scanning electron microscope, the existence of grain boundaries in the thermoelectric thin films is likely the cause of the small values, and their fragile structure causes difficulty in preparation of a test sample.

1. Introduction

The practicality of thermoelectric (TE) devices is limited mainly by the available materials, of which the performance must be improved to compete with conventional cooling and energy-generation systems. The efficiency of TE materials is directly related to a dimensionless figure of merit defined as $ZT = S^2\sigma T/k$; σ denotes electrical conductivity, S Seebeck coefficient, k thermal conductivity and T absolute temperature. An enhancement of the TE figure of merit is achievable on increasing the Seebeck coefficient (S) and the electrical conductivity (σ), or decreasing the thermal conductivity (k). Among common TE materials, bismuth telluride (Bi_2Te_3) that serves typically as an n-type material and antimony telluride (Sb_2Te_3) as a p-type material are reported to show optimal performance near 300 K in bulk form because they have a large thermoelectric figure of merit. Relative to bulk materials, TE film structures are expected to have a significantly smaller thermal conductivity because phonons are strongly scattered at both film interfaces and denser grain boundaries [1–4]; these structures thereby show a feasibility in applications of hot-spot cooling and electric generation operated at small to moderate temperature differences.

Among methods to fabricate Bi_2Te_3 and Sb_2Te_3 films, electrodeposition [5–8] is simple and cheap relative to dry processes such as molecular-beam epitaxy (MBE) [9], metal-organic chemical-vapor deposition (MOCVD) [10], pulsed laser deposition [11,12], flash evaporation [13] and sputtering [14]. Electrodeposition also enables an easy control of film thickness in a range 0.01–50 μm that shows feasibility and suitability for fabricating the micro-TE devices.

Methods to measure the thermal conductivity of thin film with a thickness in the range between 0.01 μm and 1 μm include the 3ω

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method [15,16] and others [17,18], but published methods to measure the thermal conductivity of a film of thickness greater than about 5 μm are few because of a strong heat-spreading effect in the in-plane direction of such a thick film. For instance, in a general measurement to determine the thermal conductivity of a film of thickness 10 μm heated with a strip of width 10 μm, the heat diffusing sideways into the film might be about one fifth of the total generated heat. As the thickness increases, so does the heat spreading. The significant lateral heat spreading in a thick film prevents use of Fourier's law to calculate the thermal conductivity because of inaccurate heat flow and immeasurable temperature of the film/substrate interface.

We measured the intrinsic thermal conductivity of TE materials, Bi_2Te_3 and Sb_2Te_3, prepared by electrodeposition from the aqueous solutions with and without an added ionic surfactant. The surfactant is anionic sodium dihexyl sulfosuccinate (SDSS) and commonly used in an electrodeposition process to enhance the probability of fabricating a complete micro-TE structure [19]. To prepare the sample, the TE layer (thickness 0.5–3 μm) was deposited on a silicon substrate and spin-coated with a layer of photosensitive epoxy resin (thickness 5–10 μm) that served as a dielectric layer to separate the metallic heating strip from the measured TE layer. We applied a modified parallel-strip method [20,21], an electrical heating and sensing technique, to measure the thermal resistance of such the TE film samples; the measured apparent thermal resistance (R_{app}) comprises the film's intrinsic thermal resistance ($R_{int} = t/k_{int}$) and the interfacial resistance (R_i) and is expressed as $R_{app} = t/k_{int} + R_i$. The correlation between measured thermal resistance and thickness is related to the film's thermal conductivity; hence, on measurement of TE layers of varied thickness, the measured thermal resistances of the layers could yield their intrinsic thermal conductivity.

2. The modified parallel-strip method

Our previous literature [20,21] has described a novel technique, called the parallel-strip method, for measuring the intrinsic thermal conductivity of a dielectric thin film with thickness less than 3 μm. In this job, we would also introduce the parallel-strip method and modify it to measure a thicker laminated film with thickness between 2 μm and 10 μm. The laminated structure comprises a resin layer and a electrodeposited TE layer.

The parallel-strip method originates from the analytical solutions of a heater-film-substrate heat conduction problem. Fig. 1 shows the schematic configuration of the two-dimensional steady-state problem. The method assumes a dc current is passed through a heating strip (width = $2a$) that deposited upon the measured film (film thickness is t), and thus a constant Joule heat flux (q) is generated from the strip. The designed strip's length has to be much longer than it's width for the 2D assumption. The thickness and width of substrate are c and $2b$, respectively. The correlated boundary conditions are also shown in Fig. 1; the analytical solutions are expressed as below:

$$\frac{T_f(x,d)-T_a}{(qa/hb)} = \left(1+hR_{i(f-s)}+\frac{hc}{k_s}+\frac{ht}{k_f}+\frac{hbR_{i(h-f)}}{a}\right)+\left(\frac{ha}{k_f}\right) \cdot\sum_{n=1}^{\infty}\left\{\frac{1}{(\lambda_n a)}\cdot\tanh(\lambda_n d)+\frac{\Lambda_n}{\cosh(\lambda_n t)}\right\} \cdot\frac{2\sin(\lambda_n a)}{(\lambda_n a)}\cdot\cos(\lambda_n x) \tag{1}$$

$$\frac{T_s(x,c)-T_a}{(qa/hb)} = \left(1+\frac{hc}{k_s}\right)+\sum_{n=1}^{\infty}\left\{\left(\frac{ha}{k_s}\right)\cdot\frac{1}{(\lambda_n a)}\cdot\tanh(\lambda_n c)+1\right\} \cdot F_n\cdot\cos(\lambda_n x) \tag{2}$$

$$T_{avg-f} = \left(\frac{qa}{hb}\right)\cdot\left[\left(1+hR_{i(f-s)}+\frac{hc}{k_s}+\frac{ht}{k_f}+\frac{hbR_{i(h-f)}}{a}\right)+\left(\frac{ha}{k_f}\right) \cdot\sum_{n=1}^{\infty}\left\{\frac{1}{(\lambda_n a)}\cdot\tanh(\lambda_n d)+\frac{\Lambda_n}{\cosh(\lambda_n' t)}\right\}\cdot\frac{2\sin^2(\lambda_n a)}{(\lambda_n a)^2}\right]+T_a \tag{3}$$

$$T_{avg-s} = \left(\frac{qa}{hb}\right)\cdot\left[\left(1+\frac{hc}{k_s}\right)+\left(\frac{1}{a}\right)\cdot\sum_{n=1}^{\infty}\left\{\left(\frac{ha}{k_s}\right)\cdot\frac{\tanh(\lambda_n c)}{(\lambda_n a)}+1\right\} \cdot F_n\cdot\frac{\sin(\lambda_n w)}{\lambda_n}\right]+T_a \tag{4}$$

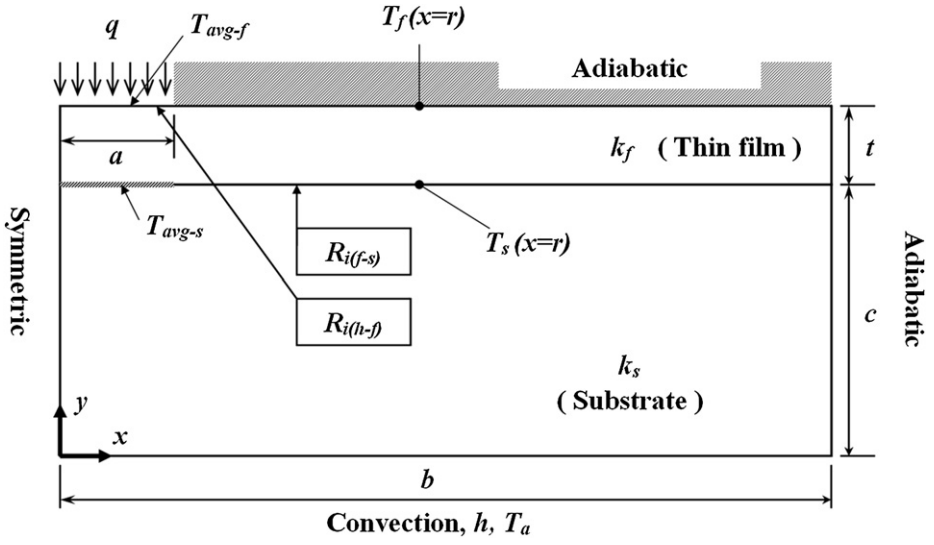

Fig. 1. Schematic model for the two-dimensional steady-state heat conduction problem of the parallel-strip method.