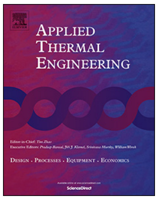
Applied Thermal Engineering 98 (2016) 683–689

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng



Research Paper

Thermal conductivity study of micrometer-thick thermoelectric films by using three-omega methods

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HIGHLIGHTS

- Thermal conductivity of electroplated Bi_2Te_3 films is determined by 3ω methods.
- Differential and slope methods produce consistent cross-plane thermal conductivity.
- Cross-plane thermal conductivity of the films ranges from 1.8 to 1.0 $Wm^{-1}K^{-1}$.
- The cross-plane thermal conductivity decreases with increasing pulse potential.
- The film's thermal conductivity anisotropy is evaluated by a two-wire 3ω method.

ARTICLE INFO

Article history:
Received 13 November 2015
Accepted 28 December 2015
Available online 11 January 2016

Keywords:
Thermal conductivity
Thermoelectric film
Three-omega method
Bi_2Te_3
In-plane
Cross-plane

ABSTRACT

Thermal conductivity is a key parameter of thermoelectric (TE) films. However, experimental reports on thermal conductivity of TE films are very limited due to the challenge in practical measurement. In this work, we report the use of some three-omega (3ω) methods to study the thermal conductivity of micrometer-thick Bi_2Te_3 TE films prepared by pulsed electroplating. The measurement devices are fabricated using sputtered SiO_2 as dielectric layer and Au lines as heaters. The differential method and the slope method are separately used to determine the cross-plane thermal conductivity of the films. The characterization methods are demonstrated to be feasible and reliable from the reasonable changes of the 3ω voltage with frequency and thickness and the consistent measurement results using these two methods. The cross-plane thermal conductivity of the electroplated film is found to decrease from 1.8 $Wm^{-1}K^{-1}$ to 1.0 $Wm^{-1}K^{-1}$ as the pulse potential increases from −100 mV to 50 mV, which is attributed to the refined microstructure of the films. In addition, the thermal conductivity anisotropy of the Bi_2Te_3 film is evaluated by using a two-wire 3ω method and the factors contributing to the measurement uncertainty are discussed.

1. Introduction

Thermoelectric (TE) materials and devices are drawing increasing interests due to their promising applications in power generation [1] and cooling [2]. In particular, growing attention has been paid to thin-film-based micro TE devices which can be used as alternative power supply for low-power microelectronic devices [3–6]. Similar to the case of bulk devices, the efficiency of micro TE devices depends to a great extent on the film's dimensionless figure of merit $ZT = \alpha^2\sigma T/\kappa$, where T is the absolute temperature, α, σ and κ are the Seebeck coefficient, electrical conductivity and thermal conductivity of the film, respectively. In order to know ZT, all the above TE parameters must be individually measured with high reliability and accuracy. At present, α and σ of TE films can be readily measured using commercial instruments. However, κ determination for TE films is not so commonly reported due to challenges in detecting small temperature differences in the film [7,8].

The most widely used techniques for the measurement of κ of thin films can be grouped into frequency-domain and time-domain methods, typically represented by the three-omega (3ω) method [9] and the time-domain thermoreflectance (TDTR) method [10], respectively. The main advantage of the TDTR method is that it is a non-contacting and non-destructive approach by using pulsed lasers for heating and sensing. The 3ω method, which is developed earlier than the TDTR method, is more popular for the measurement of thermal conductivity of thin films for its simple setup and unquestionable accuracy [8,9] and is often used to validate the TDTR measurement results [11]. For a typical 3ω measurement, a heater made of metallic wire, which also acts as a temperature sensor, needs to be deposited on the studied film. On

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http://dx.doi.org/10.1016/j.applthermaleng.2015.12.145
1359-4311/

films that are electrically insulating, the heater can be directly deposited to perform the measurement. However, TE films are semiconductive in nature, so an insulation layer must be deposited on the film of interest prior to deposition of the heater in order to ensure no current leakage, which generally requires a high smoothness of the studied film. To date, 3ω measurements of the cross-plane thermal conductivity ($\kappa_\perp$) of TE films such as Si/SiGe [12,13], half-Heusler [14], doped ZnO [15–17], and Bi_2Te_3-derivatives [18–22] have been reported. These films are all prepared by vacuum based depositions and have nanometer-scale thicknesses, for which the fabrication of pinhole-free devices is much easier.

Thick films are of particular interest for micro TE devices. In fact, micrometer-thick TE films are more desirable than nanometer-thick ones to be used in micro TE devices because thicker films are beneficial to create larger effective temperature gradient and larger power output of cross-plane devices, or to reduce the internal resistance of in-plane devices. So far, there have been only a few reports on thermal conductivity determination of micrometer-thick TE films, which are normally prepared by electroplating techniques. Chien et al. [23] studied the $\kappa_\perp$ of Bi-Te and Sb-Te films of several micrometers thick by using a modified parallel-strip method. The conventional MOCVD deposition of SiO_2 failed to insulate the TE film due to a large roughness of the film. As an alternative solution, they spin-coated an epoxy resin layer on the TE film to serve as the insulation layer. Schumacher et al. [24] reported the use of the non-contacting laser flash method, which is usually employed to measure bulk materials, to measure the thermal diffusivity (λ) of electroplated Bi-Te-Sb films. For this method, the TE films must be grown thick enough to be freestanding, and the density (ρ) and heat capacity (C_p) of the film need to be additionally measured to derive the thermal conductivity of the film ($\kappa_\perp = \rho C_p \lambda$).

In this work, the 3ω method is employed to determine $\kappa_\perp$ of micrometer-thick Bi_2Te_3 TE films. The TE films are prepared by controlled pulse electroplating, which is able to obtain much smoother surfaces than conventional potentiostatic or galvonostatic depositions and therefore ease the fabrication of pinhole-free measurement devices. The slope method and the differential method are separately used to determine $\kappa_\perp$ of the TE films, and the effect of the deposition pulse potential on $\kappa_\perp$ of the electroplated film is investigated. In addition, a two-wire 3ω method is used to evaluate the thermal conductivity anisotropy of Bi_2Te_3 film.

2. Experimental

2.1. Film deposition and characterization

Bi_2Te_3 films were electroplated on Au-coated Si substrates in a conventional three-electrode cell using a Pt sheet as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode [25]. The electrolyte used for deposition contains 30 mM Bi^{3+}, 40 mM $HTeO_2^+$ and 1.7 M HNO_3. The electroplating was controlled by a potentiostat (Princeton Applied Research, VersaSTAT 3F) with a pulsed deposition mode. The pulse-on potential (E_{on}) was varied from −100 mV to 50 mV while the pulse-off potential (E_{off}) was set as 200 mV. The pulse-on and off time are fixed as 0.1 s and 2.5 s, respectively, while the deposition time was altered to change the thickness of the film. All depositions were carried out at room temperature without stirring. After deposition, the samples were immediately rinsed with distilled water and ethanol for several times and then dried thoroughly with compressed N_2. The morphology of the films was observed with a field-emission scanning electron microscope (FESEM, FEI, Quanta 400F) and a desktop SEM (Phenom ProX).

2.2. Device fabrication for 3ω measurement

The devices for 3ω measurements have a multilayer structure as schematically shown in Fig. 1. First of all, a SiO_2 layer was deposited by magnetron sputtering on the Bi_2Te_3 films as well as on an Au-coated Si substrate (as a reference) in the same run. The sputtered SiO_2 layer must be thick enough to make sure that the final devices have no pinholes. Then, 1 mm (length) × 50 µm (width) lines were patterned by photolithography, followed by sputtering deposition of a Cr/Au layer (10/100 nm thick). Afterward, the Cr/Au line heaters were obtained by a lift-off process. Finally, the samples were mounted on a chip carrier by silver paste and bonded by Au wires (Φ 25 µm) for electrical measurement. Before each 3ω measurement, the electrical resistance between the top heater and the bottom electrode layer was measured by a multimeter. All the resistances were found exceeding the maximum range of the multimeter, indicating excellent electrical insulation of the sputtered SiO_2 layer.

3. Results and discussion

3.1. Cross-plane thermal conductivity (κ⊥)

$\kappa_\perp$ of the Bi_2Te_3 films are determined with the well-known 3ω method [9]. As shown in Fig. 1, when the sample is heated by applying an alternating current with angular frequency ω on the Au heater, the temperature drops across the sample device (ΔT_{total}) or the reference device (ΔT_{ref}), which oscillate at frequency 2ω, can be derived by

$$\Delta T = 2\frac{dT}{dR}R\frac{V_{3\omega}}{V_{1\omega}} \tag{1}$$

where R and dR/RdT are the electrical resistance and temperature coefficient of electrical resistance of the Au heater, and $V_{1\omega}$, $V_{3\omega}$ are the 1st and 3rd harmonic voltages. By subtracting the temperature drops in the reference device, the effective temperature drop across the TE film (ΔT_f) can be obtained by

$$\Delta T_f = \Delta T_{total} - (P_1/P_2)\Delta T_{ref} \tag{2}$$

where P_1 and P_2 are the electrical power ($P = V_{1\omega}{}^2/R$) applied on the heater of the sample device and of the reference device, respectively. Then, $\kappa_\perp$ of the film can be calculated by

$$\kappa_\perp = \frac{P_1 t_f}{Lw\Delta T_f} \tag{3}$$

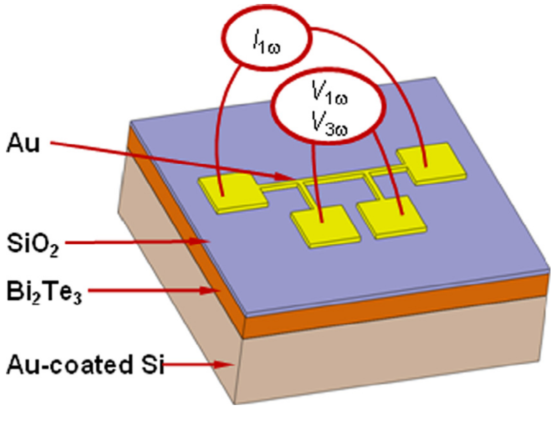

Fig. 1. Schematic of the multilayer device structure for 3ω measurements.