Multifunctional probes for high-throughput measurement of Seebeck coefficient and electrical conductivity at room temperature

Jorge García-Cañadas and Gao Min

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Multifunctional probes for high-throughput measurement of Seebeck coefficient and electrical conductivity at room temperature

Jorge García-Cañadas and Gao Min[a)]
Cardiff School of Engineering, Cardiff University, Cardiff CF24 3AA, United Kingdom

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An apparatus capable of rapid measurement of the Seebeck coefficient and electrical resistivity at room temperature is reported. The novel aspect of this apparatus is the use of 4 multifunctional probes that comprise a junction of two conductors at the tip and serve as both thermocouples and electrical contacts. In addition, one of the probes has a built-in heater that can establish a temperature gradient in the sample for the Seebeck measurement. The technique does not require special sample geometries or preparation of contacts and is suitable for bulk and thin film materials. Together with automated sample stage and data acquisition, the equipment is able to measure both the Seebeck coefficient and electrical resistivity in less than 20 s with good accuracy. Less than 5% and 4% relative errors were found for the measurement of the Seebeck coefficient and electrical resistivity, respectively. This makes the apparatus especially useful for high throughput evaluation of thermoelectric materials. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4871553]

I. INTRODUCTION

Thermoelectric materials can convert heat directly into electricity and represent a promising technology to generate electrical power from the large amount of waste heat existing in numerous applications and environments.[1] The performance of a thermoelectric material depends on the temperature difference across the material and the figure of merit Z $= \alpha^2/\rho\kappa$, where α is the Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity. The ratio α^2/ρ is usually known as the power factor. The development of new materials is focused on increasing Z and hence the determination of the three parameters that determine the figure of merit is essential. Frequently, separate equipment is needed to measure each of these quantities and is usually restricted to certain sample geometries. Although the equipment that can determine both the Seebeck coefficient and electrical resistivity with different capabilities can be found in the literature,[2–10] in most cases they involve complex setups, lengthy period of sample preparation and/or expensive equipment. Moreover, the formation of electrical and thermal contacts is sometimes required which additionally introduce more difficulties. This makes the task of characterizing thermoelectric materials more tedious, less accessible, and difficult to automate, especially when a large number of samples are needed to be screened, such as those synthesized from combinatorial methods.

In this study, we have developed a new apparatus for the high-throughput screening of the power factor at room temperature. The measurement of both the Seebeck coefficient and electrical resistivity is carried out using 4 multifunctional probes arranged as in the Van der Pauw method.[11] The new equipment can be used for different sample geometries (bulk and thin film) and the thermal and electrical contacts are easily achieved by pressure contact between the sample and the probes. Once the probes are in contact with the sample, the successive determination of α and ρ is very quick (≈20 s). To our knowledge this is the quickest measurement of both properties reported so far. In this paper, a description of the whole apparatus is first presented. Then we describe how α and ρ are obtained and finally experimental measurements are compared with well-established techniques and standard reference materials (SRM) for the evaluation of the accuracy and reliability of the equipment.

II. DESCRIPTION OF THE APPARATUS

The equipment follows a Van der Pauw setup[11] where 4 probes are contacted at the edges of the sample. Examples of similar implementation of the Van der Pauw approach can be found in the literature.[4,5,7] Differently, we have used 4 multifunctional probes, which were fabricated using a Cu tube (30 mm long and 1.6 mm diameter) and a constantan wire at the tip[12] as described in Fig. 1. The tube tip was swaged into a pencil point with a small hole in the tip. Then a constantan wire with the insulation removed from its end was threaded from the tip until the insulation bottomed out at the entrance to the hole. Finally, the constantan wire and copper sleeve were welded at the tip to form a thermocouple. In addition, a heater coil can be inserted inside the Cu tube if a "hot probe" is required. The fabrication of the probes based on our design was performed by Physitemp Instruments Inc. The tips of the probes were electroplated with Cu to ensure that the sample is always in contact with Cu. Electroplating was carried out using a brush platting pen and Cu plating solution from Technical Supermarket.

Since the Cu tube was not made of high purity Cu, this could introduce differences in the value of the Seebeck coefficient of the copper-constantan thermocouple (40.85 μV/K at 300 K).[13] In order to assess the possible deviations from this mismatch, the probe tips were immersed in stirred water heated at different temperatures by a hot plate and calibrated against a commercial K-type thermocouple. Fig. 2(a) shows

[a)]Electronic mail: min@cardiff.ac.uk

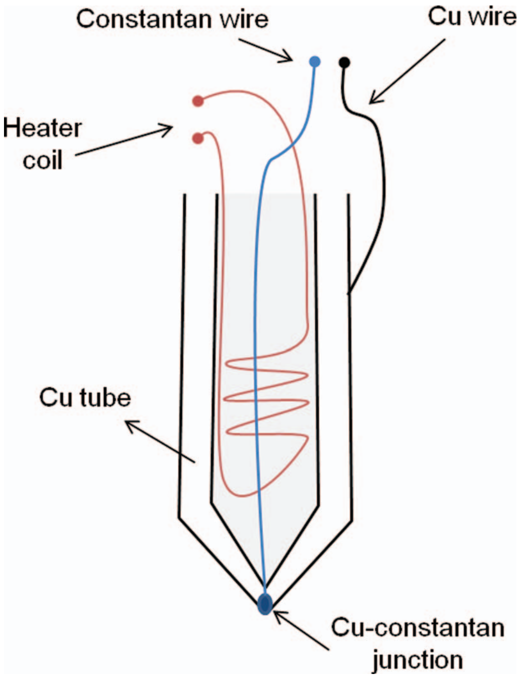

FIG. 1. Schematic diagram of the multifunctional probe with an internal heater coil.

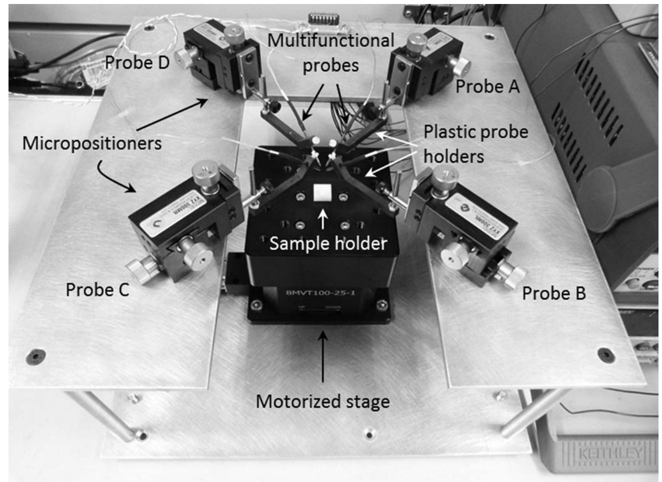

FIG. 3. The probe stage and sample holder of the novel 4-multifunctional probe apparatus.

the temperature reading from the K-type thermocouple versus the voltage output of the probe (voltage difference between Cu and constantan wires). The slope of the linear fit provides the actual Seebeck coefficient for the copper-constantan thermocouple $\alpha_{\text{Cu-con}} = 42.21\ \mu$V/K at ≈297 K, which is slightly different (1.36 μV/K) as expected. In Fig. 2(b) the temperature obtained from the multifunctional probe is calculated using the voltage output (in μV), the actual $\alpha_{\text{Cu-con}}$, and the room temperature ($T_{probe} = T_{room} + V_{output}/42.21$) and plotted versus the temperature from the commercial thermocouple. The linear fit provides origin and slope values very close to 0 and 1, respectively, proving a reliable measurement of the temperature. This calibration was performed for all probes used in the equipment and the equation provided by the linear regression (Fig. 2(b)) was used for the tip temperature calculation.

The 4 multifunctional probes were held by 4 micropositioners (Quarter Research XYZ-300-M) with custom-made plastic probe arms replacing the original metallic ones to minimize heat losses. The micropositioners were fixed to a top platform and arranged to approach the sample from 4 different directions (see Fig. 3). The use of micropositioners facilitates the movement of the probes in all directions (XYZ axes) and allows the adaptation of the apparatus to different sample geometries. The sample to be measured locates on a plastic sample holder that provides a rapid sample loading. The sample holder was fixed to a motorised stage (Altechna 8MVT100-25-1). The stage, screwed to a bottom platform (Fig. 3), can be controlled by a computer via USB and moves up and down for sample loading/unloading.

In order to provide all the necessary currents to the different elements (probes and heater) with a single power source,

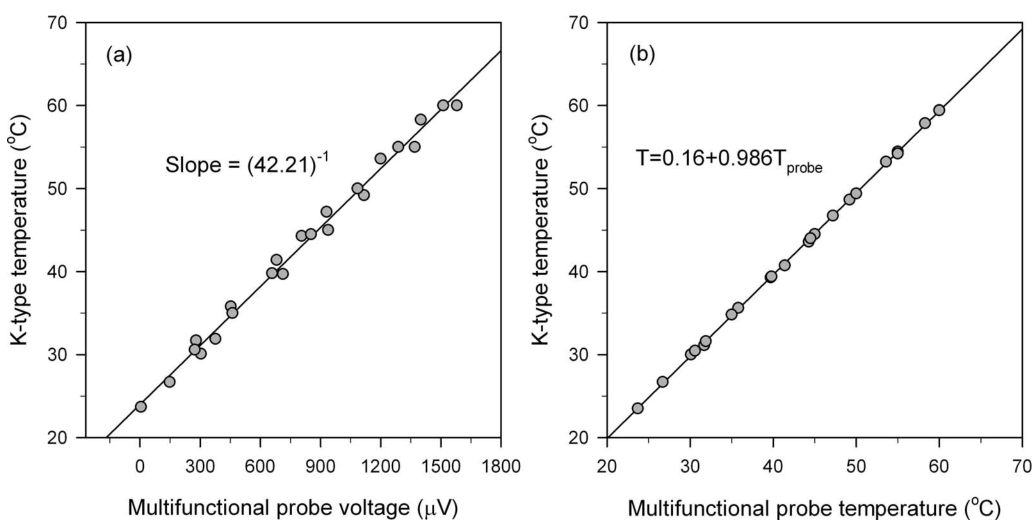

FIG. 2. Temperature from a commercial K-type thermocouple vs. voltage output of the multifunctional probe (a). The slope obtained (42.21 μV/K) was used for the calculation of the multifunctional probe temperature in (b). Lines show good linear fit to the results. The equation from the fit in (b) was used to calculate the probe tip temperature.

a triple channel DC power supply (Keithley 2230-30-1) was employed. It was connected to the computer by USB connection for automatic control. A multimeter (Keithley 2000) was used to measure resistance and all the voltage outputs. It was connected to the computer by a GPIB to USB adaptor. For the rapid switching of the current outputs and voltage readings a USB 16 channel relay module (Denkovi DAE-CB/Ro16/Di4-USB) with remote control via USB was used. All the equipment and measurement procedures were controlled using LabView 2011 in a PC. This allows a fully automated system that is able to perform all the measurement routines.

III. MEASUREMENT PROCEDURES

A. Measurement of the Seebeck coefficient

The relative Seebeck coefficient α between the sample and probes can be obtained by measuring the open-circuit voltage ΔV that is produced across a material when a small temperature difference ΔT is applied to it,

$$\alpha \equiv \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}. \tag{1}$$

It should be noted that the voltage measurement has to be taken at the same points where the temperature difference is measured. In our apparatus, this was achieved by contacting two of the multifunctional probes (probe A and probe D) to the sample. A current was supplied to the heater coil of probe A in order to achieve a temperature of ∼3 K higher than that of probe D, the temperature of which usually remained close to room temperature. Once the ΔT was established, the temperature at the probes' tips was measured as explained above for the determination of ΔT. The open-circuit voltage ΔV between the two probes was measured using a multimeter and finally the Seebeck coefficient of the sample α_s was calculated using

$$\alpha_s = \frac{\Delta V}{\Delta T} + \alpha_{\mathrm{Cu}}, \tag{2}$$

where α_{Cu} is the absolute Seebeck coefficient of Cu. For high purity Cu, the absolute Seebeck coefficient is reported to be 1.84 μV/K.[14] However, since the Cu tube employed in this study is less pure, an appropriate value for Eq. (2) is α_{Cu} = 3.2 μV/K, which was determined from the experimental results of Fig. 2(a).

In order to evaluate the accuracy of the measurements, the developed equipment was calibrated against a well-established hot probe apparatus and the reference Bi_2Te_3 material from NIST. Three samples with Seebeck coefficients in different ranges were used which include a *p*-type Bi_4SnTe_7 alloy, an *n*-type $GeBi_4Te_7$ and an *n*-type Bi_2Te_3 SRM from NIST (Ref. 3451). The values measured using both techniques are shown in Table I, together with the standard deviations and the relative errors determined from a set of 10 measurements. A low standard deviation indicates good repeatability of the measurements, while small relative errors (less than 2%) demonstrate a good agreement between the developed apparatus and the hot probe. The systematic error of the developed equipment can be estimated by directly comparing

TABLE I. Comparison of Seebeck coefficient values obtained with the 4-multifunctional probe and the hot-probe technique used as reference. A good accuracy is indicated by the standard deviations and the relative error respect to the reference (hot-probe) value.

Sample	Hot probe value (μV/K) ± st. dev.	4-multifunctional probe value (μV/K) ± st. dev.	Error (%)
p-type Bi_4SnTe_7	105.85 ± 0.76	106.21 ± 0.82	0.34
n-type $GeBi_4Te_7$	− 139.43 ± 4.46	− 138.15 ± 1.29	0.92
n-type Bi_2Te_3 SRM	− 223.77 ± 0.99	− 220.02 ± 1.15	1.63

the measured value for the SRM (−220.02 μV/K) with the standard reference value (−230.69 μV/K) provided by NIST. A relative error of 4.4% is obtained, which provides sufficient accuracy for the purpose of high-throughput evaluation of TE materials.

B. Measurement of electrical resistivity

The electrical resistivity was measured using the Van der Pauw method,[11] where 4 multifunctional probes (probes A, B, C, and D) were contacted at four different points on the perimeter of the sample. The electrical contact was ensured by checking the resistance between the probes, which change from infinite to a small value when the contact is achieved. A constant DC current was established between two probes and the voltage induced at the other two probes was measured. For example, a current I_{AB} entered the sample through probe A and left from probe B, generating a voltage $V_{CD} = V_C – V_D$ between probes C and D. A resistance $R_{AB,CD} = V_{CD}/I_{AB}$ was then obtained. In order to minimise the possible errors raising from thermoelectric effects, the direction of the current was changed and $R_{BA,DC} = V_{DC}/I_{BA}$ was calculated. Since the thermoelectric voltages can be cancelled out, probe A (with a heater coil inside) can remain hot during the electrical resistivity measurement. This avoids the need to wait for the probe to cool down and/or heat up between the measurements of the Seebeck coefficient and electrical conductivity. Consequently, a significant gain in the rapidness of the process was achieved. By switching the current applied to probes C and D and measuring the voltage in probes A and B, we obtain in the same way $R_{CD,AB}$ and $R_{DC,BA}$. Averaging these 4 resistances gives $R_A = (R_{AB,CD} + R_{BA,DC} + R_{CD,AB} + R_{DC,BA})/4$. Similarly, $R_B = (R_{BC,AD} + R_{CB,DA} + R_{AD,BC} + R_{DA,CB})/4$ was also calculated. Both R_A and R_B are required to determine the sheet resistance R_S by

$$\exp\left(-\pi R_A/R_S\right) + \exp\left(-\pi R_B/R_S\right) = 1. \tag{3}$$

Finally, the electrical resistivity is given by

$$\rho = R_s d, \tag{4}$$

where d is the sample thickness. Equation (3) can only be solved analytically when $R_A = R_B$. For the rest of the cases, it has to be solved numerically. This is achieved by implementing the iteration algorithm given by NIST[15] in LabView.

To prove the reliability of the system, a disc-shaped austenitic stainless steel SRM from the National Bureau of

TABLE II. Comparison of electrical resistivity measured using the 4-multifunctional probe and the reference value of the stainless steel SRM and the measured value using 4-probe technique for the *n*-type $GeBi_4Te_7$. The standard deviations and the relative errors respect to the reference values are indicated.

Sample	Reference value (Ω cm) ± st. dev.	4-multifunctional probe value (Ω cm) ± st. dev.	Error (%)
Stainless steel (SRM)	8.09×10^{-5}	$7.90 \times 10^{-5} \pm 0.031 \times 10^{-5}$	2.42
n-type $GeBi_4Te_7$	$2.30 \times 10^{-3} \pm 0.025 \times 10^{-3}$	$2.39 \times 10^{-3} \pm 0.0084 \times 10^{-3}$	3.96

Standards (NBS, Ref. 1461) and the same *n*-type $GeBi_4Te_7$ disc sample used above for the Seebeck coefficient evaluation (with ρ value typical of thermoelectric samples) were measured. All the measurements were carried out keeping probe A hot. The values obtained were compared with the reference value from NBS and the results using a commercial 4-probe apparatus, respectively. Table II shows the comparison and the standard deviations (from a set of 10 measurements) and relative errors which are less than 4%.

The results shown in Tables I and II demonstrate the capability of the apparatus with good accuracy. In addition, we would like to highlight a main advantage of this facility, which lies in the rapidness of the measurements. In fact, once you contact the sample with the 4 probes, it only takes around 20 s to determine both the Seebeck coefficient and electrical resistivity consecutively. When the samples have the same dimension, there is no need to reposition the probes (which can take 1 or 2 min). The contacts to the next sample can be made very quickly by placing the sample in the sample holder and elevating it with the motorised stage. Additionally, the use of plastic arms in the micropositioners with optimal contacting angle provides the flexibility of measuring the samples of different geometries and avoids the need to use solders or conductive paints to achieve satisfactory contacts with the sample.

IV. CONCLUSIONS

We have developed a new high-throughput apparatus for determination of the thermoelectric power factor. The key innovative aspect of this apparatus is the use of 4 multifunctional probes which incorporate thermocouples and heaters into the conventional Van der Pauw method. Measurement procedure and algorithm are controlled using LabView that facilitates automated determination of both the Seebeck coefficient and electrical resistivity in around 20 s. The measurements performed have been compared with well-established techniques and reference materials. A very good agreement was found for the measurement of the Seebeck coefficient with less than 5% relative errors. For electrical resistivity the relative errors are less than 4%. In addition to the rapidness of the measurements, the apparatus can be used with samples of different geometries (bulk and thin films) and do not require the complex and time-consuming formation of contacts. This makes the equipment very useful when the quick screening of the power factor is required.

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