Efficient thermoelectric van der Pauw measurements

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The development of powerful thermoelectric materials requires fast and simple characterization techniques. We combine three measurements to obtain a complete thermoelectric characterization. The electrical conductivity is measured by the van der Pauw method, while ZT is determined directly by means of a Harman measurement. Finally, exploiting the analogy between electrical and thermal physics, a thermal van der Pauw measurement is performed and the sample Seebeck coefficient and thermal conductivity can be determined. No temperature differences need to be measured; all quantities can be deduced from voltage measurements concurrently on the same sample which allows for quick and convenient material screening. © 2011 American Institute of Physics. [doi:10.1063/1.3609325]

Thermoelectric materials can convert heat into electricity and can thereby increase the energy efficiency of combustion engines or fuel cells. They can furthermore be used in thermoelectric converters to power sensors by using omnipresent small temperature gradients available in their near environment, thereby saving batteries or electrical wiring.

The conversion efficiency of a thermoelectric material is determined by its figure of merit $ZT$

$$ZT = \frac{S^2 \sigma T}{\kappa},$$

where $S$ is the Seebeck coefficient, $\sigma$ and $\kappa$ are the electrical and the thermal conductivity, respectively, and $T$ is the absolute temperature. Significant progress has been made in developing superior thermoelectric materials by nanostructuring of the material. However, for most applications, macroscopic material quantities are necessary and bulk characterization techniques are employed. The optimization of thermoelectric materials requires repeated characterization of the material, i.e., measurement of $S$, $\sigma$, and $\kappa$. It is highly desirable to measure all these properties simultaneously on a single sample in order to avoid problems with material inhomogeneities or material changes due to thermal cycling.

We have recently presented a powerful approach for a complete thermoelectric characterization on a single sample to address these issues. One drawback of that approach is the necessity to measure temperature differences. We have therefore developed the method further and want to present here a more efficient approach for a complete thermoelectric characterization that does not require the measurement of temperature differences.

Our method consists of three measurements and is based on the established van der Pauw technique for electrical characterization. As can be seen in Figure 1, the sample is equipped with four electrical contacts $E_1$ to $E_4$. Driving a current from $E_2$ to $E_1$ and measuring the potential difference between $E_4$ and $E_3$ give the 4-point resistance $R_{21,43} = U_{43}/I_{21}$; similarly $R_{31,42} = U_{42}/I_{31}$ can be obtained. Inserting these two values into the van der Pauw equation

$$\exp(-\pi \sigma d R_{21,43}) + \exp(-\pi \sigma d R_{31,42}) = 1$$

(2)
gives the electrical conductivity of the sample, provided that the sample thickness $d$ is known. The van der Pauw method requires a homogeneous sample which is free from holes and has a constant thickness, otherwise it can have an arbitrary geometry. Note also that the electrical contacts can be at an arbitrary position of the sample circumference.

The second measurement exploits the fundamental analogy between thermal and electrical transport. Provided that the parasitic heat losses are small, the van der Pauw measurement concept can be transferred to a thermal measurement and the thermal equivalent of the electrical van der Pauw equation is given by

$$\exp(-\pi \kappa d R_{21,43}^{th}) + \exp(-\pi \kappa d R_{31,42}^{th}) = 1.$$  

(3)

As discussed in Ref. 7, $\kappa$ can be obtained if $R_{21,43}^{th} = \Delta T_{33}/P_{21}$ and $R_{31,42}^{th}$ are determined by a measurement of

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the heat flow $P$ and the temperature difference $\Delta T$. However, compared to electrical measurements, temperature measurements can be much more challenging. They require the use of thermometers that can be accurately calibrated; the thermometers furthermore have to be in good thermal contact with the sample to guarantee accurate measurements. Using a different approach, we will show that all thermoelectric quantities can be obtained by pure electrical measurements, i.e., without the necessity to measure temperature differences. As presented in Figure 1, the sample is equipped with two heaters $H_2$ and $H_3$, and is in thermal contact to the environment via the heat sink $H_1$. Heat production in $H_2$ causes a heat flow $P$ from $H_2$ to $H_1$. A temperature difference between $E_4$ and $E_3$ is established which in turn causes a Seebeck voltage $U_{S,43}$ that can be measured. Using $R_{21,43}^{th} = \Delta T_{43}/P_{21} = -U_{S,43}/(SP_{21})$ and performing a second measurement with $H_3$ as heater to obtain $R_{31,42}^{th} = -U_{S,42}/(SP_{31})$, Eq. (3) can be rewritten as

$$\exp\left(+\pi d \kappa U_{S,43}^{\kappa} S P_{21}^{\kappa}\right) + \exp\left(+\pi d \kappa U_{S,42}^{\kappa} S P_{31}^{\kappa}\right) = 1. \quad (4)$$

Solving this equation gives the ratio of $\kappa$ and $S$ if $U_S$ and $P$ are measured experimentally.

In a third step, the electrical contacts are used to directly determine $ZT$ by means of a four-point Harman measurement$^{7,10,11}$

$$ZT = \frac{U_{DC} - U_{AC}}{U_{AC}}. \quad (5)$$

Using the obtained values for $\sigma$, $ZT$, $\kappa/S$, and the definition of $ZT$ (Eq. (1)), the sample thermal conductivity and Seebeck coefficient can be calculated. The sample material is then fully characterized.

In order to prove the applicability of the proposed approach, we characterized an InSb sample of $10 \text{mm} \times 10 \text{mm} \times 1.07 \text{mm}$. The charge carrier concentration and mobility were found to be $2.6 \times 10^{16} \text{cm}^{-3}$ and $6.8 \times 10^4 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, at $310 \text{K}$ using a physical property measurement system (PPMS) (Quantum Design, Inc., USA). Small resistors ($1.6 \text{mm} \times 1.2 \text{mm}$, IST, Switzerland) were used as heaters and glued on the side faces of the sample. For accurate measurements, it is indispensable that the electrical contacts and the heaters are at the same positions. We therefore glued the heaters with conductive silver paste onto the sample and used the paste as electrical contact as indicated in Figure 1. Note that the heater circuits are nevertheless insulated from the sample.

Mechanical, thermal, and electrical contacts from the heat sink to the sample are provided by a copper clamp. All measurements were performed in high vacuum $p < 5 \times 10^{-6}$ mbar in a setup as described in Ref. 7. Electrical contacts from the sample to electrical feedthroughs are made using thin copper wires ($d = 30 \mu\text{m}$, $l \approx 5 \text{cm}$). The heaters were connected to a power source using Ni wires ($d = 70 \mu\text{m}$, $l \approx 4 \text{cm}$). The heat sink and sample temperature were adjusted using a Lakeshore 332 temperature controller. In order to create a temperature gradient across the sample, the heaters were supplied with electrical power in the range of $1\text{–}10 \text{mW}$ which resulted in Seebeck voltages of $\approx 10^{-5} \text{V}$.

The results for the InSb sample are displayed in Figure 2. The red circles show the results of the presented measurement scheme, while the black lines represent a fit to reference data from Busch and Steigmeier. For further validation, a complete characterization was performed on the same sample using the method described in Ref. 7. The result of this measurement is indicated by blue crosses. As can be seen in Figures 2, the agreement between the measured data and the reference data is better than 5%; the agreement with the control measurement is excellent as well. Figure 2(d) compares the result of the direct $ZT$ measurement (Eq. (5)) with the $ZT$ obtained from the combination of the control measurement results for $\sigma$, $\kappa$, and $S$, the agreement between both is better than 10%.

Measurement errors for $\sigma$ arise due to the finite size of the contacts and uncertainties in the sample thickness. It can...
be shown that these errors can be kept well below 3%.\textsuperscript{13} Since the measurements of $ZT$ and $\kappa/\sigma$ are based on the establishment of a steady-state temperature gradient, they are affected by parasitic heat loss through the electrical connections and by radiation. These errors can be minimized by heat shielding and appropriate sample geometry as discussed in Refs. 7 and 14. For the measured sample, these effects sum up to $\approx 5\%$ at 310 K and 11\% at 410 K. Thermal contact resistances between heater and sample can be neglected as long as they are small compared to the thermal resistances of the connecting wires.

The Seebeck coefficient is calculated from Eq. (1) and the measurement results for $ZT$ and $\kappa/\sigma$. Radiation losses cause a measurement result for $ZT$ that is systematically too small, while $\kappa/\sigma$ is measured too large. Since $S$ is obtained from the product of both, $S$ is unaffected by radiation losses. Uncertainties in $S$ arise due to imperfect alignment of heaters and electrical contacts and are within 5\%. The relative error for the thermal conductivity increases from 8\% at 310 K to 14\% at 410 K and is the sum of the errors due to heat loss, finite-sized contacts, and thickness uncertainties.

The $ZT$ of the control measurement is calculated from the control measurement results for $\sigma$, $S$, and $\kappa$. Its relative error is therefore the combined error of the individual measurements minus systematic errors which affect $\sigma$ and $\kappa$ equally. The relative error increases from 15\% at 310 K to 21\% at 410 K and is significantly larger than the uncertainty for the directly measured $ZT$.

One should be aware that measured quantities $ZT$ and $\kappa/\sigma$ correspond to the material couple formed by the sample and the wire. The sample parameters $S_S$ and $ZT_S$ can be extracted from the measured quantities $\kappa/\sigma_S$ and $ZT_S$ using

$$ S_S = \frac{ZT_S}{\sigma T_S} \frac{\kappa}{\sigma_S} + S_W, \quad (6) $$

$$ ZT_S = ZT_S (S_S/\sigma_S)^2, \quad (7) $$

where the subscript $W$ indicates the wire. Please note that the correction term in Eq. (7) enters squared in contrast to what has been published previously.\textsuperscript{7} These corrections have been employed for the data shown. Using copper wires ($S_{Cu} \approx 2 \, \mu V K^{-1}$), the corrections are of the order of 1\%.\textsuperscript{15}

We have presented a measurement concept for a complete thermoelectric characterization. Based on the electrical van der Pauw method, a four-point Harman $ZT$ measurement and the fundamental analogy between electrical and thermal physics, our method allows concurrent determination of $\sigma$, $S$, $\kappa$, and $ZT$ on a single sample. In contrast to other methods,\textsuperscript{16} the proposed approach does not require a specific sample geometry except for a homogeneous thickness and a sample free from holes. Our approach avoids troublesome temperature measurements. This offers the possibility to couple the heat contactless into the sample, e.g., by local radiation heating or inductive coupling.\textsuperscript{11} In this case, only the electrical contacts are required to be physically attached to the sample. This can speed up sample preparation further and brings fully automated measurements for efficient material optimization into reach.

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