Complete Characterization of Thermoelectric Materials by a Combined van der Pauw Approach

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Most of the world’s power and mobility is provided by using fossil fuels, and large amounts of heat are dissipated uselessly. Thermoelectric materials can convert waste heat directly into electrical power and represent an important contribution to lessen energy scarcity. The search for materials with improved thermoelectric properties, however, requires simple and efficient characterization methods.\textsuperscript{[1–4]} Here we present a novel approach for a complete thermoelectric characterization, by which all relevant quantities, like the electrical conductivity, the thermal conductivity, the Seebeck coefficient, and the figure of merit, can be determined directly. The method is inherently insensitive to electrical and thermal contact resistances. It is easy to implement, and does neither require extensive sample preparation nor sophisticated equipment.

The efficiency of a thermoelectric material is to first order proportional to the dimensionless thermoelectric figure of merit \(ZT\):\textsuperscript{[5]}

\[
ZT = \frac{S^2\sigma T}{\kappa}.
\]

with \(S\) being the Seebeck coefficient, and \(\sigma\) and \(\kappa\) being the electrical and thermal conductivity, respectively. \(T\) denotes the absolute temperature. One way of determining the figure of merit \(ZT\) is to measure \(S\), \(\sigma\), and \(\kappa\) separately and calculate \(ZT\) using Equation (1).\textsuperscript{[6]} Alternatively, \(ZT\) can also be measured directly by the Harman method.\textsuperscript{[7]} In this letter we will demonstrate that an approach by van der Pauw for electrical characterization\textsuperscript{[8]} can be generalized to characterize the thermal properties of materials. By combining electrical and thermal van der Pauw measurements, \(S\), \(\sigma\), and \(\kappa\) can be determined concurrently using the same setup. Though seemingly trivial, the extreme usefulness of such a combined van der Pauw approach, especially for the characterization of thermoelectric materials, has not been recognized so far.

Furthermore we show that in addition to determining the individual quantities \(S\), \(\sigma\), and \(\kappa\), the setup can also be used to directly measure \(ZT\) via the Harman method. Such a direct \(ZT\) measurement complements the measurements of \(S\), \(\sigma\), and \(\kappa\) and is useful to cross-check the validity of the measurements. All measurements are true four-point measurements, so that their outcome is insensitive to electrical and thermal contact resistances.

The physics of electrical and thermal problems is very similar. In the same way as an electrical potential difference \(U\) induces an electrical current \(I\), a temperature difference \(\Delta T\) induces a thermal current \(P\). Due to this correspondence, some electrical characterization techniques can be adapted to measure thermal properties. In 1958 van der Pauw proposed a method for measuring the electrical conductivity of materials. This method, the van der Pauw method, became a standard technique for electrical characterization.\textsuperscript{[8]} Van der Pauw showed that the electrical conductivity can be obtained from two four-point resistance measurements (see Figure 1a), a current \(I_{2}\) is driven from contact \(E_2\) to contact \(E_1\) and the potential difference \(U_{13}\) between the other two contacts is measured. This gives \(R_{13,43} = U_{13}/I_{2}\). The second resistance, \(R_{11,42} = U_{11}/I_{1}\), is obtained by driving a current from \(E_1\) to \(E_2\) and measuring the voltage between \(E_2\) and \(E_3\). Knowing the thickness \(d\) of the sample, \(\sigma\) can then be obtained by solving the van der Pauw equation:

\[
\exp(-\pi d R_{11,42}) + \exp(-\pi d R_{13,43}) = 1.
\]

To a good approximation this equation is valid, if the sample is homogeneous and free of holes, if the size of the electrical contacts is small with respect to the sample size, if the thickness is small compared to the distance between contacts and if the contacts are located at the edge of the sample.\textsuperscript{[9–11]}

Due to the analogy of electrical and thermal problems, the van der Pauw approach can also be used to determine the thermal conductivity \(\kappa\) of materials. Although seemingly trivial, there exists to the best of our knowledge only publications by a single group wherein such a thermal van der Pauw measurement has been demonstrated.\textsuperscript{[9–11]}

The thermal van der Pauw method can best be explained by considering a sample in thermal contact (in a thermal sink) with a heat sink, and equipped with three resistance heaters/thermometers \((H_1, H_3, H_4)\), see Figure 1c. These resistance heaters/thermometers serve the double purpose of either acting as heaters (by converting supplied electrical power into Joule heat) or as thermometers (by measuring their resistance). The main difference between the electrical and the thermal van der Pauw approach lies in the fact that instead of an electrical current \(I\) a thermal current \(P\) is driven through the sample and that instead of an electrical potential difference \(U\) a temperature difference \(\Delta T\) is measured.

The arrangement shown in Figure 1c is the thermal equivalent to the electrical configuration of Figure 1a. Using \(H_1\) as a resistance heater causes a thermal current \(P_{21}\) to flow from \(H_2\) to the heat sink \(H_1\). As \(H_1\) is the only thermal contact of the sample,
characterization of thermoelectrical materials as \( \sigma \) and \( \kappa \) are two of the three key thermoelectric parameters. To combine the approaches the sample must be additionally equipped with four electrical contacts \( E_1 - E_4 \), see Figure 1c. The contact \( E_i \) can be realized by connecting the sample both thermally and electrically to the heat sink. \( \sigma \) can then be determined by the van der Pauw method.

If only the electrical and thermal conductivity were of interest, the actual positions of \( E_1 - E_4 \) could be chosen arbitrarily with respect to \( H_1 - H_4 \). However, if the electrical contacts \( E_1 - E_4 \) are placed at the same lateral position as \( H_1 - H_4 \) (see Figure 1c) the Seebeck coefficient \( S \) can be determined directly, as discussed below. Whether the contacts are placed on the top or the bottom side of the sample is irrelevant as the van der Pauw equation only considers the lateral potential distribution.

The fact that a temperature difference across a material gives rise to an electrical potential difference was first observed by T. J. Seebeck. The coupling factor between potential and temperature difference is the Seebeck coefficient \( S \), one of the quantities that constitute \( ZT \). In our setup, \( S \) can easily be measured. To determine \( \kappa \), one has to measure the two temperature differences \( \Delta T_1 \) and \( \Delta T_2 \), as discussed above. If in addition also the two corresponding voltages \( U_{14} \) and \( U_{24} \) are measured, the Seebeck coefficient \( S \) is directly at hand:

\[
S = -\frac{U_{14}}{\Delta T_{14}} = -\frac{U_{24}}{\Delta T_{24}}
\]

The circumstance that two measurement values for the Seebeck coefficient can easily and independently be obtained, is a clear advantage of the design. As one can see from Equation (1), \( ZT \) shows a quadratic dependence on \( S \), wherefore a precise determination of the Seebeck coefficient is of utmost importance.

It has been shown so far how the three key parameters \( \sigma \), \( \kappa \) and \( S \) can be determined. From these the figure of merit \( ZT \) can be calculated using Equation (1), which in principle suffices for a complete thermoelectric characterization. However, using our proposed design, \( ZT \) can also be determined directly via the Harman method.

Driving an electrical current through a thermoelectric material generally causes two effects. First, due the ohmic resistance of the material, an electrical potential difference arises, which is proportional to \( 1/\sigma \). In addition, the electrical current also creates a temperature gradient (Peltier effect), which in turn gives rise to an additional voltage drop (Seebeck effect). This purely thermoelectric contribution is proportional to \( TS^2/\kappa \). Fortunately, both contributions need different times to become fully effective. While the ohmic voltage drop arises quasi instantaneously, the thermoelectric contribution for macroscopic samples typically needs seconds to build up. Consequently, measuring the AC resistance \( R_{AC} \) at sufficiently high frequency only detects the ohmic resistance, whereas the DC resistance \( R_{DC} \) reflects both the ohmic and the thermoelectric response. For a thermoelectric sample AC measurements are therefore necessary for the determination of \( \sigma \) by Equation (2). Subtracting \( R_{AC} \) from \( R_{DC} \) yields the pure thermoelectric contribution and division by \( R_{AC} \) then gives \( ZT \).
By driving an AC and DC current from $E_2$ to $E_1$ and measuring the voltage $U_{33}$, one obtains the resistances $R^{AC}_{21,43}$ and $R^{DC}_{21,43}$, respectively, giving

$$ZT = \frac{R^{DC}_{21,43} - R^{AC}_{21,43}}{R^{AC}_{21,43}}$$

While the individual AC and DC resistances depend on the geometry of the contact arrangement, this geometrical factor cancels out since $ZT$ is given by a ratio of two resistances. Similar to the measurement of the Seebeck coefficient, also the Harman method can be performed for two configurations, giving two measurement values for $ZT$ (see Equation (5)). If $ZT$ is measured in the usual 2-terminal fashion contact resistances may affect the measurement and complicate the analysis. Here $ZT$ is measured in a true four-point manner, so that contact resistance problems are circumvented. Determining $ZT$ via the Harman method is simple, fast and especially useful if combined with measurements of $\sigma$, $S$, and $\kappa$ in order to cross-check the $ZT$ calculated from Equation (1) with the Harman $ZT$.

In order to prove the feasibility of the proposed combined van der Pauw approach, we tested the method on two different materials, Ni and InSb: Ni, because it is a standard reference material and InSb, because it has reasonably good thermoelectric properties.\(^{15,16}\)

As resistance heaters/thermometers, commercial Pt1000 temperature sensors (size 1.2 $\times$ 1.6 mm Innovative Sensor Technology AG; Switzerland) were used. All electrical wiring was realized using thin metal wires (diameter of 0.05–0.07 mm). The measurements of the Seebeck coefficient as well as the Harman $ZT$ measurements were corrected for the Seebeck voltage of the wire material. The temperature displayed in Figure 2 and 3 corresponds to the temperature of the heat sink. All measurements were performed in vacuum at a pressure lower than 5 x $10^{-4}$ mbar. Further experimental details are given in the supporting material.

The complete temperature-dependent thermoelectric characterization of pure Ni is shown in Figure 2. As can be seen, the electrical conductivity data (see Figure 2a) accurately reproduces the results of Busch et al.\(^{17}\) The measured Seebeck coefficient (Figure 2b) is the mean of the two measurements, as explained above. The data agree well with the reference data of Ref.\(^{21}\) This also holds for the thermal conductivity of Ni, see Figure 2c. Figure 2d shows the $ZT$ of Ni, calculated from the measurement data and the fits through the reference data shown in Figure 2a-c. One can see that also $ZT$ is in good agreement with the reference data. Due to the small Seebeck coefficient and low $ZT$, a complete thermoelectric characterization is challenging. Nevertheless, the results (Figure 2) prove that a complete thermoelectric characterization by the proposed approach is well feasible.

In Figure 3, the temperature-dependent thermoelectric characterization of basically intrinsic InSb is presented. The charge carrier concentration of the InSb wafer was specified as 1 – 1.5 x $10^{15}$ cm$^{-3}$ (at 77 K) by the supplier (Firebird Inc. Canada), which corresponds to about 3 x $10^{17}$ cm$^{-3}$ at room temperature.\(^{22}\) Figure 3a shows the measured electrical conductivity together with reference data from Busch et al.\(^{21}\) The data

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**Figure 2.** Temperature-dependent thermoelectric characterization of Ni (purity 99.98%, sample size $20 \times 10 \times 0.25$ mm). a) Measured electrical conductivity $\sigma$ and reference data.\(^{17}\) b) Mean measured Seebeck coefficient $S$ and reference data.\(^{17}\) c) Measured thermal conductivity and reference data.\(^{18–20}\) d) Measurement $ZT = \sigma S^2 T / \kappa$ obtained using the measurement results of a–c, and reference $ZT$ computed using the polynomial fits shown in (a–c).
sets show the same trend but do not agree exactly. However, as the electrical conductivity of a semiconductor, and especially for such a high mobility material like InSb, does critically depend on the specific impurity concentration, some variation between different “intrinsic” samples can be expected. The measured Seebeck coefficient (Figure 3b) agrees within ±10% with the reference data. As presented in Figure 3c also the agreement between measured thermal conductivity and reference data is better than 10%. Using the data of Figure 3a–c, ZT was computed for the reference and the measurement data (Figure 3d). Summing up the errors of the individual measurements leads to an overall error of the calculated ZT of 40%. In order to cross-check the validity of the calculated ZT value, also a four-point Harman measurement was performed. The data (red triangles Figure 3d) represent the mean of two separate Harman measurements. The error of this directly determined ZT value was estimated to be about 15%. The results are consistent with the ZT calculated from both the measurement data and the reference data of Figure 3a–c.

There are two types of errors related to the proposed method. The first type of errors is due to the non-ideal sample/contact geometry, as the van der Pauw equations are exactly valid only for infinitely small contacts placed at the edge of an infinitely thin sample. Errors due to finite sample thickness, finite contact size, and misplaced contacts have been investigated by different groups.\cite{8,23,24} It turns out that the van der Pauw method is quite robust. Weiss et al. found that for a square sample of side length a the relative error of the conductivity is less than 2% if the sample thickness d is less than a/2; that the error due to the contact size δ is smaller than 1% if the contacts are smaller than a/10; and that contacts placed at a distance <a/10 from the sample edge result in an error of <0.1%.\cite{25} Thus for typical sample geometries measurement accuracy is not severely affected. Furthermore, correction factors for various sample and contact geometries can be found in the literature.\cite{8,23,24}

For our measurements the total correction would be less than 1% and was therefore neglected.

The second type of errors arises from the fact that the thermal van der Pauw method – except for coupling to the heat sink – requires perfect thermal insulation. Thus unwanted heat transfer through the gas phase, through the electrical wiring, and by radiation contribute to the overall error. Of those, heat transfer through the gas is least severe and at pressures smaller 10⁻¹⁰ mbar the amount of transferred heat is negligible. With

Figure 3. Temperature-dependent thermoelectrical characterization of intrinsic InSb, sample size 10 × 10 × 0.5 mm. a) Measured electrical conductivity, b) mean measured Seebeck coefficient, and c) measured thermal conductivity compared to reference data.\cite{21} d) Comparison of the ZT = \( \sigma S T / \kappa \) calculated from measurement data shown in a-c (dark grey diamonds), reference data shown in a-c (black), and ZT directly determined via the Harman method (light grey triangles).
typical pressures of $\approx 2 \times 10^{-6}$ mbar we performed the measurements well below this limit.

Heat losses through the electrical wiring are more critical. Consider a square sample with heat sink, heater, and thermometers placed symmetrically on the middle of the sample sides, then, from solving the Laplace equation in 2D one can find that the temperature difference $\Delta T$ between heater and heat sink is related to the applied heating power $P$ approximately like

$$P = \frac{\pi \kappa d}{2 \ln(2a/d)} \Delta T. \quad (6)$$

Assuming that $\Delta T$ also corresponds to the temperature difference between both ends of the wires (which overestimates heat losses, since only some of the wires are connected to the heater), then the corresponding heat loss through the wires is given by

$$P_{\text{wire}} = \frac{n w \pi r_{w}^{2}}{l_{w}} \Delta T. \quad (7)$$

where $\kappa$, $r_{w}$, and $l_{w}$ are thermal conductivity, radius, and length of the $n$ wires. Considering the InSb measurement ($a = 1 \text{ cm}$, $\delta = 1.2 \text{ mm}$, $\kappa = 17 \text{ Wm}^{-1} \text{K}^{-1}$, $d = 0.5 \text{ mm}$) for which 70 $\mu$m thick Ni wires were employed, one can find that the heat loss through the wiring corresponds to about 2% of the heating power. For the Ni sample (using 50 $\mu$m thick Cu wires) the relative heat loss amounts to 2% as well.

For estimating the heat transfer via radiation let us consider a sample shielded by a heat shield (emissivity 1) held at the temperature of the heater, then the heat loss from the sample can be estimated as

$$P_{\text{rad}} = 4 \varepsilon \sigma T_{s}^{4} \Delta T, \quad (8)$$

where $\varepsilon$, $T_{s}$ are the Stefan-Boltzmann constant, the emissivity of the sample, and the temperature of the heat sink. In case of the InSb measurement, assuming $\varepsilon \approx 0.6$, heat losses through radiation amount to about 9% of the applied heating power. For the Ni sample radiation losses are 1% below. In general, radiative losses are more critical at higher temperatures and for materials with lower thermal conductivity, but can be compensated by reducing sample size or by improving radiation shielding.

In conclusion we have presented a combined electrical and thermal van der Pauw approach for a complete characterization of thermoelectric samples. Using this approach all three thermoelectric key parameters $\sigma$, $S$ and $\kappa$ can be measured concurrently in the same setup. We furthermore showed that the setup can also be used to directly measure $ZT$ via the Harman method. The presented method employs four-point electrical and thermal measurements, thereby avoiding problems with thermal and electrical contact resistances. It has been successfully tested by performing measurements on Ni and InSb. In distinct contrast to other characterization methods,[26–29] our approach does neither require specialized equipment nor time-consuming sample preparation.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
We are grateful to Mr. D. Hagen, Dr. M. Alexe, and the mechanical workshop staff for their assistance, as well as to the joint Fraunhofer Max-Planck project nanoSTRESS and the BMBF Project PoSiTeM (01X3539A) for financial support. We are also deeply indebted to our late director, Prof. Gösele, for support and spirit.

Note: An error was noticed in Equation (5) after Early View publication. The article has been updated with this corrected version.

Received: May 5, 2010
Revised: May 25, 2010
Published online: July 12, 2010