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Measurement of the high-temperature Seebeck coefficient of thin films by means of an epitaxially regrown thermometric reference material

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The Seebeck coefficient of a typical thermoelectric material, silicon-doped InGaAs lattice-matched to InP, is measured over a temperature range from 300 K to 550 K. By depositing and patterning a thermometric reference bar of silicon-doped InP adjacent to a bar of the material under test, temperature differences are measured directly. This is in contrast to conventional two-thermocouple techniques that subtract two large temperatures to yield a small temperature difference, a procedure prone to errors. The proposed technique retains the simple instrumentation of two-thermocouple techniques while eliminating the critical dependence of the latter on good thermal contact. The repeatability of the proposed technique is demonstrated to be $\pm 2.6\%$ over three temperature sweeps, while the repeatability of two-thermocouple measurements is about $\pm 5\%$. The improved repeatability is significant for reliable reporting of the ZT figure of merit, which is proportional to the square of the Seebeck coefficient. The accuracy of the proposed technique depends on the accuracy with which the high-temperature Seebeck coefficient of the reference material may be computed or measured. In this work, the Seebeck coefficient of the reference material, n^+ InP, is computed by rigorous solution of the Boltzmann transport equation. The accuracy and repeatability of the proposed technique can be systematically improved by scaling, and the method is easily extensible to other material systems currently being investigated for high thermoelectric energy conversion efficiency. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4754714>]

INTRODUCTION

The field of thermoelectricity has seen a resurgence of interest of late in the quest for an efficient, compact, renewable energy source. The efficiency figure of merit, $ZT = S^2\sigma T/\kappa$ is used to evaluate materials for thermoelectric applications, where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the operating temperature. The figure of merit reaches a peak at a temperature that depends on the material; the ZT of Bi_2Te_3 reaches its peak at 100 °C while that of SiGe peaks at 900 °C. Accurate and repeatable measurement of the Seebeck coefficient at high temperatures is therefore crucial in comparing various candidate materials for high-efficiency thermoelectrics.

Several techniques have been proposed in the literature for the measurement of the Seebeck coefficient of bulk materials and thin films. Scanning probe techniques^{1–3} utilize heated tips for applying highly localized temperature gradients, thereby enabling nanometer-scale spatial resolution. However, the instrumentation involved is rather elaborate, which is further complicated by the sensitivity of piezoelectric actuators to temperature, although a 750 °C atomic force microscope²⁵ has been recently reported. Integrated heater-sensor techniques^{4,5} utilize metal or polysilicon heaters and platinum resistance thermometers (PRTs) integrated into the test structure. Two-thermocouple (two-tc) techniques utilize temperature gradients created externally (off-sample) usually by Joule heating based components^{6–10} or alternately by light

pulses.¹¹ In the latter two techniques, a voltmeter is used to measure the potential difference across two contacts in open-circuit, while two resistors or tc's placed near or on the contacts measure the temperatures. In two-tc methods, often the tc leads themselves are used to probe the potential difference. The Seebeck coefficient in both methods is calculated as the negative of the ratio of the potential difference to the temperature difference. However, the simplicity of these methods is often deceptive. High-temperature measurements using integrated heater/sensors require a larger processing overhead and highly precise knowledge of the resistance of the PRT as a function of temperature, since two large temperatures will need to be subtracted to yield a small difference, a procedure inherently prone to error. Despite innovative designs of the measurement set-up and instrumentation circuit, the repeatability and accuracy of the two-tc method remains very sensitive to the quality of thermal contact between the sample and the tc's. Still, two-tc direct-voltage methods remain the most popular for high-temperature measurements on thin films (e.g., Refs. 12–15), owing to the directness of the measurement and the simplicity of the required instrumentation. Figure 1 shows a typical measurement (of $\sim 5 \times 10^{18} \text{ cm}^{-3}$ silicon-doped InP) by this method, showing a repeatability of $\pm 5\%$. For thermal contact between the thermocouples and the sample, this measurement used SPI Supplies® silver paste, part No. 05063-AB, which remains stable up to 400 °C. Indium forms excellent thermal contacts; unfortunately, it melts at 156.6 °C and flows at higher temperatures, risking the shorting of nearby structures. Martin *et al.* (Ref. 16) comprehensively reviews Seebeck

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FIG. 1. Typical high-temperature, two-thermocouple Seebeck coefficient measurement for n+ doped InP; worst case repeatability is about $\pm 5\%$. The Seebeck coefficient rolls off above 550 K due to the InP substrate (semi-insulating at room temperature) beginning to conduct appreciably.

coefficient metrology, as well as the challenges involved in the measurement.

In this work, we introduce a novel method of measuring the Seebeck coefficient of thin films by means of a thermometric reference material. A bar of the reference material is regrown in a window adjacent to a patterned bar of the material under test. An SiO_2 hard mask is used to protect the latter during regrowth, and is later lifted off in HF. Electrical contacts are deposited at both ends of each bar, with the two contacts at each end situated close to one another. Figure 2 schematically illustrates the final sample structure. The bars straddle two Joule heating-based external heaters that control the average temperature and create temperature gradients. A single tc is in thermal contact with the chip and is connected to a voltmeter to measure the average temperature on the sample surface; the placement of this tc is not critical. The Seebeck voltage of the material under test and the Seebeck voltage of the reference material are measured by two more voltmeters. Provided we know the Seebeck coefficient of the reference

FIG. 2. Schematic illustration of final sample structure. A bar of regrown n+ InP is used as a thermometric reference to characterize the Seebeck coefficient of n+ InGaAs. The geometry allows temperature differences to be measured directly.

material as a function of the temperature, the latter voltage yields the temperature difference directly. This eliminates the need to measure two large temperatures using tc's or PRTs and subtract them to yield a small difference, an error-prone procedure. Also, the Seebeck coefficient of the reference material is much larger (~ 150 – $220 \mu\text{V/K}$ in our demonstration) than conventional thermocouple coefficients (a few tens of $\mu\text{V/K}$), which improves the resolution of our technique.

SAMPLE PREPARATION AND METROLOGY

A $1 \mu\text{m}$ film of silicon-doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ (hereafter referred to as InGaAs) with a 60 nm thick unintentionally doped InP buffer layer is grown epitaxially on a $500 \mu\text{m}$ thick semi-insulating Fe:InP substrate in a horizontal-reactor metalorganic chemical vapor deposition (MOCVD) chamber. Trimethylindium (TMIn), trimethylgallium (TMGa), and tertiarybutylarsine (TBAs) are used as precursors for InGaAs growth, and H_2 is used as the carrier gas. Disilane (Si_2H_6) is used as a dopant precursor. The reactor pressure is maintained at 350 Torr during the growth, with the temperature stable at 600°C . The InGaAs film is grown under a V/III ratio of 23.7, resulting in a growth rate of $1.34 \mu\text{m/h}$. The carrier concentration of InGaAs as measured by the Hall effect, is $1.94 \times 10^{18} \text{ cm}^{-3}$ and the mobility is $\sim 4600 \text{ cm}^2/\text{V}\cdot\text{s}$. The film is then patterned into bars 2 mm wide and 1 cm long using contact photolithography followed by a 4 min wet etch in a 1:1:8 (by volume) solution of $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$, which selectively etches InGaAs over InP at $\sim 400 \text{ nm/min}$.¹⁷ A 120 nm thick SiO_2 film covering the entire sample is grown by plasma-enhanced chemical vapor deposition (PECVD) at 250°C . A 2 mm wide window of the same length (1 cm), separated by 1 mm from the InGaAs bar, is etched into the SiO_2 using buffered HF, thus exposing Fe:InP within the window. After a surface preparation that consists of solvent cleaning and a sulphuric acid dip to remove any surface oxide within the regrowth window, the sample is transferred to the MOCVD chamber for InP regrowth. A $1 \mu\text{m}$ thick film of silicon-doped InP is deposited using TMIn and tertiarybutylphosphine (TBP) as precursors, with a higher V/III ratio of 123 and a growth rate of about $1.4 \mu\text{m/h}$. A continuous film of InP is formed in the window, but polycrystalline deposits about $60 \mu\text{m}$ in diameter as visualized under the scanning electron microscope (SEM) cover the remainder of the sample, which is coated with SiO_2 (Fig. 3). With a 24 h etch in a 49% HF solution in H_2O , the SiO_2 is lifted off, thus removing the vast majority of the deposits (Fig. 4). A total of eight deposits ranging from $40 \mu\text{m}$ to $70 \mu\text{m}$ in diameter remained on the $2 \text{ mm} \times 1 \text{ cm}$ InGaAs bar after lift-off, as visualized under the SEM. Contacts of $1 \text{ mm} \times 1 \text{ mm}$, located 0.5 mm from the ends of the n+ InGaAs bar, are deposited by electron-beam evaporation of 40 nm Ti followed by 400 nm Au. The n+ InP reference bar is similarly metalized with 30 nm Ni followed by 500 nm Au.¹⁸ Room-temperature Seebeck coefficient measurements of the InGaAs bar on this sample ($119 \pm 1 \mu\text{V/K}$) compared well with the measurements on another InGaAs sample cleaved from the same Fe:InP substrate, but that did not go through the regrowth process ($116.5 \pm 1.5 \mu\text{V/K}$). This shows that the thermoelectric

FIG. 3. SEM image of the sample after InP regrowth. A continuous InP film is formed in the window on the right, where SiO_2 has been etched away, while polycrystalline deposits cover the rest of the sample. The arrow indicates the inner edge of the InGaAs bar, visible underneath the SiO_2 .

properties of InGaAs were not altered by the 600 °C InP regrowth and subsequent processing.

The sample is mounted across two independently controlled heater blocks inside a vacuum chamber, and a single thermocouple is attached to the sample surface ~ 2 mm from the bars to record the average temperature. SPI Supplies silver paste, part no. 05063-AB (stable up to 400 °C) is used to establish good thermal contact between the heaters and the sample, and between the sample and the thermocouple. The contacts on the InGaAs and InP bars are probed and the chamber pumped down to $\sim 10^{-7}$ Torr. The contacts are annealed at 250 °C in vacuum. External leads connect the InGaAs and InP bars to separate voltmeters. I-V sweeps established that all contacts were Ohmic.

Three sweeps, each consisting of five heater set-points between 60 °C and 250 °C, were used to establish the repeatability of the measurement. Around each heater set-point, five temperature differences ranging from 0 °C to 20 °C were established between the heaters. The resulting temperature differences between the ends of the bars ranged from 0 to ~ 10 K,

FIG. 4. SEM image of the sample after SiO_2 lift-off. Two parallel bars of InGaAs and InP are clearly visible; two deposits are seen on the InGaAs bar to the left.

FIG. 5. Linearity of the raw data; heater set-point = 200 °C resulting in a temperature of 490 K on the sample surface. The slope of the best-fit line, multiplied by the Seebeck coefficient of InP at 490 K, yields the Seebeck coefficient of InGaAs at 490 K.

while the average temperature on the sample surface remained constant to within 2 K. The voltages on the bars were allowed to stabilize at each temperature difference before the values were recorded. The voltages across the InGaAs bar ΔV_{InGaAs} were then plotted with respect to the corresponding voltages across the reference InP bar ΔV_{InP} , and the slope of the best-fit straight line was calculated. This slope, multiplied by the Seebeck coefficient of InP at the average temperature (discussed below), gives the Seebeck coefficient of InGaAs. All measurements showed good linearity, with the norm of the residuals $< 100 \mu\text{V}$ (the measurement range was ~ 1 –2 mV). A typical plot of ΔV_{InGaAs} vs. ΔV_{InP} at 490 K is shown in Fig. 5.

It remains to calculate the Seebeck coefficient of InP as a function of temperature. First, we note that the room-temperature Seebeck coefficient measured by the two-tc direct voltage method in ambient is highly repeatable ($\pm 2\%$) since the integrity of the thermal adhesive is not compromised by any heat treatment. Second, the Seebeck coefficient of III-V compound semiconductors can be quite accurately calculated by numerical solution of the Boltzmann transport equation (BTE) beyond the relaxation time approximation (RTA).¹⁹ Optical-mode phonon in-scattering, which cannot be described by the RTA, is included by an extension of the iterative method first developed by Rode.²⁶ This is significant at high temperatures due to the increased occupation of optical modes. Pauli's exclusion principle as well as conduction band non-parabolicity are included, as are all significant scattering mechanisms in the scattering rate calculations. The full BTE solution correctly reproduces experimental Seebeck coefficients of III-Vs to within 10%, compared to 20% for the usual RTA formula.²⁰ More details about the BTE solution can be found in Ref. 19. However, even this accuracy (10%) is too low for a thermometric reference. We choose therefore to extract the carrier concentration by fitting the simulated room-temperature Seebeck coefficient to the measured value, $147 \mu\text{V/K}$. The concentration thus obtained is $2.15 \times 10^{18} \text{ cm}^{-3}$, which is to be

TABLE I. Simulated Seebeck coefficient of $2.15 \times 10^{18} \text{ cm}^{-3}$ Si doped InP vs. temperature. See text for details.

T (K)	$S_{\text{InP}}(T)$ ($\mu\text{V/K}$)
300	147
350	166
400	183
450	198
500	212
550	224
600	235

compared to the Hall electron concentration of the regrown InP film, $2.4 \times 10^{18} \text{ cm}^{-3}$. The simulated Seebeck coefficient of $2.15 \times 10^{18} \text{ cm}^{-3}$ InP as a function of temperature, $S_{\text{InP}}(T)$ is shown in Table I. Since Si is a shallow donor in InP (activation energy $\sim 5.7 \text{ meV}$ ²¹), we do not expect an increase in electron concentration with temperature at this doping level.

If $S_{\text{Test}}(T)$ denotes the measured Seebeck coefficient of the test material at temperature T , and $S_{\text{Ref}}(T)$ the Seebeck coefficient of the reference material at temperature T , we have

$$S_{\text{Test}}(T) = \left[\frac{\Delta V_{\text{Test}}}{\Delta V_{\text{Ref}}} \right]_T \cdot S_{\text{Ref}}(T), \quad (1)$$

where the square brackets denote the slope of the best-fit straight line at temperature T .

RESULTS AND DISCUSSION

$S_{\text{InGaAs}}(T)$ calculated using Eq. (1) from three temperature sweeps performed over a period of three days is shown in Fig. 6. $S_{\text{InGaAs}}(T)$ is repeatable to within $\pm 2.6\%$ (worst-case), which compares well with the $\pm 5\%$ repeatability of two-tc measurements. In order to assess the measurement ac-

FIG. 6. High-temperature measurements are consistent with simulation. The repeatability bars for the proposed technique measure $\pm 2.6\%$ (worst case) from the mean value. Two-thermocouple measurements (repeatability $= \pm 5\%$) are also shown to provide another independent point of verification.

curacy, the carrier concentration of InGaAs is extracted by fitting the BTE simulations of Ref. 19 to the measured room-temperature Seebeck coefficient ($117 \mu\text{V/K}$), and it is determined to be $1.65 \times 10^{18} \text{ cm}^{-3}$ (Hall-effect measurements place the actual electron concentration at $1.94 \times 10^{18} \text{ cm}^{-3}$). The Seebeck coefficient of $1.65 \times 10^{18} \text{ cm}^{-3}$ InGaAs is then simulated over the temperature range of interest. The carrier concentration is temperature-independent at this doping since Si is a shallow donor in InGaAs.²¹ Figure 6 shows that the measured values are in line with simulations, except for an aberration at 377 K. There are smaller deviations at 490 K and beyond; it is possible that these are due to errors in InGaAs and InP Seebeck coefficient simulations, which have been optimized to fit the reliable room-temperature data. Direct two-thermocouple measurements performed on InGaAs are also shown in Fig. 6 and provide a second independent point of verification of the proposed method.

Although we have conducted high-temperature measurements only up to 550 K, this is not a limitation of the proposed technique per se; the semi-insulating InP substrate conducts appreciably¹² and corrupts thin-film measurements beyond this temperature, as was seen in the typical two-tc measurement shown in Fig. 1.

For this proof-of-concept test, the distance between the centres of the InGaAs and InP contacts at each end was 3 mm, while the length of the bars was 10 mm. There is a systematic route to improving the repeatability and accuracy of these measurements: by reducing the bar widths and separations relative to the bar lengths, we reduce the impact of lateral temperature gradients (our analysis assumes a longitudinal gradient, i.e., parallel to the bars). These features are defined by photolithography, and can be resolved to within a few microns with contact lithography. This scalability contrasts strongly with two-tc measurements, where the thermal impedances between the tc's and the sample decide the quality of the data, and no further improvements are possible.

The proposed technique therefore reduces the problem of characterizing an entire epitaxial system to that of characterizing one reference material in that system. In extending the technique to material systems other than InP, two limitations become apparent: (a) the accuracy of the measurement is proportional to the accuracy with which the reference material can be computationally characterized, and (b) care must be taken to ensure that the reference material regrowth and subsequent processing do not affect the transport properties of the material under test. As regards the accuracy of the reference material characterization, a material with a large effective mass, if available, must be chosen as the thermometric reference, since optical-mode phonon effects as well as deviations from parabolic bands are less pronounced in such materials, for the same carrier concentration. If a reference material must be chosen that has not been as extensively studied as, for example, InP, GaN, or Si, it is to be noted that the Seebeck coefficient is the most sensitive to the effective mass and the carrier concentration, and depends only logarithmically on the scattering rate. Therefore, effective mass determination by the Shubnikov de-Haas effect, combined with Hall effect measurements at such high magnetic fields that the Hall

factor tends to 1, would enable one to calculate the Seebeck coefficient of the reference to sufficient accuracy. Density functional theory also furnishes a viable means of band-structure calculation. The issue of the reference material regrowth being compatible with the material under test is highly platform-dependent and must be examined on a case-by-case basis; n-type doped InP, GaN, and Si thin films are all appropriate reference materials for evaluating other materials that can be grown on semi-insulating InP, sapphire, and semi-insulating Si substrates, respectively.

CONCLUSIONS

We have demonstrated an attractive alternative to two-thermocouple techniques for the measurement of the high-temperature Seebeck coefficient of thin films. The method presented here can be directly applied to the characterization and optimization of high- ZT alloys and nanocomposites of InGaAs such as ErAs:InGaAlAs.²² A variant of this technique involves using silicon-doped InGaAs regrown on semi-insulating Fe:InP as the reference material; this will help directly compare the Seebeck coefficient of the material under test to that of the control instead of indirect comparison through InP. Nor is the applicability of this method limited to the InP platform; regrown GaN can be used as the thermometric reference to characterize AlInN, which has been demonstrated^{23,24} to have exceptional ZT . In systems where a good lattice-matched electrical insulator is available, such as SiO₂ in the silicon platform, the regrowth step itself may be unnecessary. The reference layer may be buried under the insulator, and the material to be characterized may be deposited epitaxially on the insulator. Isolated parallel bars may be patterned by photolithography, alternate bars etched down to the reference layer, and contacts made as before to the material under test and to the reference material. The insulator would isolate the Seebeck voltage of the material under test from the reference layer buried underneath.

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