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A hot probe setup for the measurement of Seebeck coefficient of thin wires and thin films using integral method

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An experimental setup is developed for the measurement of the Seebeck coefficient of thin wires and thin films in the temperature range of 300–650 K. The setup makes use of the integral method for measuring the Seebeck voltage across the sample. Two pointed copper rods with in-built thermocouples serve as hot and cold probes as well as leads for measuring the Seebeck voltage. The setup employs localized heating and enables easy sample loading using a spring loaded mounting system and is fully automated. Test measurements are made on a constantan wire and indium tin oxide (ITO) thin film for illustration. The Seebeck voltage obtained for constantan wire is in agreement with the NIST data for copper constantan couple with an error of 1%. The calculated carrier concentration of ITO film from the Seebeck coefficient measurement is comparable with that obtained by electrical transport measurements. The error in the Seebeck coefficient is estimated to be within 3%. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2869039]

I. INTRODUCTION

The study of transport properties, particularly thermopower or the Seebeck coefficient, of a material is of both fundamental and technological importance. With the ever increasing demand for nonconventional energy sources, thermoelectric materials and hence suitable techniques to evaluate the performance of the materials have gained immense interest. Of the two basic techniques for measuring the Seebeck coefficient, viz., the integral and the differential methods, the former conforms more closely to the conditions of operation if the sample under investigation finds application in high temperature thermoelectric energy conversion.

Experimental techniques based on the differential method to measure the Seebeck coefficient at low and high temperatures, wherein a small temperature gradient is established along the length of the sample, are well covered in literature.[1–4] Differential method using a pointed hot probe for determining the Seebeck coefficients of bulk specimens has been reported by several workers. One of the earliest reports is due to Cowles and Dauncey[5] who used a copper hot probe with a thermocouple soldered to its end. The hot probe, heated externally using resistive heaters, was pressed on the sample resting on a huge brass block, which acted as a heat sink. A direct reading potentiometer circuit yielded the differential Seebeck coefficient of the specimen with respect to copper as compared with that of a chromel-alumel couple held at the same temperature gradient. Gee and Green[6] have described a hot probe setup in which a gold ball, melted on the thermocouple, was heated by an incandescent bulb. Though it is applicable for bulk and thin film samples alike, the setup facilitates studies at room temperature and below only. In addition, the electrical contact between the thermocouple and the hot probe may lead to spurious results. This was avoided by Goldsmid,[7] who modified the apparatus of Cowles and Dauncey by isolating the couples from both the probe and heat sink. A simplified electrical circuit was also introduced. However, a suitable choice of resistors was necessary to obtain the desired sensitivity over a limited range of the Seebeck coefficient. Platzek *et al.*[8] extended the hot probe method to measure the spatial variation of the Seebeck coefficient by mounting the hot probe over a linear translational stage. Peltier elements were integrated for heating and cooling of the probe and the sample. The setup facilitated measurements on bulk specimens over a temperature range of −10 to +60 °C.

In comparison, fewer papers are available on the integral method, where one end of the sample is held at a fixed temperature (generally either 273 K or room temperature) and the temperature of the other end of the sample is raised to the desired value. Large thermal gradients are an inherent feature of this method. The Seebeck voltage generated in the sample is recorded as a function of temperature of the hot end. The Seebeck coefficient of the sample with reference to the probe at any temperature can be obtained from the slope of the Seebeck voltage versus temperature curve at that temperature. The integral and differential methods yield the same results for metals, semimetals, and degenerate semiconductors. However, in the case of nondegenerate semiconductors and insulators, the methods could give contrasting results and hence, the integral method is limited to the analysis of the former class of materials alone.[9]

Wood *et al.*[9] described a setup that measures Seebeck voltages using the integral method in which the sample was pressed between a resistance-heated molybdenum furnace and a water cooled copper plate. The setup facilitated measurements up to 1000 °C but was limited to short rod shaped samples. A brief mention of the integral method applied to thin film samples, but with no detailed description of the

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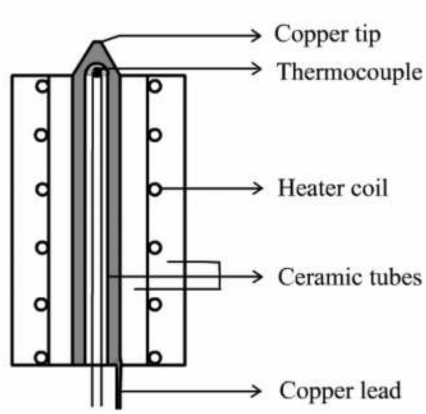

FIG. 1. A schematic view of the hot probe.

setup used, appears often in literature.[10,11] The sample is usually pressed between large copper blocks and heated externally. The thermocouple is mounted either inside the copper block or pressed to the sample and hence, the measurement of the Seebeck voltage and temperature at the same point of the sample is not possible. Moreover, the range of temperature reported is only 300–450 K.

We have designed, fabricated, and report here a hot probe apparatus using the integral method. The setup measures the Seebeck voltage of thin wires and thin films in the temperature range of 300–650 K by employing localized heating using the hot probe, which also acts as the voltage measuring lead. The hot and cold probes have in-built thermocouples and proper calibration enables the accurate measurement of the temperature of the hot and cold points on the samples. Test measurements carried out using a standard constantan wire and an ITO thin film have yielded results comparable with the reported data.

II. EXPERIMENTAL DETAILS

A. Description of the setup

The hot probe is made from a high purity copper rod, with a tapered end. A schematic of the probe is shown in Fig. 1. The tapering extends to ~2 mm so that the area of contact with the sample is defined by a circle of ~1 mm diameter. This prevents mechanical damage, especially to thin film samples, due to sharply pointed probe. A hole that extends up to ~1 mm from the tapered end is drilled in the copper rod. A copper-constantan thermocouple (wire diameters of ~0.25 mm each) is first inserted through a double holed ceramic tube of diameter of 3 mm. This assembly is then inserted into the hole in the copper rod. The tip of thermocouple is electrically isolated from the copper rod using an epoxy. A thin copper wire directly attached to the copper rod serves as the electrical lead for measuring the Seebeck voltage. This arrangement is placed inside another ceramic tube, over which a heater coil is wound and then packed inside a third ceramic tube using a high temperature cement such that only the tapered end of the copper rod is exposed. The cold probe is fabricated in the same manner. The probes are mounted inside holders covered by copper radiation shield using stainless steel screws and fixed on a water cooled copper base plate, as shown in Fig. 2. The separation between the probes is ~40 mm. The samples were pressed to the probes by a spring loaded mounting arrangement erected on four stainless steel posts. This arrangement ensures good thermal contact between the probes and the sample, which is critical in high temperature measurements. This pressure contact is not influenced by thermal expansion of the various parts of the hot probe, as the springs are far away from the hot probe and are held essentially at room temperature. The setup is mounted inside a vacuum chamber ($\sim 5\times 10^{-6}$ Torr) and trial heating is done to enable degassing. The temperature of the hot probe is varied over the range of interest using a proportional–integral–derivative (PID) controller (Shinko PCD-33A), which is fed by the temperature sensed by the thermocouple implanted inside the hot probe. A slow heating rate (~0.7 K/min) is used. The corresponding Seebeck voltages are acquired using a Keithley 196 system digital multimeter (DMM), interfaced to a computer. The wires coming out of the probes are shielded. Also the same metal wires for both voltage leads as well as thermocouples are brought out of the vacuum chamber using a specially designed feed through to eliminate any artifacts due to dissimilar junctions.

FIG. 2. (Color online) Photograph of the setup. The probes are mounted inside the radiation shields, on the water cooled base plate. The stainless steel (SS) posts for mounting the spring loaded sample holder are also seen. For details, refer text.

B. Experimental procedure and data analysis

Prior to actual measurements, the temperature at the tip of the hot probe is measured using a thin copper-constantan couple pressed at the exposed tip. The temperatures sensed by this couple and the couple which is implanted inside the tip remained the same during the initial stages of heating. However, we have observed differences between the temperatures sensed by the couple at the tip and the couple inside the tip as the temperature reached 650 K. A difference of 0.1 K is observed at ~550 K and at 650 K (as measured by the inside couple); the outside couple recorded 670 K. This indicates that the thermocouple inside the tip is not in good thermal contact with the tip. The difference in temperature arises due to the low thermal conductivity of the epoxy used to electrically isolate the inside couple from the tip. The test is repeated several times, keeping the heating rate the same. The results are found to be reproducible with an error of less than 1%. A relationship between the temperatures measured by the internal and the external couples has been arrived at. This is used to obtain the actual temperature of the hot probe from the temperature sensed by the inside thermocouple.

In the setup, the hot probe is connected to the positive of the voltmeter. Hence *n*-type samples yield a positive Seebeck voltage *V*. The Seebeck coefficient of the sample at any temperature with respect to copper, $\alpha(T)$ is then given by the simple relation

$$\alpha(T) = -\left(\frac{dV}{dT}\right)_T. \quad (1)$$

For analyzing the data and extracting the Seebeck coefficient, we follow the method of global least squares curve fitting on the plot of the Seebeck voltage versus temperature. A third order polynomial fits all the data with a coefficient of regression greater than 0.9999. The derivative of the fitted data at any temperature gives the Seebeck coefficient of the sample with reference to copper at that temperature. The absolute Seebeck coefficient of the sample, $\alpha_{\text{sample}}(T)$, is obtained by using the relation

$$\alpha_{\text{sample}}(T) = \alpha(T) + \alpha_{\text{Cu}}(T), \quad (2)$$

where $\alpha_{\text{Cu}}(T)$ is the absolute thermopower of copper, obtained using the empirical interpolation function given by Burkov *et al.*[3]

Using the setup, the Seebeck voltage was measured with an accuracy of 1 μV and the temperature with an accuracy of 0.1 K. The third order polynomial regression used to extract the Seebeck coefficient introduces error that varies with sample response. The total error in the Seebeck coefficient for any sample is estimated to be within 3%.

The cold probe is kept at a temperature of 285 K. Hence, all acquired data have been compensated to obtain Seebeck voltages with reference to the ice point (273.16 K). Though the cold probe is shielded from the hot probe by a copper radiation shield and mounted on a water cooled copper base plate, the temperature of the cold tip is found to increase by ~4 K when the hot probe reaches 650 K. This is unavoidable in the integral method and is attributed to the thermal conduction through the sample as well as the glass plate in the spring loaded mounting system. Hence, all data have been corrected accordingly. It is to be noted here that such a correction is not necessary if the temperature difference between the probes are measured directly.

III. EXPERIMENTAL RESULTS

Test measurements are carried out using a standard constantan wire (diameter of ~0.25 mm) The Seebeck voltage obtained for the constantan wire with reference to copper as a function of temperature is shown in Fig. 3, along with the standard data for copper-constantan couple.[12] The experimental data are found to be in excellent agreement with the standard with an error of 1%.

To check the capability of the setup to make measurements on thin films, experiments were done on an ITO film on glass substrate. The ITO film was deposited by reactive dc sputtering of an indium tin target containing ~10 at. % tin under a gas mixture of oxygen and argon. ITO is a *n*-type degenerate semiconductor with high carrier concentration,

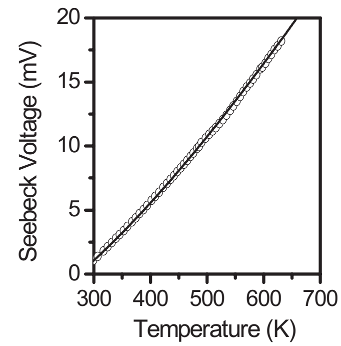

FIG. 3. Seebeck voltage obtained for constantan wire with reference to copper (open circles), as a function of temperature, along with the standard data (continuous line) for the copper-constantan couple.

low resistivity, and high optical transparency.[13] The variation of the Seebeck voltage with temperature for the ITO film (open circles) is shown in Fig. 4, along with the third order polynomial fit to the data (continuous line). The calculated value of the Seebeck coefficient (open triangles) for the ITO film is also shown in Fig. 4. As expected for a *n*-type semiconductor, the Seebeck coefficient is negative in the entire range of temperature. Moreover, the temperature dependence behavior of the Seebeck coefficient is typical of a degenerate semiconductor with high carrier concentration. From the data, we have calculated the value of carrier concentration of the ITO film using the method outlined in Ref. 14. The calculated value (1.6×10^{20} cm^{-3}) is found to be in good agreement with the reported values for ITO films.[15,16] This has also been confirmed by room temperature Hall effect measurements and the slightly lower value of carrier concentration in our film is due to the higher resistivity of the film (9.4×10^{-4} Ω cm). A systematic study on ITO and indium oxide films has been made using this setup and the results will be published elsewhere.

The setup offers the following benefits:

(a) The presence of small spurious voltages that affect the measurements is common in conventional setups using the differential method. This is largely overcome in the integral method due to large Seebeck voltages generated by the large thermal gradients.

(b) Accurate measurement of temperature at the electrical contact to sample is not possible with thermocouples in

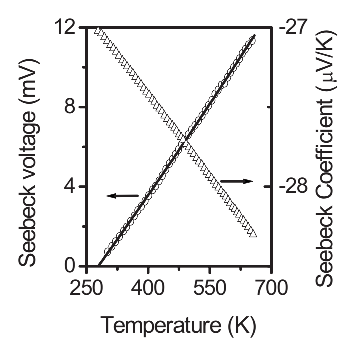

FIG. 4. Seebeck voltage (open circles) and Seebeck coefficient (open triangles) obtained for the ITO thin film with reference to copper, as function of temperature. The third order fit to the Seebeck voltage curve is shown as the continuous line.

conventional setups as the contact and thermocouple have to be kept apart at a finite distance. This problem is overcome by implanting the thermocouple inside the probe, with suitable electrical isolation.

(c) The sample needs to be pressed using the spring loaded mounting system to only two probes with in-built thermocouples and hence no additional care is required for changing of samples, thereby making it simple and easy.

(d) Any degradation of the electrical contacts at high temperatures is minimized by the operation under high vacuum condition.

Further, the finite size of the probe tips facilitates localized heating of the thin film samples and hence is expected to help in studying any local variation of the Seebeck coefficient, though such an attempt has not been made in this report. Also, the temperature range of interest may be increased beyond 650 K by implanting a chromel-alumel couple or a platinum resistance thermometer, instead of the copper-constantan couple, inside the probe tip.

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[1] O. Boffoue, A. Jacquot, A. Dauscher, B. Lenoir, and M. Stölzer, Rev. Sci. Instrum. **76**, 053907 (2005).
[2] Z. Zhou and C. Uher, Rev. Sci. Instrum. **76**, 023901 (2005).
[3] A. T. Burkov, A. Heinrich, P. P. Konstantinov, T. Nakama, and K. Yagasaki, Meas. Sci. Technol. **12**, 264 (2001).
[4] V. Ponnambalam, S. Lindsey, N. S. Hickman, and T. M. Tritt, Rev. Sci. Instrum. **77**, 073904 (2006).
[5] L. E. J. Cowles and L. A. Dauncey, J. Sci. Instrum. **39**, 16 (1962).
[6] W. Gee and M. Green, J. Phys. E: J. Sci. Instrum. **3**, 135 (1970).
[7] H. J. Goldsmid, J. Phys. E: J. Sci. Instrum. **19**, 921 (1986).
[8] D. Platzek, G. Karpinski, C. Stiewe, P. Ziolkowski, C. Drasar, and E. Müller, Proceedings of the 24th International Conference on Thermoelectrics (ICT), 2005 (unpublished), p. 13.
[9] C. Wood, A. Chmielewski, and D. Zoltan, Rev. Sci. Instrum. **59**, 951 (1988).
[10] M. Muhibbullah, M. O. Hakim, and M. G. M. Choudhury, Thin Solid Films **423**, 103 (2003).
[11] V. Damodara Das and J. C. Mohanty, J. Appl. Phys. **54**, 977 (1983).
[12] http://srdata.nist.gov/its90/main
[13] J. Ederth, P. Johnsson, G. A. Niklasson, A. Hoel, A. Hultaker, P. Heszler, C. G. Granqvist, A. R. van Doorn, M. J. Jongerius, and D. Burgard, Phys. Rev. B **68**, 155410 (2003).
[14] Z. Q. Lia and J. J. Linb, J. Appl. Phys. **96**, 5918 (2004).
[15] F. O. Adurodija, H. Izumi, T. Ishihara, H. Yoshioka, and M. Motoyama, J. Appl. Phys. **88**, 4175 (2000).
[16] N. Kikuchi, E. Kusano, H. Nanto, A. Kinbara, and H. Hosono, Vacuum **59**, 492 (2000).