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DIGITAL OBJECT IDENTIFIER
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The article by Thorne Lay and Hiroo Kanamori is an excellent review of the energy released by the 1994 Chilean earthquake. The authors used the relation for seismic energy release rather than total strain energy release. The seismic energy underestimates the total strain energy release by a factor of about 3, or 10 times if one uses a 100-megaton rather than a 30-megaton value for the energy released by the earthquake. The authors also state that the seismic energy released by the earthquake is approximately five times as much energy as that of a 100-megaton atmospheric explosion. This is not right. If the authors were to use a 100-megaton value for the energy released by the earthquake, they would find that the seismic energy released by the earthquake is approximately five times as much energy as that of a 100-megaton atmospheric explosion. The article does not have any references.

Comment on this article
By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck ball. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon, later becomes released in a new event. Perhaps calculations of one added that in, while another's calculations did not. E.M.C.
Written by Edgar McCarroll, 14 July 2012 19:59

Apparatus for measuring the Seebeck coefficients of highly resistive organic semiconducting materials

H. Y. Cai,^{a)} D. F. Cui,^{a)} Y. T. Li, X. Chen, L. L. Zhang, and J. H. Sun

State Key Laboratory of Transducer Technology, Institute of Electronics, Chinese Academy of Sciences, China

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A Seebeck coefficient measurement apparatus for high resistance organic semiconductor materials has been designed and built. It can measure materials with resistance over $7 \times 10^{12} \Omega$. This is the highest material resistance value ever reported for Seebeck coefficient measurement. A cyclic temperature gradient generation technique and a corresponding algorithm are proposed to eliminate the negative effects of the long term drift of Seebeck voltage. Sources of errors in these measurements are discussed. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4799968>]

I. INTRODUCTION

Seebeck coefficient (SC) is a key parameter for organic electronic and optoelectronic device research, necessary to understand the nature and dynamics of charge carriers in semiconductor materials. The SC gives the sign of the majority carrier in a semiconductor and can be used to obtain carrier density.

Many organic semiconductor materials show promising thermoelectric characteristics because they have a relatively large SC (>1 mV/K) and low thermal conductivity compared to inorganic materials.^{1–4} However, measuring the SC of high resistance organic materials is a challenge. There are a limited number of studies on the thermoelectric properties of these materials. Trakalo *et al.* introduced an experimental system for high resistance semiconductor films, only a $1 \times 10^{11} \Omega$ sample was measured.⁵ Nakamura *et al.* tried another apparatus for organic semiconductor films, but the experimental result of the approximated $10^{12} \Omega$ sample was barely distinguishable.⁶ The main problem is that high resistance and distributed capacitance cause large time constants, so the Seebeck voltage signal will drift.

In this paper, a Seebeck coefficient apparatus that can measure materials up to $7 \times 10^{12} \Omega$ is described. This is the highest material resistance value ever reported. Special techniques to minimize leakage current and distributed capacitance are also introduced.

II. EXPERIMENTAL DETAILS

A. Description of apparatus

Figure 1 is a diagram of the apparatus. A vacuum chamber is evacuated with a turbo pump (PFEIFFER HiCUBE), which can reach as high as 1×10^{-8} bar. A self-made high input resistance signal conditioning instrument and two temperature controllers (Cryocon 32, USA) are connected to the chamber. These three devices are controlled by a computer.

In the following, we will discuss the steps taken to design and build this apparatus.

B. Temperature control and measurement

A sample test stage is mounted inside the vacuum chamber, as shown in Figure 2(a). This stage can be separated into four layers: (1) thermostat layer, (2) temperature gradient arms, (3) sapphire layer, and (4) sample holder.

The thermostat layer provides a stable base temperature (T_{base}) for the sample stage. The bottom of this layer is a square shape peltier device, which serves as a heater or cooler, depending on the current direction. Above it is a heater layer with an embedded power film resistor (50Ω , 30 W). On the top is an oxygen-free copper block with a round-shape ceramic packaged PT-100 temperature sensor (RS components, 397-1595) inside. A first temperature control instrument named CC32Stage controls the stage heater and measures the T_{base} value, as shown in Figure 2(c). Such design provides convenient ways to control temperature quickly and automatically, compared with a liquid nitrogen cooling method, since both the cooler and heater can be easily controlled by computer software. However, the peltier cooling method cannot reach temperatures as low as the liquid nitrogen method.

Layer 2 consists of the temperature gradient arms. Inside each arm is a ceramic packaged 25Ω resistance heater. Using a solid-state MOSFET relay (G3VM-81HR, OMRON), the hot or cold side heater can be selectively powered by a second temperature control instrument named CC32Delta, so a positive/negative temperature gradient (ΔT) can be generated between the hot and cold side, as shown in Figure 2(b). By tuning the power, up to 5 K ΔT in either direction can be established.

Two $100 \mu\text{m}$ thick sapphire plates are placed on top of the arms. Sapphire is a good heat transfer media and an excellent insulator. So, heat can be transferred between the arms and the sample holder, while the holders are electrically insulated from the arms. This is a key point for the $T\Omega$ high resistance SC measurement.

Two sample holders are mounted on top of the sapphire plates with a U-shape sample clamping mechanism. When

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: hycui@mail.ie.ac.cn and dfcui@mail.ie.ac.cn.

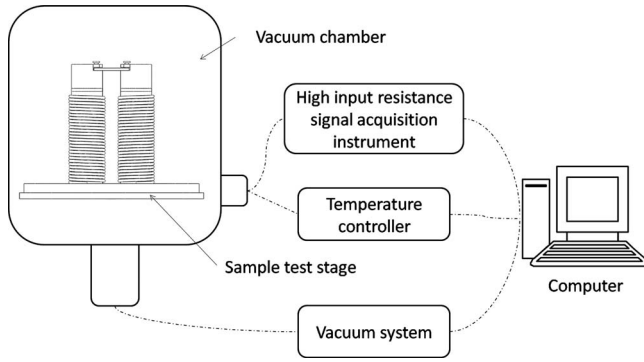


FIG. 1. Diagram of the apparatus.

rectangle shaped sample chips are placed between the two surfaces, they can be fixed firmly by two screws. Some commercial instruments recommend fixing samples between electrodes with conductive silver paste. However, this only works for low resistance ($<100 \text{ k}\Omega$) samples. For high resistance samples, conductive cracks inside the paste induce signal noise as large as mV levels, which overwhelms the Seebeck voltage signal.

Separate miniaturized ceramic packaged PT-100 temperature sensors are installed in the two sample holders.

Briefly, the temperature control procedure is as follows: (1) CC32Stage heats or cools the stage to a user defined temperature. (2) After the temperature is stable, CC32Delta operates in a programmed manner, and steps of ΔT are generated between the two arms.

C. Seebeck coefficient measurement

In principle, Seebeck coefficient measurement can be quite simple, as shown in Figure 3: A sample of interesting material is placed in the holder, between the hot and cold sides. A temperature gradient is set up between the ends of the sample, and the Seebeck voltage (V_s) between hot and cold sides was measured with a volt meter. By convention, this potential is measured with respect to the hot side.

The SC can be calculated as follows:

$$T_{\text{sample}} = (T_{\text{hot}} + T_{\text{cold}})/2, \quad (1a)$$

$$\Delta T = (T_{\text{hot}} - T_{\text{cold}}), \quad (1b)$$

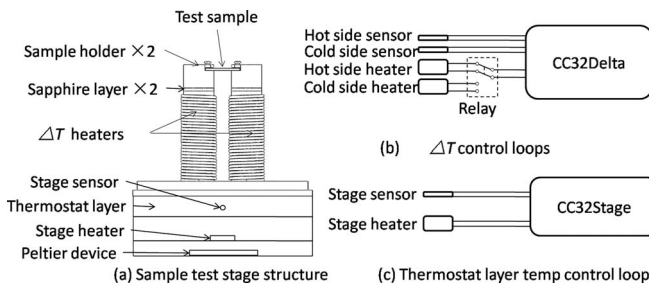


FIG. 2. (a) Structure of the sample test stage; (b) temperature control loop of sample gradient; and (c) temperature control loop of thermostat layer.

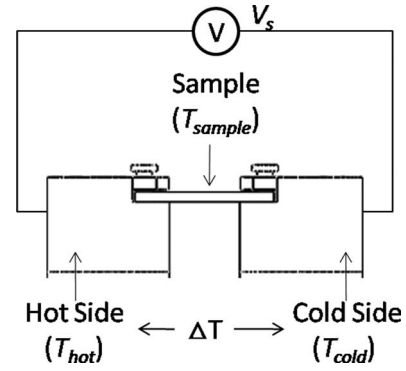


FIG. 3. The schematic of SC measuring principle. T_{sample} is sample temperature, T_{hot} is hot side temperature, T_{cold} is cold side temperature, ΔT is the difference between cold and hot sides, and V_s is the Seebeck voltage with respect to the hot side.

$$V_s = V_{\text{cold}} - V_{\text{hot}}, \quad (1c)$$

$$\text{SC} = \frac{V_s}{\Delta T}. \quad (1d)$$

There are several special consideration when carrying out high resistance voltage source ($>100 \text{ M}\Omega$) measurement:⁷ (1) the signal conditioning circuit should have ultrahigh input resistance, i.e., at least 100 times higher than the sample resistance. For sample resistance as high as $1 \times 10^{12} \Omega$, the circuit should have over $1 \times 10^{14} \Omega$ input resistance. (2) The circuit should be designed and operated carefully to minimize leakage current and distributed capacitance. Any leakage current will cause false voltage readout, and any distributed capacitance increases response time. (3) Noise from variant sources should be carefully controlled, such as pickup from heaters, noise generated by vibrations, etc.

Figure 4 illustrates the Seebeck voltage signal conditioning circuit. Connections are made from the sample holder to operation amplifier input. To minimize noise, low triboelectric effect shielded cable is used, the shield connected to the guard voltage output to eliminate distributed capacitance.

An ultrahigh input impedance operation amplifier (National Semiconductor LMP7721) is chosen.⁸ According to its datasheet, input bias current as low as $<\pm 20 \text{ fA}$ at 25°C is guaranteed. However, one must pay special attention to the printed circuit board (PCB) design in order to achieve that.

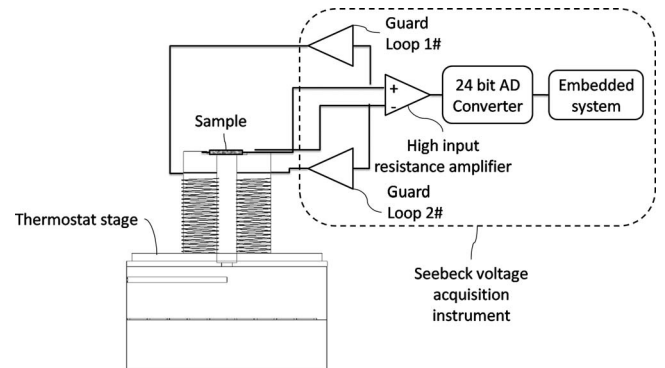
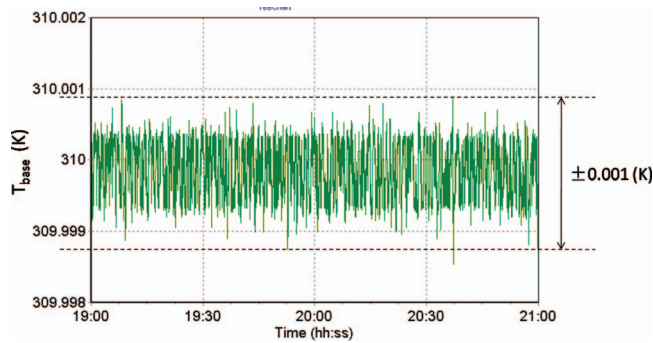


FIG. 4. Seebeck voltage signal conditioning circuit diagram.

FIG. 5. Temperature variance of thermostat layer (T_{base}) over 2 h.

To avoid leakage current on the PCB, “guard” patterns surround the amplifier’s input lead. This ensures that the entire amplifier circuitry is fully protected by the guard potential, minimizing leakage current.

Either hardware or software low pass filter technologies are used. The cutoff frequency is as low as 0.1 Hz. Low cutoff frequency increases system response time; however, since the Seebeck voltage varies in several minute intervals, 0.1 Hz cut-off is a compromise between noise suppression and response time.

III. EXPERIMENTAL RESULTS

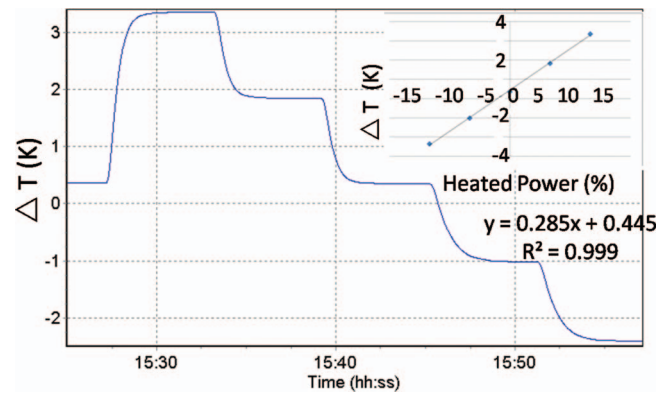
A. Temperature control

Figure 5 shows the temperature control accuracy experimental result over 2 h. An input of 310 K was the control set point (T_{base}). The thermostat layer was heated to 310 K from room temperature. T_{base} reaches 310 K within 5 min. As shown in Figure 5, the T_{base} readouts varied within the limit of 309.999–310.001 K, i.e., the T_{base} peak-to-peak variance is less than ± 0.001 K. The ultrahigh temperature control accuracy provides essential low noise levels for accurate SC measurement. It should be noted that there is about 0.5 K temperature different between T_{base} and T_{sample} . The accurate sample temperature should be acquired by Eq. (1a).

In addition to stable thermostat temperature, generation of dual-way gradient between the ends of the sample is also critical. Figure 6 shows the gradient experimental result. Steps of heated power difference were applied to the two heater arms, i.e., 5, 2.5, 0, -2.5 , -5 W, and ΔT was established between the sample holders. Inset of Figure 5 shows a perfect linear relationship between ΔT and the heater power output, the correlation coefficient $R^2 = 0.999$. The transition time between steps is about 2 min. The peak-to-peak noise level is less than ± 0.001 K in 2 min, meaning that the Seebeck voltage variance due to ΔT noise will be less than ± 0.1 μ V for sample $S = 100$ μ V/K, so can be neglected during noise source analysis.

B. Seebeck coefficient measurement

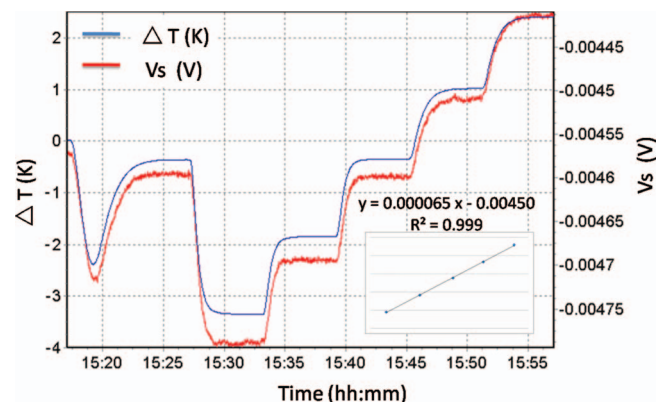
In order to verify the ability to measure the SC of high resistance materials, samples with different resistance are tested. Phthalocyanine and its metal complexes are a model

FIG. 6. Steps of temperature gradient between two sample holders. (Inset) The linear regression line of ΔT and the heated power difference, the correlation coefficient $R^2 = 0.999$.

substance in thermoelectric material research. Because of its high resistance to chemical influences, copper phthalocyanine has been in use in organic crystal carrier transport research for a long time.⁹

Figure 7 shows an experimental result for one kind of organic material—doped copper (II) phthalocyanine ($C_{32}H_{16}CuN_8$). The sample film thickness is about 50 nm and the sample resistance is 1.4×10^8 Ω . As shown, the V_s (red line) and the ΔT (blue line) correlate very well. Inset shows the linear regression curve of the V_s and ΔT ($R^2 = 0.999$). By calculating the slope of the linear regression line, the SC can be obtained ($SC = +65$ μ V/K), which is consistent with the reported value.¹⁰ The negative sign of SC means that the major charge carrier in the material is hole.

However, as sample resistance increases up to 1×10^{12} Ω , things become completely different. Figure 8 shows a V_s curve decreasing exponentially over 1 h in another organic material (iron phthalocyanine). The sample’s resistance is as high as 7×10^{12} Ω (measured by Agilent 4339B). By fitting the V_s curve with an exponential mathematical model, the RC time constant can be evaluated, which is about 450 s. This exponential decrease will affect the SC measurement severely, since no flat V_s step can be obtained, although steps of ΔT are applied.

FIG. 7. Seebeck measurement result of doped copper (II) phthalocyanine ($C_{32}H_{16}CuN_8$), with resistance of 1.4×10^8 Ω .

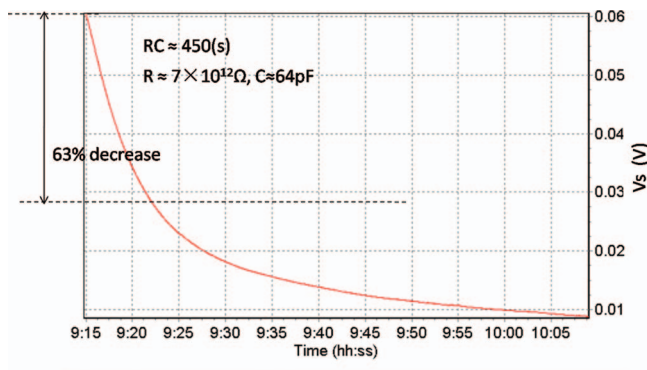


FIG. 8. Seebeck voltage curve decreases exponentially when sample resistance is $7 \times 10^{12} \Omega$.

To overcome this problem, a novel cyclic temperature method is proposed and tested. This involves waiting 1 h for the V_s to reach a relatively stable decrease trend, which is about $1000 \mu\text{V}/\text{min}$. Then cyclic temperature gradients are applied to the ends of the sample. As expected, the V_s becomes cyclic at the same interval, as shown in Figure 9(a).

Figure 9(b) shows the V_s signal after removing low frequency baseline shift and the corresponding temperature gradient curve. By calculating the dV/dT at the maximum

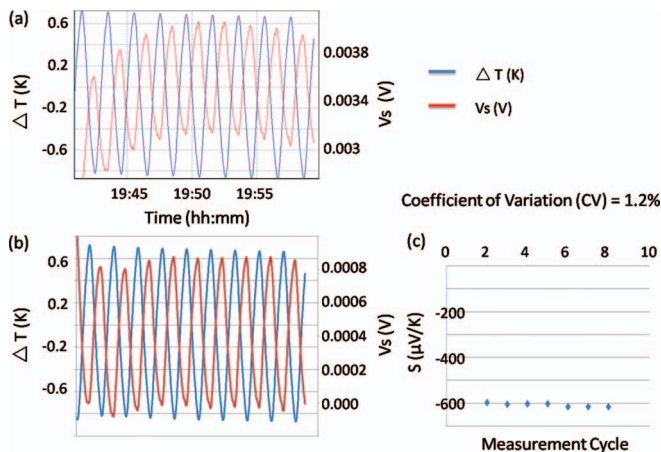


FIG. 9. Experiment result of $7 \times 10^{12} \Omega$ resistance sample.

slope of T every cyclic interval, SC can be acquired, as shown in Figure 9(b) inset. Figure 9(c) shows the SC calculated at every cyclic interval, the coefficient of variance (CV) is 1.2%, which shows the data have little variance. The averaged SC is $-606 \mu\text{V}/\text{K}$, indicating that the major charge carrier is electron.

IV. CONCLUSION

In summary, we have designed and built a Seebeck coefficient measurement apparatus for high resistance materials. SC of iron phthalocyanine which has resistance as high as $7 \times 10^{12} \Omega$ can be measured reliably. This is the highest material resistance value ever reported. A cyclic temperature gradient generation technique and corresponding algorithm are proposed to eliminate negative effects due to long term drift of Seebeck voltage. Sources of errors in high resistance SC measurement are also discussed.

ACKNOWLEDGMENTS

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⁸See <http://www.ti.com/product/Imp7721> for detailed description of Imp7721, a ultralow input bias current precision amplifier.

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