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HIGH-SPEED EVALUATION OF THERMOELECTRIC MATERIALS USING MULTI-CHANNEL MEASUREMENT SYSTEM

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Abstract

We have developed a multi-channel measurement system for combinatorial investigation of thermoelectric materials. The measurement apparatus has ten series of pin-probe array which enables us to measure the Seebeck coefficient and electric conductivity of 10 samples simultaneously. A successful measurement on a composition-spread thin films library indicated that this measurement system is highly useful for the high-speed exploration of thermoelectric materials by combinatorial approach.

Keywords: combinatorial chemistry, high-speed screening, oxide, thermoelectric, thin film

Introduction

Thermoelectric conversion has been considered as an effective way to convert waste-heat into electricity. The advantages of the themroelectric generation devices are compact, easy installation, and maintenance-free. With such advantages, the thermoelectric conversion devices have been employed in the area where high reliability is required (e.g. power sources for the space crafts and pace makers). However, no significant improvement on conversion efficiency has been reported since the discovery of Bi_2Te_3 system in 1950's [1]. Oxide materials have been neglected as a candidate of thermoelectric materials because they were presumably regarded as insulating. Nevertheless, subsequent discoveries of the highly conductive oxides in the last decade associated with the extensive studies on the high temperature superconductors gave rise to the thermoelectric applicability of the several oxide materials. Oxides have two advantageous features compared with the conventional thermoelectric materials. Firstly, they can withstand the high temperature operations because they are already oxidized. This brings high potential for the waste heat power generations. In

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high temperature operations, we can appreciate higher conversion efficiency with the increase of the non-dimensional figure of merit *ZT* (here *Z*: figure of merit [K^{-1}] ($Z=\sigma S^2/\kappa$, where σ: electric conductivity, *S*: Seebeck coefficient, and κ: thermal conductivity, and *T*: temperature). Secondly, oxides may possess variety of physical properties depending on the crystal structures and the combination of the elements due to *d* or *f* electron. The cause of such properties cannot be explained by the conventional semiconductor theory that has constrained the progress in the thermoelectric materials for the past 4 decades. Therefore, oxide materials have been attracting much attention in the last few years as there are vast numbers of the oxide materials composed of a variety of elemental combinations yet to be investigated. However, with the increasing complexity of new materials for the superior physical properties, the conventional 'one by one' approach of synthesis, which is predominantly a process of trial and error, yields a low success rate needing high expenditure and long timelines. Combinatorial approach offers a unique way to overcome this barrier. Combinatorial chemistry is a development which has already had its most profound impact in the field of organic and bio-organic synthesis in general and medicinal synthesis in particular [2–4]. The combinatorial approach involves synthesis of vast number of compounds by reacting a set of components in the pre-designed combinations within a single experiment. This yields the microscale quantities of diverse materials in a library which can be then evaluated to identify the most promising candidates quickly. Indispensable for the combinatorial technology is not only the high-speed synthesis but also the high throughput characterization. The three main stages involved in the successful application of combinatorial strategies for the innovative materials technology are: (i) design, (ii) high throughput synthesis, and (iii) rapid characterization. Thus, high throughput synthesis methods must be coupled with different mass screening analysis techniques. In this paper, we report on the exploration method of thermoelectric materials consisting of parallel sample fabrication system and high-throughput evaluation system, which may significantly accelerate the speed of the explorations.

System construction

One of the obstructions towards the high-speed exploration of the thermoelectric materials is the slow measurement process that is inherent to the thermal analysis. However, if one could do such tasks for multiple samples, the evaluation time can be reduced significantly, resulting in the acceleration of the exploration speed. The time for setting up the specimen to the measurement system is also a time consuming routine. Taking into account of these facts, we have developed a multi-channel measurement system for thermoelectric properties.

Figures 1a and b show the schematic diagram and photographic images of the measurement apparatus, respectively. The apparatus can measure up to 10 specimens with a dimension of 1×7.5×0.5 mm. The size of the apparatus is 20×30×8 mm. In this setup, we employed spring pin probes so that one can reduce the time for lead connections as well as the contamination problem. It takes only 5 min to mount the samples (or a library) to

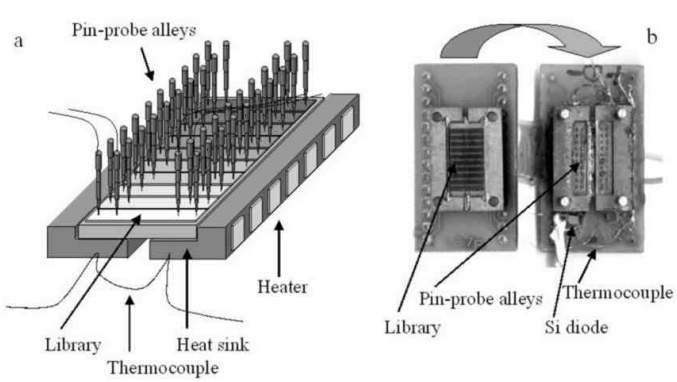

Fig. 1 a – Schematic diagram and b – photographic image of the apparatus developed for the multi-channel measurement of the resistance and thermopower

the apparatus. In order to assure the heat conduction between the probe and heat sink, the insulation gap between the heat sink and pin accepters was set as small as 20 μm using varnish. Most parts of the spring pins were embedded into the heat sink in order to reduce the temperature difference between the probe top and the heat sink. A Si-diode thermometer was attached to the low temperature side of the heat block to monitor the base temperature and the copper–constantan–copper thermocouple was attached on the side of the each heat sink to monitor the temperature difference between two heat sinks. This measurement apparatus is placed either in air or under vacuum.

Figure 2 shows the schematic diagram of the whole measurement system. In this system, wires were connected between the pin probes and a multiplexer (Keithley #7400) to select a measurement channel. The selected channel was then connected to a voltmeter (Keithley #2700) to measure the voltage output for the contact of thermopower. The inner pins or outer pins can be selected. In case of conducting 4-wire resistance measurement to obtain the resistance of the specimen under the selected sample, the outer pins are connected to a source meter (Keithley #2400) while inner pins to a voltmeter. The current-voltage curves are generated on every channel. One can also conduct 2-wire resistance measurement to check the contact resistance. When conducting thermopower measurement, an electric current is applied to a heater (Kyowa strain gauge) to generate the desired temperature difference between two heat sinks with PID control using a temperature controller (Lakeshore #340). One can apply temperature difference up to 10 K. The thermopower was measured using inner pins after the temperature was stabilized.

System performance and discussion

In order to get the reliable data, there were two major concerns; one was the relatively high contact resistance at the tip-sample interface and the other was the temperature discrepancy among the measurement channels. The first concern is not a significant

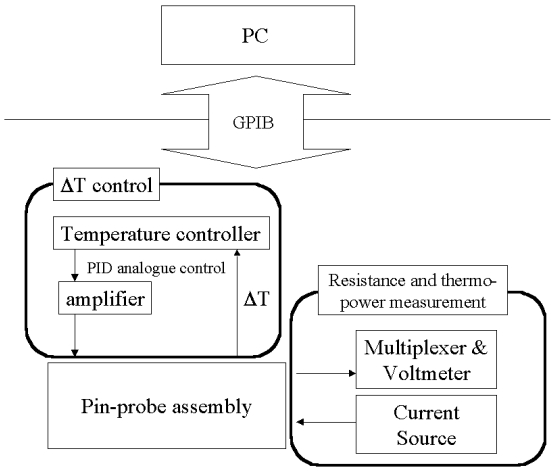

Fig. 2 Schematic diagram of the multi-channel measurement system

issue for resistance measurement because 4-wire resistance measurement can cancel such surface resistance. However, for thermopower measurement there is always some offset voltage associated with the contact resistance. In order to compensate such an offset value, Seebeck coefficient was obtained by taking a linear fit to the thermopowers measured at the several ΔT's. The real temperature difference is recorded before and after the thermopower measurement of all channels, and the average value is regarded as a real ΔT value. Examples of the thermopower measurement on Ni foils at room temperature (300 K) in air and under vacuum condition are shown in Figs 3a, and b, respectively. The average and standard deviation of Seebeck coefficient in air and under vacuum condition were -18.40 ± 0.26 μV K^{-1}, and -19.16 ± 0.07 μV K^{-1}, respectively, which were similar to the reported value of

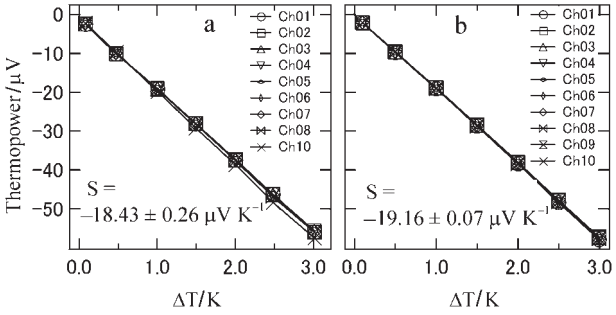

Fig. 3 Thermopower as a function of ΔT's for different channels at room temperature measured a – in air and b – under the vacuum condition. The samples are the 100 μm-thick Ni foils with a dimension of 7.0×1.0 mm attached on a 500 μm-thick TiO_2 substrate

–18.6 μV K^{-1} at room temperature (300 K) in air [5]. Therefore, our system can detect Seebeck coefficient with accuracy of the order of 1 μV K^{-1}.

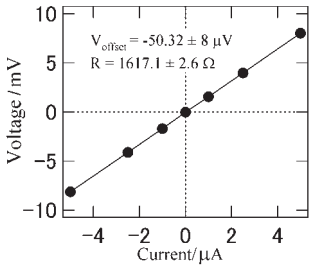

Fig. 4 Typical I–V plot obtained by multi-channel measurement system at room temperature (300 K). The sample is non-doped ZnO thin film

Both of the results indicated the high accuracy of ΔT measurements and its uniformity in the measurement assembly, which are enough for material screening. The accuracy of the current-voltage measurement was also confirmed. An example of the measurement for non-doped ZnO thin film is shown in Fig. 4. The film was deposited on an Al_2O_3 (0001) substrate heated at 200°C under the oxygen pressure of $5 \cdot 10^{-3}$ torr. The conductivity was found to be 104 S cm^{-1}, which was similar to the one fabricated on a Corning #7059 substrate at 180°C by rf-sputtering (~70 S cm^{-1}) and almost identical to the one fabricated on an Al_2O_3 (0001) substrate at 400°C by pulsed laser deposition (~100 S cm^{-1}) [6, 7]. The major factors of error in the electric conductivity among 10 different channels were contact resistance that is critical for highly resistive materials and the accuracy of the sample size estimation that is caused by the accuracy of pin-probe configuration (gives an error of about ±1.25% without electrode) and thickness profile of the individual specimens (gives an error of about ±1% for 200 nm-thick film). With this measurement system, Seebeck coefficient and the electric conductivity of 10 specimens at a fixed temperature can be measured in about 15 min. As a demonstration, we have measured a $Zn_{1-x}Al_xO$ ($0.00 \leq x \leq 0.03$) composi-

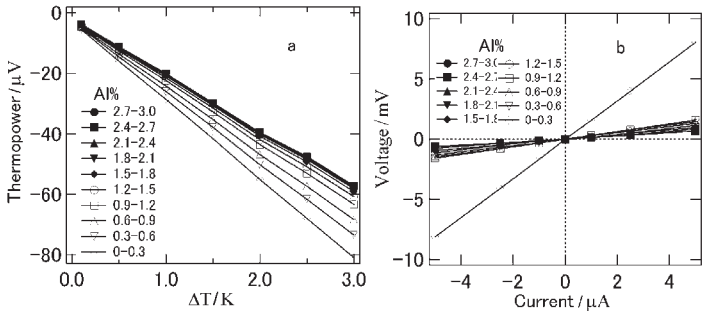

Fig. 5 a – Thermopower as a function of ΔT and b – I–V curves of a $Zn_{1-x}Al_xO$ ($0.00 \leq x \leq 0.03$) composition-spread thin-film library

tion-spread libraries prepared with a combinatorial pulsed laser deposition chamber. The thin film library with the thickness of about 200 nm was fabricated with the same condition as the non-doped ZnO film. The detailed fabrication procedures of the composition spread-library are described in [8]. The library was separated into the 10 pieces with a dimension of 1.0 mm width and 7.0 mm length by wet etching after the deposition to measure the electric conductivity and Seebeck coefficient of the limited composition range. Figure 5 shows (a) voltage as a function of current and (b) thermopower as a function of temperature difference measured in air. As a result, the electric conductivity, Seebeck coefficient, and calculated power factor ($PF=\sigma S^2=\kappa Z$) as a function of Al substitution ratio were quickly obtained as shown in Fig. 6.

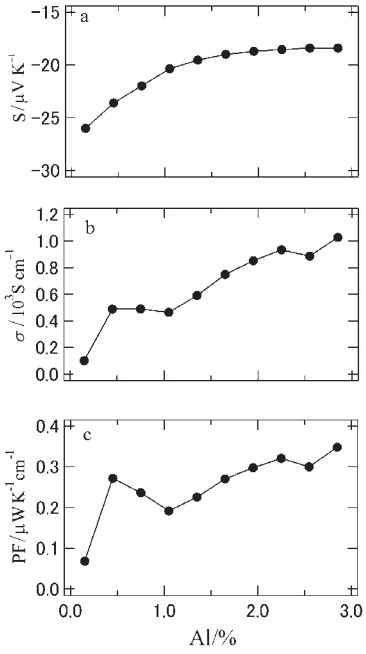

Fig. 6 a – Seebeck coefficient, b – electric conductivity, and c – power factor of $Zn_{1-x}Al_xO$ ($0.00 \leq x \leq 0.03$) composition-spread thin-film library as a function of the Al substitution ratio

For the exploration of the good thermoelectric materials, it is also very important to know the optimum operation temperature. Thus, we have also developed the measurement system to obtain thermoelectric properties at various base temperatures. In the system, the pin-probe measurement assembly was built into a cryogenic-cooler (Advanced Research Systems Inc., CSR204). The base temperature was controlled with PID using a temperature controller (Lakeshore #340) and can be varied from 10 to 400 K. The base temperature is measured by a Si diode embedded in the cooler head. Another silicon diode was also attached to the low temperature side of the heat sink of the measurement assembly. The temperature difference at an arbi-

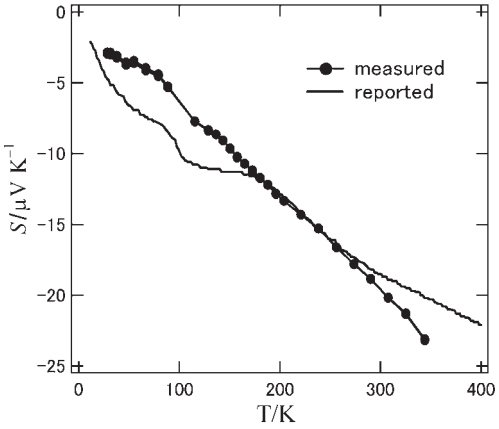

Fig. 7 Seebeck coefficient of Ni foil as a function of temperature measured with the multi-channel measurement system. Reference data is taken from [5]

tral base temperature was estimated using $\Delta S/\Delta T$ curve obtained for the copper–constantan thermocouple. A computer program was developed for the complete automation of arbitral combinations of the measurement procedures specified above. In order to check the reliability of this measurement system, Seebeck measurements of Ni foil at various base temperatures were conducted (Fig. 7). The result generally showed a good agreement with the reported values above 180 K [5]. The deviation below 180 K may be attributed to the different impurity concentrations in the sample. For the electric conductivity measurement, metal pads must be fabricated on the film surface on which the pin probes are placed in order to keep the path length constant as well as to assure the Ohmic contact.

Conclusions

We have developed a novel multi-channel thermoelectric measurement system. Its easy sample setting, high evaluation speed (15 min to measure 10 samples at a fixed temperature) and complete automation of the measurement procedures in the system verified that this system is essential for the high-speed exploration of the thermoelectric materials with the use of combinatorial approach.

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