Development of a high-throughput thermoelectric screening tool for combinatorial thin film libraries

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Abstract

We have developed a high-throughput thermoelectric screening tool for the study of combinatorial thin films. This tool consists of a probe to measure resistance and Seebeck coefficient on an automated translation stage. A thin film library of the $(Ca_{1-x-y}Sr_xLa_y)_3Co_4O_9$ ternary system has been fabricated on a Si (1 0 0) substrate, using combinatorial pulsed laser deposition by the natural-composition-spread method. We have demonstrated successful mapping of the resistance and Seebeck coefficient of this film library. The mapping indicates that the substitution of La for Ca results in an increase of both resistance and Seebeck coefficient, and that of Sr results in a decrease of resistance. The screening tool allows us to measure 1080 data points in 6 h.
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1. Introduction

There has been considerable interest in thermoelectric materials for more than 40 years because of their attractive applications, which include all-solid-state refrigerators based on the Peltier effect, and thermoelectric power generation devices using waste heat based on the Seebeck effect [1]. However, due to the low efficiency of the materials, as well as system performance, large-scale industrial applications of thermoelectric materials have been limited. Recently, promising results have been reported on a number of new thermoelectric materials, including ternary or quaternary systems [2]. These new discoveries have ignited renewed interest in the field.

Combinatorial methodology is a powerful and efficient technique for exploring novel materials, and for the optimization of material properties in multi-component systems [3]. Composition-spread synthesis is one of the combinatorial methods for fabricating films with continuously varying compositions between two or three different materials on a substrate [4,5]. Property measurements on such film "libraries" require high-throughput characterization tools. Although there are a number of literature reports concerning high-throughput characterization tools for composition-spread films [6–8], only two address thermoelectric properties. However, these techniques are not applicable for ternary composition-spread films [9,10]. The goal of this paper is to report our recent development of a high-throughput thermoelectric screening tool, and its use to demonstrate mapping of resistance and Seebeck coefficient measurements on a $(Ca,Sr,La)_3Co_4O_9$ ternary composition-spread film.

2. Experimental setup

Fig. 1a shows the high-throughput thermoelectric screening tool, and the corresponding schematic diagram is illustrated in Fig. 1b. The screening tool consists of a measurement probe to measure resistance and Seebeck coefficient, an automated translation stage to move the probe in the x–y–z directions, and various electric measuring instruments. Fig. 1c shows an enlargement of the measurement probe, which consists of four spring probes as sample contacts, a heater to generate temperature differences between two of the spring probes,

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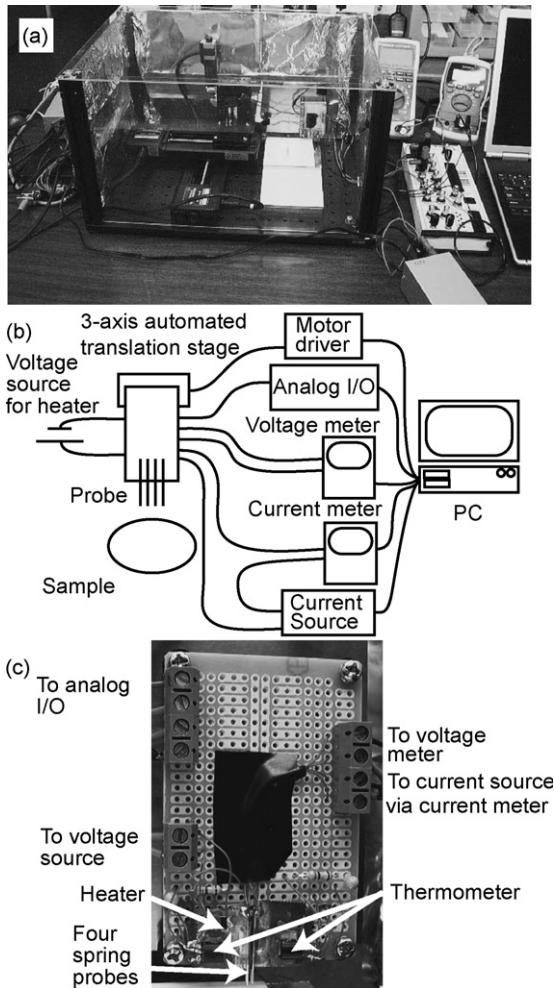E-mail address: motani@nist.gov (M. Otani).

Fig. 1. (a) A high-throughput thermoelectric screening tool, consisting of a measurement probe, a 3-axis automated translation stage, and electric measuring instruments, (b) a schematic diagram, and (c) an enlarged view of the measurement probe.

Fig. 2. Time profiles of temperature difference measured with and without a case for stabilizing the temperature measurements of a probe.

and two thermometers to measure the temperature of these probes. Among the four spring probes, two are connected to a voltage meter, and the other two are connected, via a constant current source, to a current meter. The heater and the thermometers are connected to a constant voltage source and a multi-channel analog-to-digital converter, respectively. To achieve full automation, the voltage and current meters, current source, analog-to-digital converter, and a motor driver are all connected to a laptop computer. In order to stabilize the temperature of the measurement probe, it is further placed inside a protective case. The importance of the use of the case is illustrated in Fig. 2, where time profiles of temperature differences (ΔT) between the two spring probes are shown with and without the use of the case. The fluctuations in ΔT are 0.025 K (0.59%) and 0.47 K (13%), respectively, for the measurements with and without the use of the case. This result concludes that the use of the case is indeed critical for stabilizing ΔT.

Fig. 3 is a block diagram of a typical measurement procedure for the resistance and Seebeck coefficient. In brief, before measurement, we apply a constant voltage to the heater to
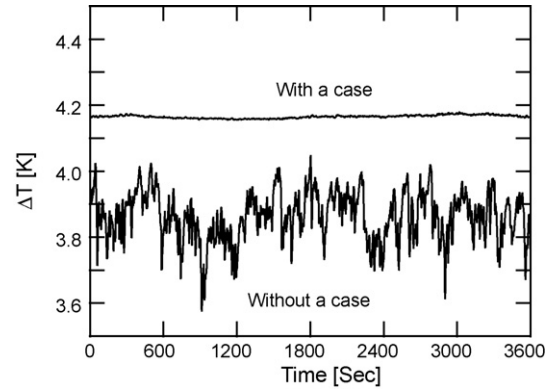
generate a temperature difference. The duration of this step usually lasts for about 20 min in order to achieve temperature stabilization. The probe is then moved to a measurement point and placed in contact with the sample. The Seebeck Voltage, V_{TP}, and temperatures of each probe (T_1, T_2), are then measured. V_R^+ is obtained by sending a fixed current, I, through two probes and measuring the voltage across the other two. V_R^- is obtained by reversing the polarity of the current and measuring the voltage. After the completion of this measurement step, the probe is moved to the next measurement point. The Seebeck coefficient, S, is defined as the Seebeck voltage divided by the temperature difference (ΔT) between the two probes:

$$S = \frac{V_{TP}}{\Delta T} = \frac{V_{TP}}{(T_1 - T_2)} \qquad (1)$$

The resistance, R, is calculated according to the expression:

$$R = \frac{(V_R^+ - V_R^-)}{2I} \qquad (2)$$

Measurement of one sample point usually takes about 20 s. Therefore, this tool allows us to measure 1080 sample points in 6 h.

3. Sample fabrication and measurement

As a demonstration of our high-throughput thermoelectric screening tool, we have mapped the resistance and Seebeck coefficient data of a ternary-natural-composition-spread film of
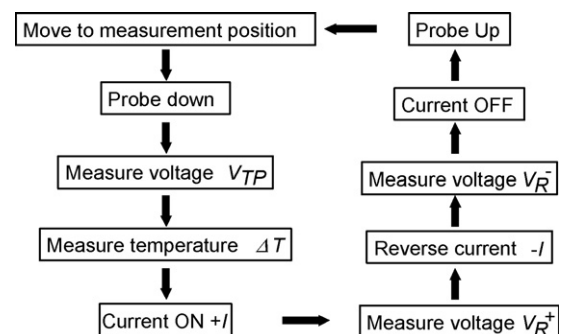

Fig. 3. A block diagram of a typical measurement procedure to measure resistance and Seebeck coefficient concurrently.
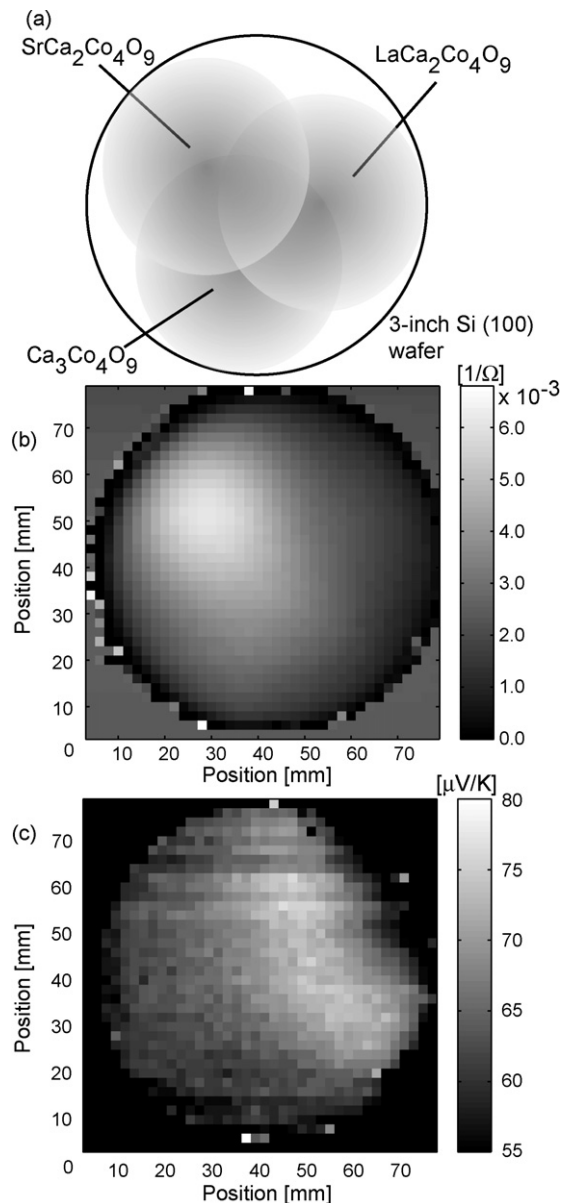
Fig. 4. (a) A schematic of $(Ca_{1-x-y}Sr_xLa_y)_3Co_4O_9$ ternary-composition-spread film. The inverse of resistance (b) and Seebeck coefficient (c) image of the composition-spread film.

the $(Ca_{1-x-y}Sr_xLa_y)_3Co_4O_9$ system. The composition-spread film was fabricated on a 76.2 mm Si (1 0 0) wafer by combinatorial pulsed laser deposition at a substrate temperature of 750 °C and oxygen pressure of 80 Pa. A KrF excimer laser (248 nm in wavelength) was used for ablation. The fabrication procedure of the ternary-composition-spread film is as follows (See Fig. 4a). First, a $Ca_3Co_4O_9$ target was ablated by the pulsed laser, resulting in $Ca_3Co_4O_9$ film deposition. The film had a thickness distribution, the center of which was away from that of the substrate. The substrate was then rotated 120° and a

$(SrCa_2)Co_4O_9$ film was deposited. The substrate was rotated yet another 120° and a $(LaCa_2)Co_4O_9$ film was deposited. This process was repeated 360 times to obtain the desired thickness for the film library, suitable for characterization. Fig. 4b and c show the inverse of resistance and Seebeck coefficient, mapped for the $(Ca_{1-x-y}Sr_xLa_y)_3Co_4O_9$ film library, respectively. The substitution of La for Ca results in an increase of both resistance and Seebeck coefficient that could be attributed to the decrease of hole concentration resulting from the substitution of a trivalent for a divalent cation [11]. The substitution of Sr for Ca, on the other hand, results in a resistance decrease that is consistent with reported results for bulk samples [12]. The total combined fabrication and measurement time of the present ternary-composition-spread film was about 14 h (8 h and 6 h, respectively). This is a much more efficient approach for composition screening as compared to conventional approaches using bulk.

4. Conclusion

We have constructed a new high-throughput thermoelectric screening tool for combinatorial thin film libraries. Using the $(Ca_{1-x-y}Sr_xLa_y)_3Co_4O_9$ ternary-natural-composition-spread film as a demonstration, we have shown that this new tool has the capability of measuring 1080 resistance and Seebeck coefficient data points in the relatively short timeframe of 6 h. We conclude that a combination of the composition-spread method and the screening tool will lead to an acceleration of thermoelectric materials research.

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