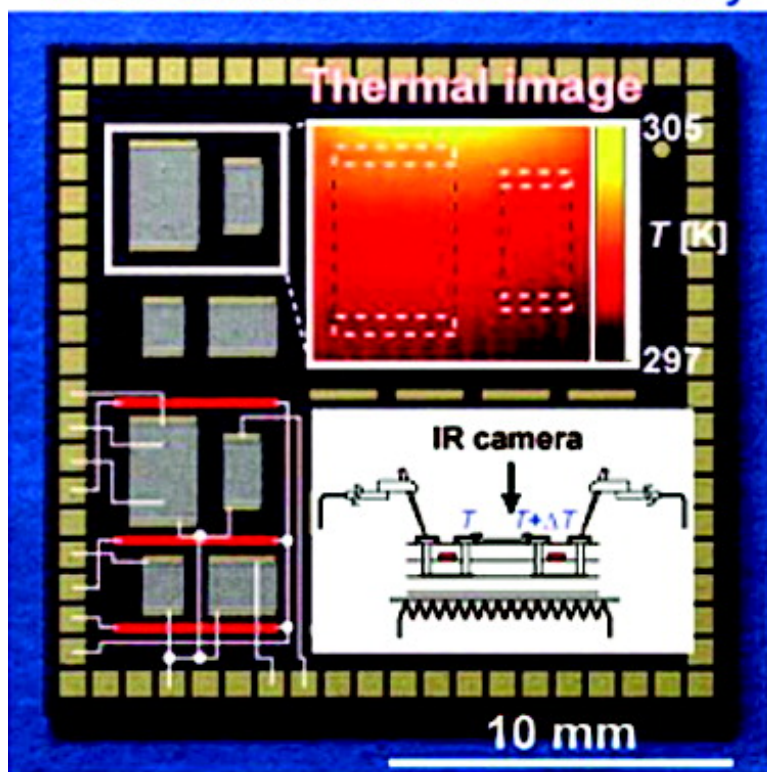## Article

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High-Throughput Screening for Combinatorial Thin-Film Library of Thermoelectric Materials

Masaki Watanabe,[†] Takuji Kita,[†] Tomoteru Fukumura,[‡] Akira Ohtomo,[‡] Kazunori Ueno,[‡] and Masashi Kawasaki*,[‡,§]

Toyota Motor Corporation, Toyota 471-8571, Japan, Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan, and WPI Advance Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Received June 12, 2007

A high-throughput method has been developed to evaluate the Seebeck coefficient and electrical resistivity of combinatorial thin-film libraries of thermoelectric materials from room temperature to 673 K. Thin-film samples several millimeters in size were deposited on an integrated Al_2O_3 substrate with embedded lead wires and local heaters for measurement of the thermopower under a controlled temperature gradient. An infrared camera was used for real-time observation of the temperature difference ΔT between two electrical contacts on the sample to obtain the Seebeck coefficient. The Seebeck coefficient and electrical resistivity of constantan thin films were shown to be almost identical to standard data for bulk constantan. High-throughput screening was demonstrated for a thermoelectric Mg−Si−Ge combinatorial library.

Introduction

Thermoelectric materials have been of great interest because of increasing technological demands for energy conversion between heat and electricity. However, the thermoelectric conversion efficiency is severely limited even when using state-of-the-art thermoelectric materials. Therefore, high-performance materials are urgently needed.[1] Recently, studies have focused on raising the thermoelectric figure of merit $\alpha^2/(\rho\,\kappa)$ that dominates the conversion efficiency (α = Seebeck coefficient, ρ = electrical resistivity, κ = thermal conductivity). Since such efforts including bulk synthesis and evaluation of the thermoelectric properties are time-consuming, the combinatorial approach is considered a powerful tool to explore thermoelectric materials.

Combinatorial methods have already been developed for the synthesis of inorganic materials.[2–5] For thermoelectric materials, several combinatorial studies have been performed using custom-made screening tools.[6,7] The difficulty in screening was the quantitative evaluation of α, which usually requires both electrical and thermal contacts with the sample, together with a well-controlled temperature gradient to produce thermopower.

In this study, we developed a high-throughput screening method for measuring the thermoelectric properties of a combinatorial thin-film library. We used an infrared (IR) camera to observe the temperature distribution of the library because this technique has been successfully used to search for catalysts via exothermic reactions.[8,9] The library was fabricated on a custom-developed integrated Al_2O_3 substrate
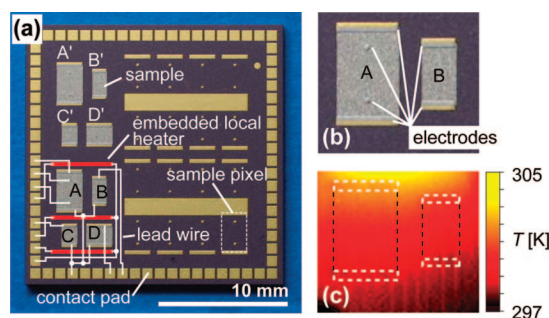

Figure 1. (a) Photograph of an integrated Al_2O_3 substrate having eight constantan thin films (samples A−D and A′−D′ in gray) on the left side and 16 blank sample areas on the right side (represented by a white dashed square). The sizes of samples A−D are 3 mm × 2 mm, 2.5 mm × 1 mm, 1.5 mm × 1 mm, and 1.5 mm × 2 mm, respectively. Four electrodes in sample A, two electrodes in samples B−D, and embedded local heaters (red lines) are connected with contact pads at the substrate edges via embedded lead wires (white lines). (b) Close-up view of samples A and B. (c) A typical thermal image of the same area as in b during operation of the local heater.

with embedded lead wires and local heaters for measurement of α and ρ. First, we evaluated α and ρ for a constantan thin-film library consisting of four different sizes from room temperature to 673 K to test the capability of our method. Second, we evaluated α and ρ for an $Mg_xSi_yGe_{1-y}$ ($2.3 \leq x \leq 4.1$, $0.45 \leq y \leq 1$) thin-film library consisting of 16 samples in the same temperature range. The composition range is close to that of well-characterized $Mg_2Si_yGe_{1-y}$ ($0 \leq y \leq 1$) solid solutions possessing moderate thermoelectric properties in the temperature range of 500–800 K.[10–12]

Experimental Section

Constantan Thin-Film Library. Constantan thin films of 0.2 μm thickness were deposited using the pulsed laser

Table 1. Compositions of Each $Mg_xSi_yGe_{1-y}$ Sample Measured by Electron Probe Microanalysis

composition	1			2			3			4		
	x	y	$1-y$	x	y	$1-y$	x	y	$1-y$	x	y	$1-y$
A	3.8	0.49	0.51	3.5	0.47	0.53	2.8	0.50	0.50	2.4	0.45	0.55
B	3.5	0.69	0.31	3.2	0.66	0.34	2.8	0.67	0.33	2.6	0.63	0.37
C	4.1	0.84	0.16	3.2	0.85	0.15	2.8	0.81	0.19	2.3	0.81	0.19
D	3.4	0.94	0.06	3.5	0.97	0.03	2.7	0.96	0.04	2.5	0.97	0.03

deposition method; the films were grown on an integrated Al_2O_3 substrate (designed by us and manufactured by Kyocera Corp.) through a stencil mask by ablation of a constantan (Cu 55.41 wt %, Ni 43.55 wt %, Mn 1.04 wt % alloy) target with 248 nm KrF excimer laser pulses (6.0 J cm^{-2}). The thin films were grown at room temperature in an ultrahigh-purity Ar-H_2 (1%) gas at a pressure of 6.7×10^{-3} Pa and annealed for 20 min at 773 K in the flow of the same Ar-H_2 gas for crystallization. After the samples were annealed, the sample surface was coated with a blackbody paint (emissivity $= 0.94 \pm 0.009$) to enable reliable thermal imaging.

The substrate with the samples was placed on a common heating stage to control the temperature in a vacuum probing system. Electrical contacts for measurement of α and ρ were made with probes placed on contact pads at the edges of the substrate, where the contact pads were connected to each sample via the embedded lead wires as shown in Figure 1a. Sample A had four electrodes for measurement of α and ρ, and samples B−D had only two electrodes for measurement of α (Figure 1b). ρ was measured by a conventional four-

probe configuration by application of a typical current of 1 mA with both current polarities. For the measurement of α, the embedded local heaters in the substrate were fed with currents (typically 0.1–0.4 A) through the contact pads to produce a temperature difference, ΔT, within each sample. It is noted that the substrate is inexpensive (several tens of dollars per piece) and disposable because mass production is possible.

Temperature measurements were performed by thermal imaging with an IR camera (Nippon Avionics Co., Ltd., TVS-8500) detecting IR emissions of 2–5 μm from outside the vacuum probing system through a CaF_2 window with temperature and spatial resolutions of <0.025 K and 0.1 mm, respectively. A typical thermal image is shown in Figure
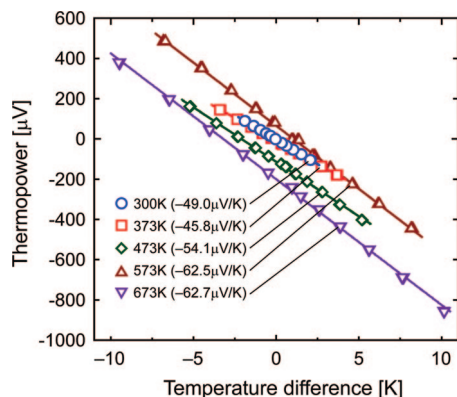
Figure 4. (a) Seebeck coefficients of the constantan thin films (samples A−D) (α_{sample}) and the lead wire (α_{lead}). (b) Electrical resistivity of the constantan thin film (sample A) (ρ) as a function of temperature. Standard data from the bulk specimen (filled triangles) are also plotted.[14] The horizontal error bars indicate the accuracy of absolute temperature evaluated by the IR camera. Note that the accuracy of ΔT is much better because of the subtraction between the data in a same thermal image, yielding in negligible errors in the values of Seebeck coefficient.

Figure 2. Thermopower (V_{meas}) as a function of temperature difference (ΔT) at various temperatures. Solid lines are least-squares fits of the data. The Seebeck coefficient (α_{meas}) at each temperature is also shown.
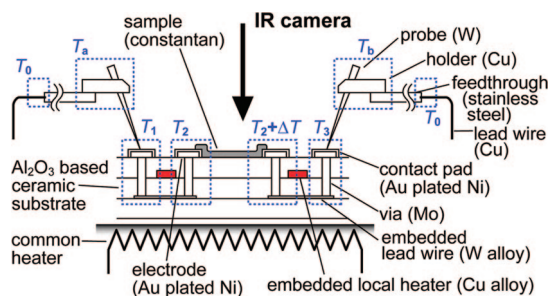
Figure 3. Schematic experimental configuration for measuring the Seebeck coefficient and electrical resistivity. T_0 is room temperature; T_a and T_b are the temperatures at the connections between the probe holder and the probe needle, and T_1, T_2, and T_3 are the temperatures at the contact pads and the sample electrodes.
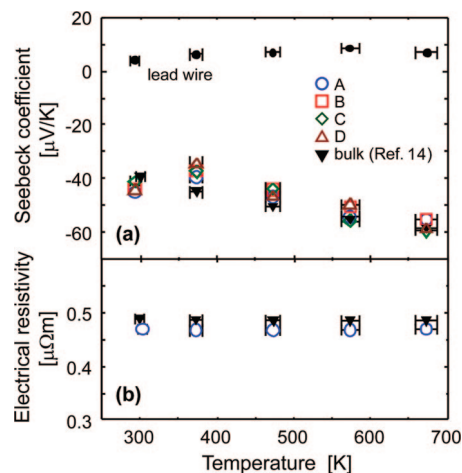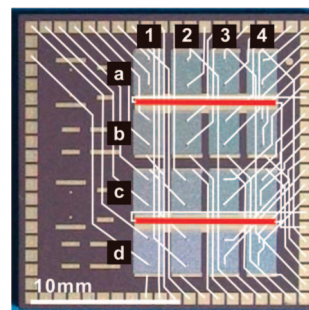
Figure 5. Photograph of the Mg−Si−Ge library consisting of 16 thin-film samples on an integrated Al_2O_3 substrate. The size of each sample is 3 mm × 2 mm. The characters (a−d and 1−4) address each sample in Table 1 and Figure 6. Local heaters (red lines) and lead wires (white lines) are embedded.
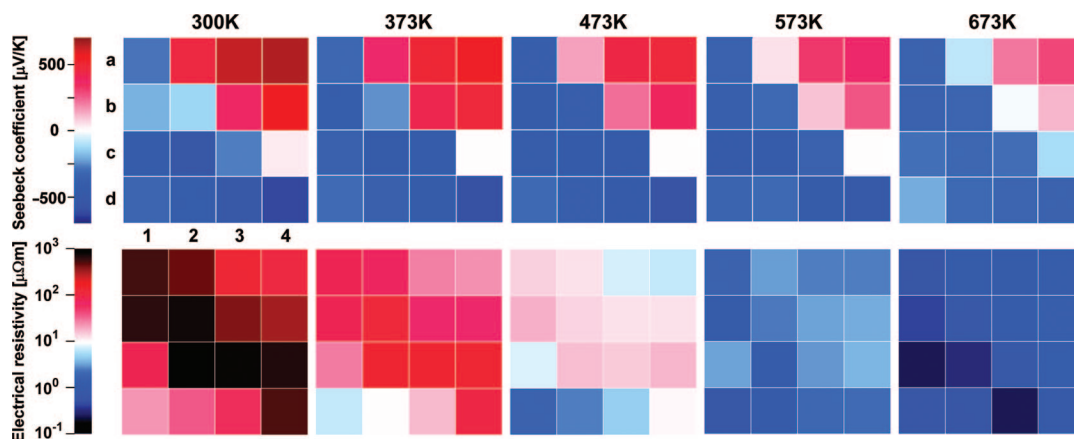
Figure 6. Compositional dependence of the Seebeck coefficient (α) and electrical resistivity (ρ) at different temperatures for the Mg−Si−Ge library. Characters a−d (column) and 1–4 (row) correspond to locations in Figure 5.

1c. All measurements of α were performed for four samples A−D with different dimensions to ensure sample size independence.

Mg−Si−Ge Thin-Film Library. Two $Mg_xSi_yGe_{1-y}$ ($2.3 \leq x \leq 4.1$, $0.45 \leq y \leq 1$) thin-film libraries of 0.2 μm thickness were fabricated on an integrated Al_2O_3 substrate and a BN substrate by the pulsed laser deposition method and annealed for an hour at 673 K in a flow of Ar-H_2 (1%) gas. One library consisting of 16 samples was fabricated on the right side of the integrated Al_2O_3 substrate (Figure 5) to measure α and ρ. Another library was fabricated on the BN substrate to evaluate the composition of each sample by electron probe microanalysis because the boron nitride substrate consisted of elements lighter than Mg, Si, and Ge, enabling quantitative measurement of the composition. The samples on the integrated Al_2O_3 substrate were analyzed by X-ray diffraction (Bruker D8 Discover with GADDS). Thermoelectric measurements were performed as described above.

Results

Constantan Thin-Film Library. Figure 2 shows the measured thermopower V_{meas} versus ΔT curves at various temperatures, where ΔT was evaluated from the thermal image by taking the difference of the temperatures averaged over each electrode corresponding to the white dashed squares in Figure 1c. At each temperature, V_{meas} is almost proportional to ΔT. The linearity indicates the proper evaluation of ΔT in this range; however, it is noted that the slope is not identical to α of the sample as described below. Hence the slope is called α_{meas} hereafter. A sizable offset of V_{meas} at $\Delta T = 0$ for higher temperature is attributed to the thermopower of various parts other than the sample, which are independent of ΔT and thus are irrelevant to α_{meas}.

In our experimental setup, the sample is connected in series to various materials, including lead wires (Cu), a probe holder (stainless steel), a probe needle (W), electrodes and contact pads (Au plated Ni), vias (Mo), and embedded lead wires (W alloy). Therefore, V_{meas} is the sum of the thermopower of each component. Provided that these materials are homogeneous and that the tem-

perature at each connection is defined as shown in Figure 3, V_{meas} is expressed as[13]

$$V_{meas} = \int_{T_0}^{T_a} \alpha_{holder}(T)dT + \int_{T_a}^{T_1} \alpha_{probe}(T)dT +$$
$$\int_{T_1}^{T_2} \alpha_{lead}(T)dT + \int_{T_2}^{T_2+\Delta T} \alpha_{sample}(T)dT +$$
$$\int_{T_2+\Delta T}^{T_3} \alpha_{lead}(T)dT + \int_{T_3}^{T_b} \alpha_{probe}(T)dT + \int_{T_b}^{T_0} \alpha_{holder}(T)dT \quad (1)$$

where T_0 is room temperature, T_a and T_b are the temperatures at the connections between the probe holder and the probe needle, T_1, T_2, and T_3 are the temperatures at the contact pads and the sample electrodes (see Figure 3), and $\alpha_k(T)$ is the Seebeck coefficient of each segment k. Since $T_2 - T_1$, $T_2 - T_3$, and ΔT are as small as a few Kelvin, $\alpha_{lead}(T)$ and $\alpha_{sample}(T)$ are approximately proportional to the temperature. This approximation simplifies eq 1 as follows

$$V_{meas} = \alpha_{lead}\left(\frac{T_1+T_2}{2}\right)(T_2 - T_1) + \alpha_{sample}(T_2 +$$
$$\Delta T/2)\Delta T + \alpha_{lead}\left(\frac{T_2+\Delta T+T_3}{2}\right)(T_3 - T_2 - \Delta T) +$$
$$\left(\int_{T_0}^{T_a} \alpha_{holder}(T)dT + \int_{T_a}^{T_1} \alpha_{probe}(T)dT + \int_{T_3}^{T_b} \alpha_{probe}(T)dT +$$
$$\int_{T_b}^{T_0} \alpha_{holder}(T)dT\right) \quad (2)$$

As can be seen from eq 2, the thermopower contributions from the lead wires, probes, and probe holders do not cancel out if the temperature distribution is asymmetric, that is , if $T_a \neq T_b$, $T_1 \neq T_2$, or both, leading to a finite offset of V_{meas} at $\Delta T = 0$ as seen in Figure 2. However, only differentiation of V_{meas} with respect to ΔT is necessary to evaluate α_{meas}. Hence, α_{meas} is expressed as

$$\alpha_{meas} = dV_{meas}/d(\Delta T) = \alpha_{sample}(T_2 + \Delta T/2) - \alpha_{lead}$$
$$\left(\frac{T_2+\Delta T+T_3}{2}\right) \quad (3)$$

Thus, α_{meas} obtained from Figure 2 is attributed to the difference in α between the sample α_{sample} and the lead wire α_{lead}; α_{lead} is evaluated from $dV_{lead}/d(\Delta T)$ by measuring the thermopower V_{lead} between the electrode at $T_2 + \Delta T$ and the adjacent contact pad at T_3.

Figure 4a shows the temperature dependence of α_{lead} and α_{sample} for the samples A−D. α_{sample} was deduced from eq 3,

where $T_2 + \Delta T/2$ and $(T_2 + \Delta T + T_3)/2$ were approximated by T_2 because of the small temperature dependence of α_{lead} and the difference between T_2 and T_3 being as small as a few Kelvin. α_{lead} is less than $10\ \mu$V K^{-1} at each temperature, whereas the amplitude of α_{sample} is 4–6 times larger than that of α_{lead} and shows weak temperature dependence: from -45 μV K^{-1} at 300 K to -58 μV K^{-1} at 673 K. The value of α_{sample} for this temperature range shows good agreement with the standard data for bulk constantan.[14] Figure 4b shows the temperature dependence of ρ for sample A, which is nearly independent of temperature, and also shows good agreement with the standard data.[14]

Mg−Si−Ge Thin-Film Library. X-ray diffraction patterns of the films only showed peaks of the polycrystalline $Mg_2Si_yGe_{1-y}$ phase without Mg, Si, and Ge phases in all of the samples in the library. Table 1 shows the composition of thin-film samples in the library (see Figure 5). The Mg contents were four different values from ~4 to ~2.5 (from column 1 to column 4), and the Si contents were varied from Si/Ge ~1 to Si-rich (from row a to row b). Figure 6 shows the measured α and ρ of the library at different temperatures. The α is *p*-type in the Ge-rich region and *n*-type in the Mg- and Si-rich regions at each temperature, and the amplitude decreases with increasing temperature. The ρ rapidly decreases as temperature increases and shows a discernible trend with composition at higher temperatures. Whole measurements to evaluate both the α and ρ at these different temperatures took only 4 h so that our measurement system will be useful for exploration of thermoelectric materials.

Conclusion

A high-throughput method has been developed to evaluate the Seebeck coefficient and electrical resistivity of combi-natorial thermoelectric thin-film library. Noncontact temperature measurement was performed by thermal imaging with an IR camera, and sample integration was achieved by using a custom-made substrate with embedded lead wires and local heaters to control the temperature gradient. Quantitative and high-throughput measurements of the Seebeck coefficient and electrical resistivity were successfully demonstrated.

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