Feasibility Study of Thin Film Thermocouple Piles
(MSFC Center Director’s Discretionary Fund Final Report, Project No. 99–41)

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April 2001
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Acknowledgments

This work was supported by funding from the National Aeronautics and Space Administration Center Director’s Discretionary Fund at Marshall Space Flight Center.

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1. INTRODUCTION

A thermocouple circuit is formed when two dissimilar metals or semiconductors joined by wires on each end form a closed loop, as shown in figure 1. When one end is heated, a continuous current flows in the circuit that is proportional to the temperature difference and composition of the junction. If this circuit is broken in the middle, the Seebeck voltage is expressed across the open leads to the junction. Thomas Seebeck discovered this effect in 1823 by observing compass needle movements near the circuit, indicating current flow in the wires. 1 The Seebeck coefficient, a material property, relates this voltage output to junction temperature and is given in volts per degree Celsius. The voltage produced from a single, metal thermocouple is commonly used to measure temperature over large ranges. Typical Seebeck coefficients for dissimilar metal junctions range from 6 to 40 μV/°C while semiconductors may have Seebeck voltages in the hundreds of microvolts per degree. A thermocouple pile or thermopile makes use of many single thermocouples joined in series or parallel combinations to increase overall output from the available heat source.

![Diagram of thermocouple circuit](image)

Figure 1. The Seebeck effect is observed when the junctions in a closed loop formed by two dissimilar metals or semiconductors are at different temperatures.
Published information from literature searches revealed thin films as electrical generators have been investigated as early as 1965.\textsuperscript{2} Limited success with vacuum-deposited thin films for very small DC power supplies had occurred as early as 1972. Several cardiac pacemaker batteries using thermoelectric tapes and junctions have been developed by manufacturers utilizing a radioactive heat source generating power from 3 to 600 $\mu$W. A silicon-on-sapphire technique was also demonstrated using ion implantation to form the thermopile junctions and was patented in 1988.\textsuperscript{3} Fabrication of thermopile devices in the milliwatt power range is well developed but usually powered by a radioisotopic energy source and may have restricted use. The pressure to develop localized power sources in the microwatt range for the microelectromechanical systems (MEMS) revolution will continue to drive advances in the thermoelectric power generation arena.\textsuperscript{4}
2. APPROACH

A thermocouple pile or thermopile makes use of many single thermocouples joined in series or parallel combinations to increase overall output from the available heat source. Even though the use of thin films as thermoelectric generators does not appear to have widespread use today, the potential use will increase as a result of advancing MEMS technology. Power outputs of only microwatts could be utilized in nanotechnology applications.

The first design arranges the thin film hot junctions at the center of a spoked-wheel pattern and the cold junctions around the rim. Thermoelectric voltage is produced when the center junctions are heated. The heat is supplied by closed-cycle water heaters/refrigerators in the laboratory for testing purposes, but focused solar energy or any other suitable waste heat could be used in a real application. Several of these thin thermopile discs could be physically stacked and connected electrically in parallel to enhance output.

The photolithography masks used in the patterning for the spoked-wheel circuit were designed with Adobe® Illustrator® and printed on clear film with an Epson Stylus Pro® printer. Two masks shown in figure 2 were used to form the bilayer thermocouple pile pattern. One-inch-square Corning 7059 glass was first radio frequency (rf) sputter coated with a 3,500-Å copper thin film over the complete surface. The film was “spin coated” with a Shipley® positive type photoresist for 20 sec at 8,000 revolutions/sec. Step 3 in figure 3 shows the resulting pattern after the initial mask exposure in a Kepro® ultraviolet exposure frame and development with Shipley photoresist developer. Exposure times ran =3 min with development times of 20 sec in a 50:50 mix of distilled water and developer. The remaining photoresist will protect the copper underneath while the unprotected areas are chemically removed. This photoresist pattern was etched in a very weak solution of ferric chloride, revealing the copper pattern in figure 3, step 4. The copper pattern was then spun coated again with the same type resist (fig. 3, step 5) and exposed with the complementary mask in figure 2. Careful registration between the mask and existing pattern was done with a × 10 magnifier. After the second exposure and development, the substrate was placed back in the rf sputter chamber for the nickel coating. A nickel film thickness of 815 Å overcoated the complete surface as shown in figure 3, step 6. The nickel-coated photoresist was removed (lifted off) while submerged in acetone for several minutes. Figure 3, step 7 shows the final copper-nickel thermocouple pile with 48 junctions ready for testing. A thin film copper/indium-tin oxide and a silicon/germanium thermopile were fabricated with the same design.
Figure 2. Spoked-wheel pattern photolithography masks.

Figure 3. Thin film thermopile fabrication steps.

**Fabrication Steps:**
- Step 1: Thin film deposition
- Step 2: Spin coat resist
- Step 3: Expose and develop first pattern
- Step 4: Etch pattern
- Step 5: Spin coat resist
- Step 6: Thin film deposition
- Step 7: Lift-off
The test fixture shown in figure 4 maintains a temperature difference across the thermopile by controlling the temperature of two separate circulating water solutions through the heat source and sink. The thermopile center junctions are heated from below by a stinger protruding upward from the heat source. The outer junctions are cooled by inside contact with the recessed heat sink. During testing the temperature of the cold and hot junctions are recorded along with the voltage and current output of the thermopile as a function of time. An automated data acquisition system acquires and stores all pertinent information for later analysis. Typical no-load thermopile voltage and short-circuit current plots are shown in figures 5 and 6.

A second design was fabricated, using similar techniques, to reduce the large series electrical resistance inherent in the spoked-wheel design. A schematic of the design and a microphotograph of the device can be seen in figure 7. The metal thin film conductors join the alternating p-type (positive) and n-type (negative) thin film semiconductor junctions. The electrical resistance path is lowered since electrical current flows along good metal interconnects and only through the thickness of the higher resistance junctions. When there is a temperature difference between the two heat sinks, the thermal voltage generated by each junction is added together.
Figure 5. Typical thermopile voltage output from test fixture.

Figure 6. Typical thermopile current output from test fixture.
Figure 7. A schematic and × 10 microphotograph of the short interconnect thin film thermopile design.
3. RESULTS

Power output for the spoked-wheel design is 0.5 pW into a 1-Ω load. The large electrical resistance of the conducting path between the hub and rim of several thousand ohms and low Seebeck coefficient materials prevents the device from producing useful amounts of power. This design was fabricated with other materials, including indium-tin oxide, silicon, and germanium. The higher voltages produced in semiconductor versions of this design were offset by higher electrical resistance along the current path. This high-resistance series path is undesirable and was reduced to 600 Ω in a second design (fig. 7). During testing it was discovered that temperature gradients of only a few degrees could be established across the thin film junctions of silicon and germanium. It is desirable for the thermal conductance through the junction to be small. This design suffers from high thermal conductance through the few thousand angstroms-thick junctions. Sufficient temperature gradients could not be established across the junctions to produce measurable power.
4. CONCLUSIONS

Thin film thermopile geometries were successfully fabricated utilizing rf sputtering and photo-resist lift-off techniques. Power output from these devices falls well below any usable values of power by orders of magnitude. These designs suffer from high internal electrical resistance in the spoked-wheel design and high thermal conductance in the short interconnect design. Designs to improve these shortcomings may include thicker films beyond the capability of rf sputtering, clever multilayer geometries, and incorporating newer materials as they are discovered.
REFERENCES


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M-1013

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NASA/TM—2001–210963

Prepared by Microgravity Science and Applications Department, Science Directorate

Historically, thermopile detectors, generators, and refrigerators based on bulk materials have been used to measure temperature, generate power for spacecraft, and cool sensors for scientific investigations. New potential uses of small, low-power, thin film thermopiles are in the area of microelectromechanical systems since power requirements decrease as electrical and mechanical machines shrink in size.

In this research activity, thin film thermopile devices are fabricated utilizing radio frequency sputter coating and photoresist lift-off techniques. Electrical characterizations are performed on two designs in order to investigate the feasibility of generating small amounts of power, utilizing any available waste heat as the energy source.