Thermoelectric microdevice fabricated by a MEMS-like electrochemical process

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Microelectromechanical systems (MEMS) are the basis of many rapidly growing technologies, because they combine miniature sensors and actuators with communications and electronics at low cost. Commercial MEMS fabrication processes are limited to silicon-based materials or two-dimensional structures. Here we show an inexpensive, electrochemical technique to build MEMS-like structures that contain several different metals and semiconductors with three-dimensional bridging structures. We demonstrate this technique by building a working microthermoelectric device. Using repeated exposure and development of multiple photoresist layers, several different metals and thermoelectric materials are fabricated in a three-dimensional structure. A device containing 126 n-type and p-type $(Bi, Sb)_2Te_3$ thermoelectric elements, 20 μm tall and 60 μm in diameter with bridging metal interconnects, was fabricated and cooling demonstrated. Such a device should be of technological importance for precise thermal control when operating as a cooler, and for portable power when operating as a micro power generator.

Electrochemical MEMS allows the incorporation of a greater variety of materials, particularly metals and semiconductors, into devices. Most MEMS devices are made only from materials compatible with silicon integrated circuit processing, such as silicon, silicon dioxide and silicon nitride. Although numerous MEMS devices are used in the automotive, communications and chemical industries[1], and their influence is expected to grow with the increased interest in micromachines for optoelectronics and biotechnology, the processing limits the number of materials that can be used, and therefore limits their functionality. In electrochemical deposition (ECD), dissolved species are deposited as a film by reduction at a conducting surface. A non-conducting mould is used to guide the deposition only onto select areas. This allows the fabrication of tall structures (and high aspect ratios) from a variety of electrically conducting materials without deep etching.

The most used method of electrochemical MEMS is referred to as LIGA after the German words for lithography, electroplating and moulding[2]. Synchrotron X-ray radiation is typically used in LIGA to produce high-aspect-ratio moulds, around which the electrodeposited material is formed. After removing the mould, the resulting structures can be used to produce additional moulds for injection moulding. The cost and complication of using synchrotron radiation has lead to the development of methods that use ultraviolet lithography and commercial photoresist (UV-LIGA) to pattern the initial moulds.

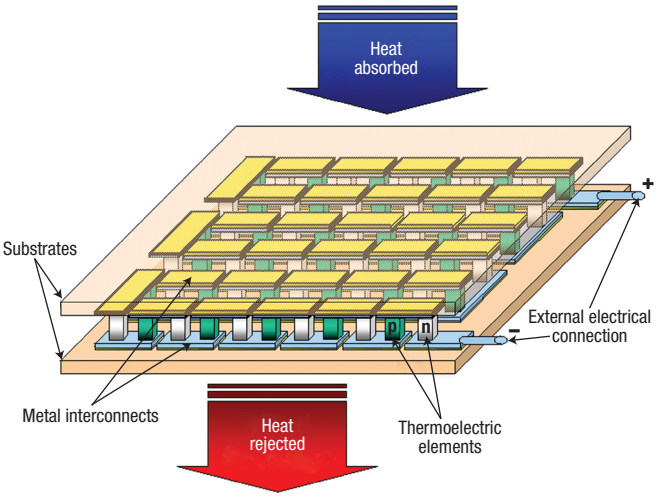


Figure 1 A typical thermoelectric device. Both n-type and p-type $(Bi, Sb)_2Te_3$ thermoelectric elements are sandwiched between two high-thermal-conductivity substrates. With alternating top and bottom interconnects, the n- and p-type elements are connected sequentially in series. The heat flow is from the top substrate to the bottom, making all thermoelectric elements thermally in parallel. In cooling mode, an externally applied current forces the heat to flow from the top to the bottom. In power-generation mode, heat flowing from the top to the bottom drives a current through an external load.

Using standard LIGA techniques, only tall two-dimensional structures can be produced. For structures with bridges or overhangs more than one level is required. By using a metal as a mould[3], multilevel structures can be produced with repeated electrochemical deposition and polishing. However, the metal mould cannot be modified once formed to allow structures with more than one material in a single layer, which is required in an efficient thermoelectric device.

Thermoelectric devices are used for both cooling and power generation[4]. The ideal thermoelectric device (shown schematically in Fig. 1) contains over one hundred n–p couples connected electrically in series, but thermally in parallel between two planar surfaces. When used for cooling, an electric current in the thermoelectric device produces a temperature difference between these two surfaces because of the Peltier effect. For power generation, a temperature difference between the surfaces drives electrical power through the

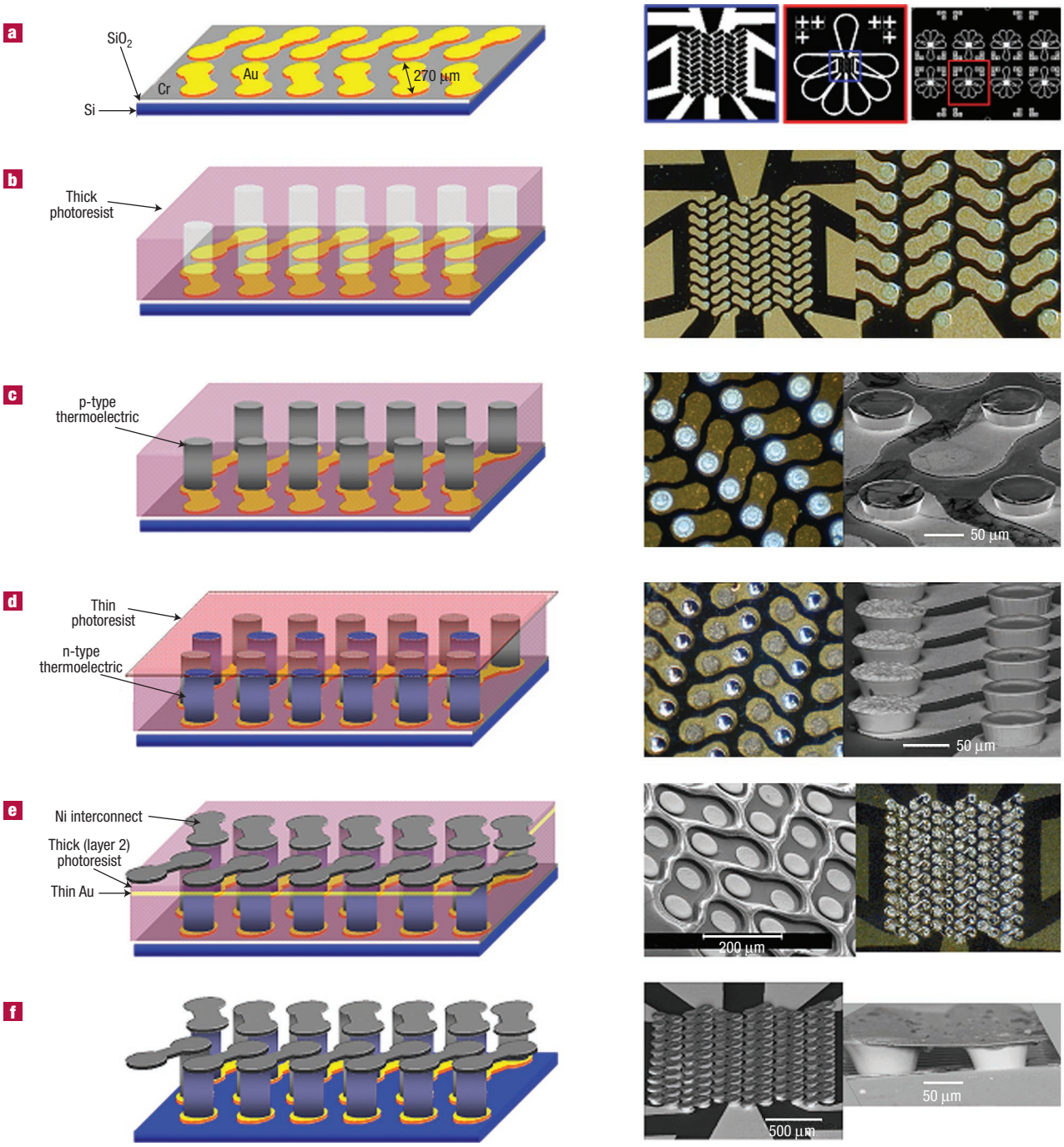


Figure 2 Electrochemical MEMS fabrication steps for thermoelectric microdevice. Illustrations are shown on the left, and optical and SEM images on the right. **a**, Bottom interconnect pattern of 3-μm-thick Au pads on oxidized Si sputtered with a 0.1-μm-thick layer of Cr. The mask pattern is shown (with zoom out to show entire device and batch of eight) on the right. **b**, Thick positive photoresist with one set of holes developed. **c**, First set of thermoelectric elements electrochemically deposited in openings. Images are of p-type Sb_2Te_3 from above and close-up with the photoresist removed. **d**, A thin positive photoresist covers the first set of elements before the second set is exposed and developed. Close-up image shows both n-type and p-type elements on interconnects (photoresist removed). **e**, The thin photoresist from the previous step is removed, thin Au film is sputtered for uniform electrical connection, and then the top interconnect pattern is formed with a second layer of thick photoresist. The photographs show the surface before and after the top Ni interconnects are deposited. **f**, The completed device after sequential removal of the top photoresist, the thin Au film, the thick photoresist and finally, Cr was etched to electrically isolate the bottom interconnects. Photographs show the entire structure and a close-up of a 40-μm-tall couple.

circuit due to the Seebeck effect. Because the Peltier and Seebeck effects are directly related, the best materials for thermoelectric cooling are also optimized for power generation. Near room temperature, the most efficient materials are heavily doped p-type and n-type $(Bi, Sb)_2Te_3$. Remarkably high efficiency has been demonstrated in nanostructured thermoelectric materials[5,6], but have not yet been fabricated into useful devices.

A viable thermoelectric microdevice therefore requires a structure difficult or impossible to produce with existing MEMS techniques. Most challenging are the two different types of tall, heavily doped compound semiconductors structured on the same surface. The thermoelectric elements must be connected electrically in series with bridging metal interconnects on both the top and bottom surface. These interconnects must maintain low contact resistance with high mechanical strength while operating at high current densities and temperature gradients. Such constraints have, up to now, limited thermoelectric microdevices to either in-plane devices (as opposed to the out-of-plane structure of Fig. 1), where the substrate will act as a thermal short that reduces performance, or to relatively large structures with a small number of thermoelectric elements[7].

Using a novel, low-cost electrochemical MEMS process, we have demonstrated these key requirements in a working thermoelectric microdevice with a configuration shown schematically in Fig. 1. Commercially available gold (Technic TG25E, –600 mV versus SCE) and nickel (Technic TechniS nickel sulphamate, –924 mV versus SCE) bath solutions are used for ECD of metals. Thermoelectric semiconductors Bi_2Te_3 (n-type) and Sb_2Te_3 (p-type) are deposited at room temperature from a nitric acid solution[8–10]. With multiple photoresist layers, true three-dimensional structures (overhangs and bridges) are fabricated. Repeated exposure and development of the photoresist allows two different thermoelectric elements to be deposited in the same layer.

Fabrication of thermoelectric microdevices uses a multistep process. The demonstration microthermoelectric device (Fig. 2) contains 126 thermoelectric elements 60 μm in diameter and 20 μm tall[10]. Because the resistance of two $(Bi, Sb)_2Te_3$ elements is about 0.14 Ω, the metal interconnects must be several micrometres thick to not contribute overwhelmingly to the device resistance. We use 3-μm-thick gold for the bottom interconnects and 3-μm-thick nickel for the top, which have resistances of about 0.02 Ω and 0.05 Ω respectively.

We use 400-μm-thick oxidized silicon as a substrate because of its high thermal conductivity and compatibility with integrated circuit and MEMS applications. The oxidation layer prevents electrical shorting of the bottom interconnects through the substrate. Onto the substrate is sputtered 0.1 μm Cr, 0.3 μm Au, and then a thicker 3 μm Au layer is deposited by ECD. Using commercial thin positive photoresist (Clariant AZ 1518) and simple transparency film mask, the regions for the bottom interconnects are protected and the surrounding Au is etched (iodine solution). The Cr layer remains and is thick enough to allow further ECD on the isolated Au interconnects (Fig. 2a).

The thermoelectric layer is formed using a 20-μm-thick photoresist mould of positive commercial photoresist (Shipley SJR5740). By aligning a glass mask, 60-μm-diameter holes are patterned on one end of each gold interconnect (Fig. 2b). The first set of thermoelectric elements (p-type Sb_2Te_3) is electrodeposited onto the top of the photoresist (Fig. 2c).

By performing the ECD under yellow light, the same photoresist is used for the second set of thermoelectric elements. First, a thin layer of positive photoresist is added to cover the p-type elements. Next, a second set of 60-μm-diameter holes is opened in the thick photoresist on the other end of the gold interconnects. Then the n-type Bi_2Te_3 elements are grown by ECD (Fig. 2d).

The top interconnects must be formed on a new photoresist layer to build a freestanding bridge between the n-type and p-type elements. First, the thin photoresist layer is selectively removed with a short flood exposure and development to expose the top of the p-type elements.

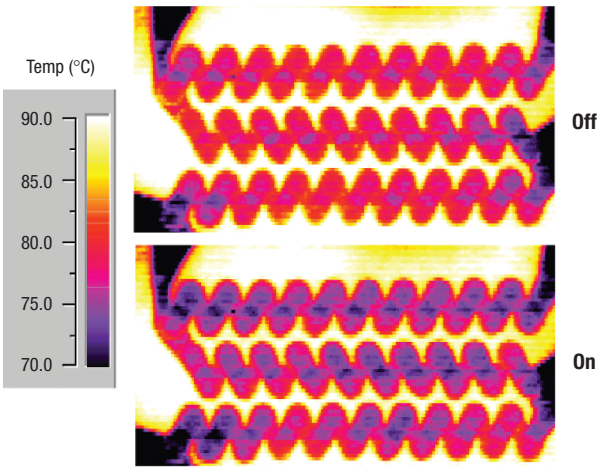


Figure 3 Split-screen thermal image of a thermoelectric microdevice functioning as a cooler. On (100 mA) and Off states of the same region are shown. Images were captured by an infrared camera.

To ensure uniform electrodeposition, the entire top surface is sputtered with a very thin layer (< 0.01 μm) of gold. A fast developing layer of positive photoresist (soft baked SJR5740) is used to form the top interconnect mould. About 3 μm of nickel is grown by ECD into the top interconnect mould (Fig. 2e). A low stress ECD process is used to ensure that the interconnects do not pull off the thermoelectric elements.

Having completed the ECD steps, the photoresist moulds and thin gold layer is removed in reverse order (Fig. 2f). Wet and dry etches and solvents are selected to prevent damage to neighbouring structures.

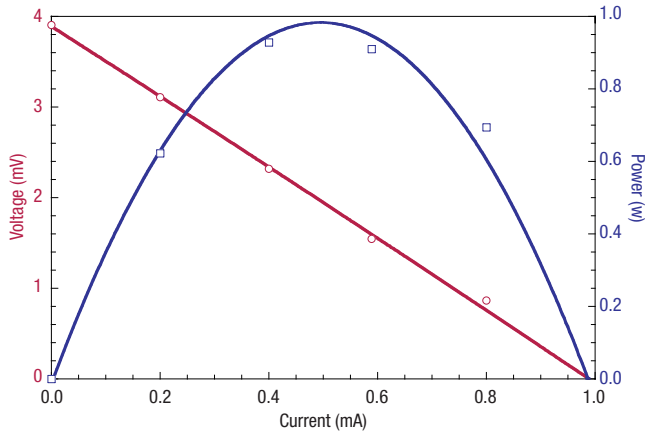
Before operation, samples are annealed in forming gas (7.2% H_2 in Ar) at 250 °C for 2 hours. Annealing improves the mechanical and electrical contacts between the thermoelectric elements and interconnects, and also improves the thermoelectric figure of merit[4] of the thermoelectric materials.

The final Cr etch (with $KMnO_4$ solution) electrically isolates the bottom interconnects. All 126 thermoelectric elements are electrically in series, but each of the six rows can be individually addressed with the seven external contacts.

Device performance was evaluated on a number of thermoelectric microdevices. Typical device resistances range from 12 to 30 Ω indicating that most of the resistance is due to the thermoelectric material, which should have a resistivity of about 1×10^{-3} Ωcm.

To demonstrate cooling, a device was mounted on a temperature-controlled heat sink in a vacuum chamber (~10^{-6} torr) and monitored with an infrared camera. For maximum resolution on the low-emissivity metallic surfaces, measurements were taken at 82 °C. A decrease in temperature on the top interconnects is clearly visible immediately after the application of a current (100 mA) (Fig. 3). The average temperature drop was 2 K for the optimal applied current of 110 mA and average resistance of 0.26 Ω per couple[10]. From these values we calculate that the heat flux at zero temperature difference was 7 W cm^{-2}.

To demonstrate power generation, the top interconnects were coated with black antimony telluride by ECD. The sample was then heated by illumination with a lamp (Fig. 4) and the voltage output measured as current was changed. As expected for a thermoelectric generator, the voltage decreases linearly, while the power output rises to a maximum (about 1 μW or 40 μW cm^{-2} for this sample) before decreasing. At zero load resistance the current produced is 1 mA or 40 mA cm^{-2}.



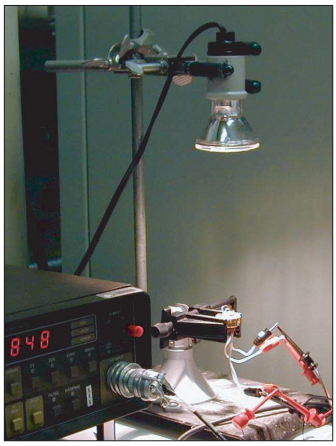


Figure 4 Voltage and power produced by a thermoelectric microdevice on illumination by a lamp.

The demonstrated cooling shows the functionality of electrochemical MEMS for building complex structures out of metals and semiconductors. With further optimization of the thermoelectric material, much larger temperature differences and heat fluxes are expected. Optimally doped $(Bi, Sb)_2Te_3$ has absolute thermopower of about 200 μV K^{-1} at room temperature. The electrodeposited material has the expected elemental composition and crystal structure, but the defect structure produces a high concentration of low mobility carriers such that the room-temperature thermopower is 40 to 100 μV K^{-1}. On achieving the thermoelectric properties of optimally doped $(Bi, Sb)_2Te_3$, temperature differences of 70 K are expected.

Microthermoelectric devices have inherent advantages that could revolutionize thermal management, power generation and heat-detection technologies. Certainly, the low cost of batch processing compared to state-of-the-art fabrication processes will be a driver for many applications. In addition, ECD allows the incorporation of thermoelectric nanostructures[8,11] to greatly enhance the thermoelectric efficiency[5,6].

The small size of microthermoelectric coolers can profoundly affect their performance. Shorter thermoelectric elements can in principle produce higher heat fluxes (greater than 100 W cm^{-2})[9,11]. Efficient thermoelectric elements must be taller[7] than about 10 μm due to the electrical resistance of contacts and thermal resistance of the substrate[9]. Shorter elements will also operate much faster, which can be exploited to allow temporary, enhanced cooling[12]. The small thermoelectric element pixel sizes will enable unprecedented resolution for thermal management, allowing dynamic control of the temperature profile for optoelectronics or lab-on-a-chip applications.

By connecting thousands of elements in a microthermoelectric generator, even small temperature gradients can be used to generate useful electric power. Small microcombustors[13,14] could use high-energy-density fuels to supply the heat to the thermoelectric. Even with low (3%) conversion efficiency, a combustor/thermoelectric generator will exceed the power density of lithium-ion batteries. The possibility to use waste heat from natural temperature gradients is particularly attractive. For example, thermoelectric wristwatches[15] convert body heat into electricity.

Because a thermoelectric is an efficient solid-state thermal-to-electric energy conversion device, it is also an excellent transduction method for heat detection[16]. A thermoelectric microdetector with many small thermoelectric couples individually addressed, can be used to create a sensitive infrared camera.

The electrochemical MEMS described in this paper allows the fabrication of complex, multifunctional metal and semiconductor parts at low cost. Dramatically increasing the number and variety of materials available for MEMS should aid the further development of the MEMS industry.

We have demonstrated the electrochemical MEMS technique by fabricating the first (standard configuration) thermoelectric microdevice with over 100 elements[7]. This process is easily scalable to batch-produce devices with thousands of thermoelectric elements at low cost. A micrometre-sized thermoelectric cooler will enable fast, reliable and integrated microthermal control for thermal sensors, labs-on-a-chip, and optoelectronics. Thermoelectric microdevices can also be used to power microelectronics with waste heat or in conjunction with microcombustors.

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Competing financial interests

The authors declare that they have no competing financial interests.