MEMS/ECD Method for Making $Bi_{2-x}Sb_xTe_3$ Thermoelectric Devices

Devices containing diverse materials in complex three-dimensional shapes can be fabricated.

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A method of fabricating $Bi_{2-x}Sb_xTe_3$-based thermoelectric microdevices involves a combination of (1) techniques used previously in the fabrication of integrated circuits and of microelectromechanical systems (MEMS) and (2) a relatively inexpensive MEMS-oriented electrochemical-deposition (ECD) technique. The devices and the method of fabrication at an earlier stage of development were reported in "Submillimeter-Sized $Bi_{2-x}Sb_xTe_3$ Thermoelectric Devices" (NPO-20472), *NASA Tech Briefs*, Vol. 24, No. 5 (May 2000), page 44. To recapitulate: A device of this type generally contains multiple pairs of n- and p-type $Bi_{2-x}Sb_xTe_3$ legs connected in series electrically and in parallel thermally. The $Bi_{2-x}Sb_xTe_3$ legs have typical dimensions of the order of tens of microns. Metal contact pads and other non-thermoelectric parts of the devices are fabricated by conventional integrated-circuit and MEMS fabrication techniques. The $Bi_{2-x}Sb_xTe_3$ thermoelectric legs are formed by electrodeposition, through holes in photoresist masks, onto the contact pads.

Heretofore, most MEMS have been made from materials compatible with silicon integrated-circuit processing, such as silicon, silicon dioxide, and silicon nitride. Moreover, commercial MEMS fabrication techniques have been mostly limited to structures of a substantially two-dimensional character. However, to be useful, thermoelectric microdevices must consist of a variety of materials (including metals and semiconductors), and complex, three-dimensional shapes are needed to effect the required series electrical and parallel thermal connections. In a typical case, the n- and p-type $Bi_{2-x}Sb_xTe_3$ thermoelectric legs must be connected electrically in series with bridging metal interconnections on top and bottom surfaces (see Figure 1). These interconnections are required to be have low contact resistance and high mechanical strength and must be capable of withstanding large current densities and temperature gradients. Most challenging is the requirement to form the p- and n-type tall, heavily doped compound semiconductor legs protruding from the same surface.
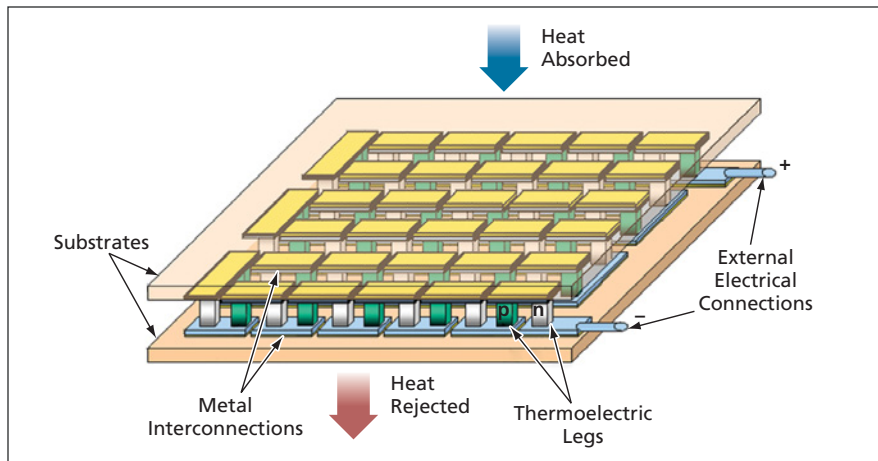

Figure 1. A **Typical Thermoelectric Device** includes multiple n-type and p-type thermoelectric legs sandwiched between two high-thermal-conductivity substrates. The n- and p-type legs are electrically connected in series by alternating top and bottom metal contact pads. Because heat flows from the top to the bottom, all of the thermoelectric legs are thermally connected in parallel. In the cooling mode, an externally applied current forces the heat to flow from the top to the bottom. In the power-generation mode, heat flowing from the top to the bottom drives an electric current through an external load.

The present method overcomes the limitations of prior MEMS fabrication techniques and makes it possible to satisfy the aforementioned requirements. The method is implemented in a process (see Figure 2) that includes the following main steps:

1. In a subprocess that includes sputtering, electrodeposition, photolithography, and etching, a bottom interconnection pattern of Au contact pads (typically 3 μm thick) is formed on a layer of Cr (typically 0.1 μm thick) that has been sputtered onto the oxidized upper surface of an Si substrate.
2. A photoresist having a thickness corresponding to the desired height of the thermoelectric legs is deposited, exposed, and developed to form through-the-thickness holes ending at those portions of the Au contact pads to which the p-type thermoelectric legs are to be bonded.
3. Sb_2Te_3 (p-type) thermoelectric legs are electrodeposited in the holes.
4. A thin layer of photoresist is deposited to cover the tops of the p-type thermoelectric legs.
5. Step 2 is repeated to form holes at the intended locations of Bi_2Te_3 (n-type) thermoelectric legs.
6. The n-type thermoelectric legs are deposited in the holes.
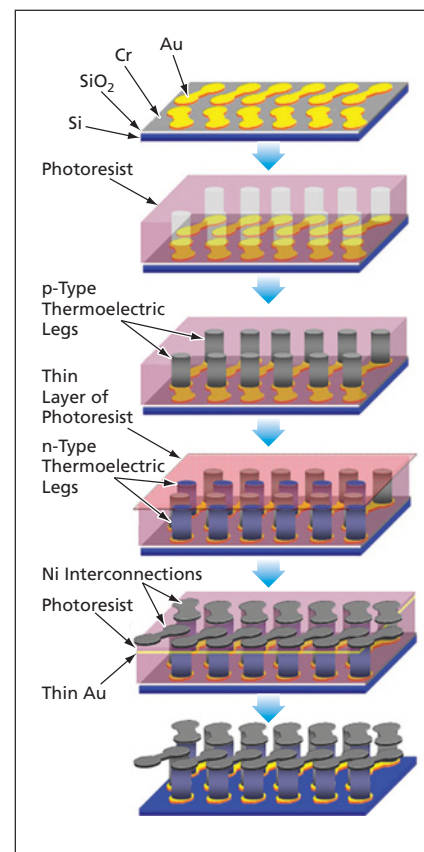

Figure 2. **Metal Interconnections and Thermoelectric Legs** constituting a three-dimensional structure are formed in a multi-step process.

7. The thin top photoresist layer deposited in step 4 is removed.
8. A partly sacrificial layer of gold <0.01 µm thick is deposited to ensure uniform ECD in step 10.
9. A thicker top photoresist layer is deposited and patterned to form a mold for a top interconnection pattern of Ni contact pads.
10. The Ni contact pads, typically 3 µm thick, are electrodeposited in the holes in the mold. The electrodeposition parameters are chosen to keep stresses in the pads low so that the pads do not pull off the thermoelectric legs.
11. In a series of etches, the excess Cr between the bottom contact pads, the excess Au between the top contact pads, and the photoresist layers are removed.

A device containing 63 Bi_2Te_3 (n-type) and 63 Sb_2Te_3 (p-type) thermoelectric legs, each 20 µm tall and 60 µm in diameter, was fabricated by this method and demonstrated to be capable of thermo-electric cooling. This device can be considered a prototype of future devices for exerting precise thermal control in microscopic regions and for extracting small amounts of electric power from temperature gradients.

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Low-Temperature Supercapacitors

Electrolyte compositions are designed to extend the low-temperature operational limit.

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An effort to extend the low-temperature operational limit of supercapacitors is currently underway. At present, commercially available non-aqueous supercapacitors are rated for a minimum operating temperature of –40 °C. A capability to operate at lower temperatures would be desirable for delivering power to systems that must operate in outer space or in the Polar Regions on Earth.

Supercapacitors (also known as double-layer or electrochemical capacitors) offer a

Co-Solvent	freezing point, °C
ethyl acetate	-72.0
methyl formate	-71.0
methyl acetate	-70.0
1,3–dioxolane*	-67.9
triethylamine	-62.3
* with 2% by volume triethylamine stabilizer	

Freezing Point of electrolyte solvent formulations in a 3:1 by volume ratio of acetonitrile to co-solvent.

high power density (>1,000 W/kg) and moderate energy density (about 5 to 10 Wh/kg) technology for storing energy and delivering power. This combination of properties enables delivery of large currents for pulsed applications, or alternatively, smaller currents for low duty cycle applications. The mechanism of storage of electric charge in a supercapacitor — at the electrical double-layer formed at a solid-electrode/liquid-electrolyte interface — differs from that of a primary or secondary electrochemical cell (i.e., a battery) in such a manner as to impart a long cycle life (typically >10^6 charge/discharge cycles).

Commercially available non-aqueous supercapacitors are limited in operation to temperatures ≈–40 °C due to the relatively high melting point of the solvent used. Typical electrolytes in commercially available supercapacitors consist of a tetraethyl-lammonium tetrafluoroborate (TEATFB) salt dissolved in one or more solvent(s) that can include acetonitrile [AN (which freezes at –45.7 °C)] and/or propylene carbonate [PC (which freezes at –49 °C)]. Moreover, the viscosities of these solvents increase at lower temperatures, with a consequent increases in the equivalent series resistance (ESR) of the supercapacitor cell. This increase in ESR limits the power that can be delivered by the supercapacitor cell at low temperatures.

Therefore, efforts to enable operation at lower temperatures have focused on tailoring electrolytes with lower melting points (to extend the temperature range) and higher ionic conductivities and lower viscosities (to minimize increases in ESR). The approach followed thus far has targeted the use of co-solvents to depress the melting point of TEATFB/AN electrolytes while maintaining sufficient solubility of TEATFB at low temperature. These electrolytes are used in conjunction with appropriate electrode materials capable of exhibiting a suitable energy density.

The electrolytes investigated comprise the basic AN/TEATFB formulation in combination with various proportions of co-solvents that include methyl formate, methyl acetate, ethyl acetate, and 1,3-dioxolane (DX) (see table). Coin cells for evaluating the performance of these electrolytes have been fabricated using electrodes made of a commercially available high-surface-area porous carbon-based material. The electrodes were electrically isolated from each other by use of a polyethylene-based separator material. From measurements on these cells, it was concluded that the use of suitable co-solvents can enable retention, at temperatures <–45 °C, of room-temperature capacitance values. For one elec-
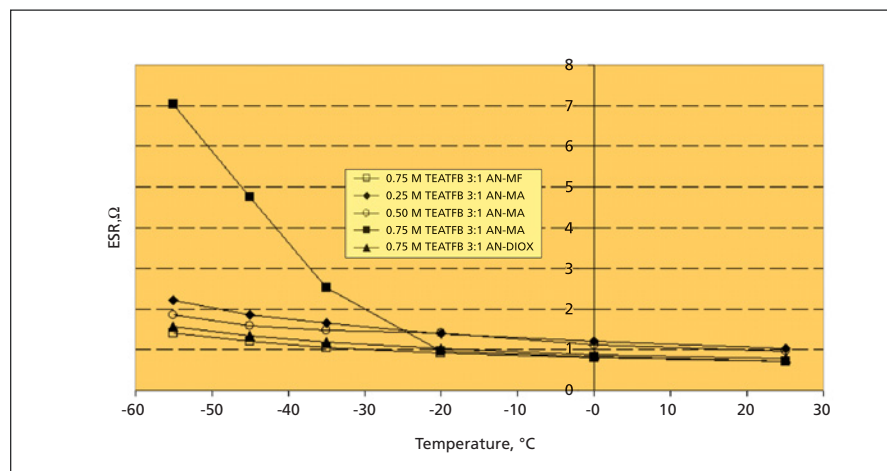
ESR of Supercapacitor Test Cells is shown down to –55 °C, using various low-temperature electrolytes.