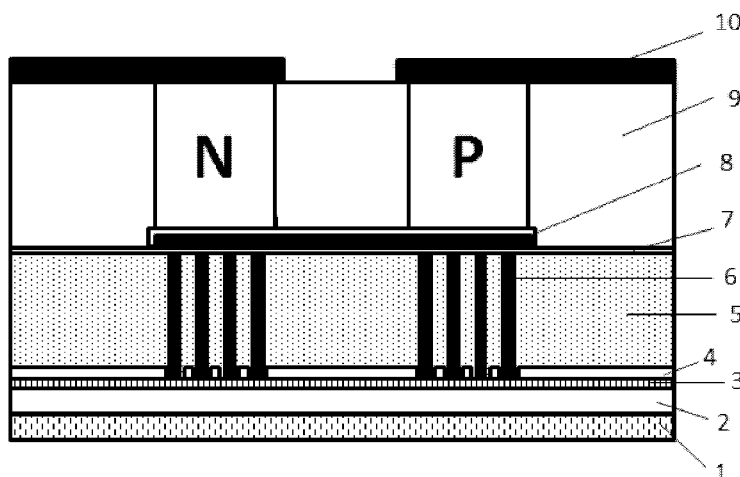




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Figure 3



(57) Abstract: Flexible thermoelectric modules and processes of fabrication are disclosed. In one aspect, a method of fabricating a thermoelectric nanowire module is disclosed, which includes forming a polymer mold pattern on a substrate and depositing nanowires in nanoporous templates. In another aspect, the flexible thermoelectric module fabricated herein includes a flexible layer comprising a polymer which is stable at a temperature of at least 200 °C, a plurality of pillars embedded in the flexible layer. The plurality of pillars extends through the flexible layer and contacts an insulation layer on one side of flexible layer and a back layer on the other side of the flexible layer.



FLEXIBLE THERMOELECTRIC MODULES AND METHODS OF FABRICATION

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of and priority to U.S. Provisional Patent Application No. 61/981,724, filed April 18, 2014, the entire content of which is hereby incorporated by reference.

GOVERNMENT RIGHTS NOTICE

[0002] This invention was made with government support under grant number EEC-1160483, awarded by the National Science Foundation (NSF). The government has certain rights in the invention.

FIELD

[0003] The present invention generally relates to thermoelectric modules. More particularly, the present subject matter relates to flexible thermoelectric modules and methods of fabrication.

[0004] Thermoelectric modules are devices that convert heat directly into electrical energy using a phenomenon called the Seebeck effect. They can also act as a heat pump if electrical energy is provided as an input. Typical thermoelectric generators either rely on bulk polycrystalline materials and have relatively low performance (i.e., low ZT (thermoelectric figure-of-merit)), or they have crystalline materials grown by expensive epitaxial techniques to improve the ZT. Nanostructured thermoelectric generators are more effective (i.e., higher ZT). Although advances have been made, there is a need for improved flexible thermoelectric generators and techniques for their manufacture.

SUMMARY

[0005] In one aspect of the present technology, a method of fabricating a flexible thermoelectric nanowire module is disclosed. In one embodiment, the method of fabricating a thermoelectric nanowire module includes depositing or bonding a polymer on a substrate and patterning, the pattern defining a first recess and a second recess that each extend towards the substrate. Further, the method includes forming a plurality of conductive pillars within

each of the first recess and the second recess. The method also includes converting the conducting pillars to insulating nanoporous channels followed by filling the pores to form p-type and n-type semiconductor nanowires thus creating bundles of p-type and n-type nanowires in original polymer recesses. The method also includes attaching a plurality of contacts on one side of the nanowires. Further, the method includes attaching a plurality of contacts on the other side of the nanowires to connect the p-type and n-type bundles electrically in series.

[0006] In another aspect of the present technology, the method of fabricating a flexible thermoelectric nanowire module includes forming insulating nanoporous pillars on a first area and a second area of a substrate. The method also includes depositing semiconducting nanowires in the nanopores. The method also includes attaching a first contact on top of the nanowires on the first area of the substrate. Further, the method includes attaching a second contact on top of the conductive pillars and the nanowires on the second area of the substrate. The method also includes attaching a third contact on a bottom of the conductive pillars and nanowires, the third contact extending between the conductive pillars and nanowires of the first and second areas.

[0007] In yet another aspect of the present technology, a process for fabricating a flexible thermoelectric module (cooler or generator) is disclosed. In one embodiment, the process includes the steps of: providing a back layer having an outer surface and an inner surface; optionally providing an adhesion layer attached to the outer surface of the back layer; providing a flexible layer attached to the adhesion layer and opposite to the back layer, wherein the flexible layer comprises a polymer which is stable at a temperature of at least 200 °C; and forming a plurality of pillars embedded in the flexible layer, wherein each pillar has a first end and a second end, wherein the first end of each pillar extends through the flexible layer in a direction opposite from the adhesion layer, and wherein the second end of each pillar extends through the flexible layer and the adhesion layer and contacts the back layer. The process may further include the steps of: depositing an insulation layer on the flexible layer, wherein the insulation layer is thermally conductive but electrically insulative, and wherein the insulation layer contacts the first ends of the pillars; depositing a base electrode on the insulation layer, wherein the base electrode has a first area and a second area; and attaching a first thermoelectric material to the first area of the base electrode, and attaching a second thermoelectric material to the second area of the base electrode. The process may

further include the steps of: applying a stretchable polymer on the base electrode, wherein the first thermoelectric material and the second thermoelectric material are embedded in the stretchable polymer; attaching a first electrode to the first thermoelectric material; and attaching a second electrode to the second thermoelectric material.

[0008] In yet another aspect of the present technology, a flexible thermoelectric module is disclosed. In one embodiment, the flexible thermoelectric module includes: a first electrode; a second electrode; a base electrode having an outer surface and an inner surface, wherein the outer surface has a first area and a second area; a first thermoelectric material connecting the first electrode and the base electrode at the first area of the base electrode; a second thermoelectric material connecting the second electrode and the base electrode at the second area of the base electrode; an insulation layer attached to the inner surface of the base electrode, wherein the insulation layer is thermally conductive but electrically insulative; a flexible layer attached to the insulation layer and opposite to the inner surface of the base electrode, wherein the flexible layer comprises a polymer which is stable at a temperature of at least 200 °C; an optional adhesion layer attached to the flexible layer and opposite to the insulation layer; a back layer attached to the adhesion layer and opposite to the flexible layer; and a plurality of pillars embedded in the flexible layer, wherein each pillar has a first end and a second end, wherein the first end of each pillar extends through the flexible layer and contacts the insulation layer, and wherein the second end of each pillar extends through the flexible layer and the adhesion layer and contacts the back layer.

[0009] Other aspects of the invention will become apparent by consideration of the detailed description and accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a flow diagram of exemplary steps for fabricating a flexible nanowire thermoelectric module in accordance with embodiments of the present disclosure.

[0011] Figure 2 is a flow diagram of other exemplary steps for fabricating a flexible nanowire thermoelectric module in accordance with embodiments of the present disclosure.

[0012] Figure 3 shows a non-limiting illustration of the process for fabricating a thermoelectric module which includes a flexible polyimide layer and copper pillars embedded therein.

[0013] Figures 4A-4D show a non-limiting representative module fabricated by the present process. Figure 4A shows the present module containing a flexible polyimide substrate (corresponding to the polyimide layer 5 in Figure 3). Figure 4B shows a top view of a typical arrangement for copper studs embedded in polyimide layer, the semiconductor leg soldered on top of the copper studs, and the copper/gold interconnect between a pair of semiconductor legs. Figure 4C show a flexible module after drop casting and planarization of PDMS. Figure 4D shows a flexible module after forming the printed metal electrodes. Figure 4E shows a cross-section of the layered structure of a representative complete module fabricated by the present process, which has the same numbered layers as defined in Figure 3 but does not contain the supporting polyimide (layer 2) or the silicon wafer (layer 1).

DETAILED DESCRIPTION

[0014] Before any embodiments of the invention are explained in detail, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of components set forth in the following description or illustrated in the following drawings. The invention is capable of other embodiments and of being practiced or of being carried out in various ways.

[0015] The use of "including," "comprising," or "having" and variations thereof herein is meant to encompass the items listed thereafter and equivalents thereof as well as additional items. Any numerical range recited herein includes all values from the lower value to the upper value. For example, if a concentration range is stated as 1% to 50%, it is intended that values such as 2% to 40%, 10% to 30%, or 1% to 3%, etc., are expressly enumerated in this specification. These are only examples of what is specifically intended, and all possible combinations of numerical values between and including the lowest value and the highest value enumerated are to be considered to be expressly stated in this application.

[0016] The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (for example, it includes at least the degree of error associated with the measurement of the particular quantity). The modifier "about" should also be considered as disclosing the range defined by the absolute values of the two endpoints. For example, the expression "from about 2 to about 4" also discloses the range "from 2 to 4." The term "about" may refer to plus or minus 10% of the indicated number. For example, "about 10%" may indicate a range of 9% to 11%, and "about 1" may mean

from 0.9-1.1. Other meanings of “about” may be apparent from the context, such as rounding off, so, for example “about 1” may also mean from 0.5 to 1.4.

[0017] Thermoelectric devices are modules that are used to convert a heat differential or gradient into electricity based on the electric potential or voltage difference (ΔV) generated between the two ends of a thermoelectric material (e.g., a semiconductor) where there exists a net temperature differential (ΔT) between the two ends. This phenomenon is known as the Seebeck effect and is expressed as $\Delta V = S\Delta T$, where S is the Seebeck coefficient, which is a property of the thermoelectric material. For semiconductor materials, the type of doping (i.e., P- or N-type) determines the polarity of the thermoelectric voltage generated across the semiconductor.

[0018] High performance thermoelectric modules traditionally employ bulk crystalline thermoelectric materials, which can be grown by epitaxial techniques. It is noted that a challenge with thermoelectric generators is to maintain a large temperature differential between the two sides and this requires materials with poor thermal conductivity (λ).

[0019] The electrical conductivity of the thermoelectric material is also important for at least two reasons. According to the maximum power transform theorem, the resistance of any load powered by a voltage source should match the internal resistance of the source. This forces the open-circuit voltage of the generator to divide between the internal resistance and the load, yielding the equation:

$$P = \frac{\Delta V^2}{4R}$$

where P is power delivered to the load and R is the resistance. Therefore, the power generated by a thermoelectric generator is inversely proportional to its internal source resistance. For a thermoelectric generator, the internal resistance is the sum of the electrical resistances of the individual legs since they are all in series. Therefore, higher electrical conductivity and lower source resistance lead to higher generated power. The second reason why the electrical conductivity is important stems from the fact that when current flows through the legs, there is certain power dissipation and heating, which can reduce the temperature differential. Therefore, semiconductors with high electrical conductivity are needed for successful thermoelectric generators.

[0020] Three important parameters (i.e., Seebeck coefficient, thermal conductivity, and electrical conductivity) are included in a single thermoelectric figure-of-merit, referred to as the ZT of a material given by:

$$ZT = \frac{\sigma S^2}{\lambda} T$$

It has been shown by nano-structuring these materials, the thermoelectric figure of merit ZT, which describes the quality of the material, can be increased beyond standard bulk ZT values. The improvement is mainly due to reduction in phonon transfer either by introducing a series of barriers (superlattices) or by changing the surface-to-volume ratio to enhance the impact of surface roughness scattering (nanowires). However, it has been proposed that nanostructuring can also have a positive impact on the Seebeck coefficient of the material. Both superlattice and nanowire techniques have been implemented to obtain high ZT materials.

[0021] Flexible modules using electrodeposition techniques have been realized but only with bulk materials. Electrodeposition of thermoelectric nanowires remains unrivaled in comparison to other deposition techniques as far as deposition rate, thermal budget, large scale integration, and cost. In one aspect, the present disclosure relates to a flexible, large-area, high-performance thermoelectric module based on nanostructuring of the thermoelectric material. Processes are disclosed for implementing thermoelectric nanowires into high performance, flexible thermoelectric modules. In one embodiment, anodized aluminum oxide (AAO) templates may be isolated in a polymer mold that can be used to control the synthesis of thermoelectric nanowire bundles. Hence, a larger voltage can be obtained by connecting alternating p-type and n-type semiconductor legs in series as shown in Figure 1, which illustrates a flow diagram of exemplary steps for fabricating a flexible nanowire thermoelectric generator in accordance with embodiments of the present disclosure. It can be seen that while the legs are electrically in series, they are thermally in parallel.

[0022] The present disclosure provides techniques for realizing a structure that allows for thermoelectric nanowires to be included in a flexible structure that does not require the AAO template to remain in the final module. This can solve two key issues with using template assisted nanowires. First, modules based off AAO require the AAO to remain in the module for mechanical stability. Because AAO has a non-negligible thermal conductivity, the overall temperature difference across the module is reduced, which severely degrades module

performance. Secondly, both the AAO templates and nanowires are fragile. The nanowires are too fragile to be suspended without the template, but the template itself is very fragile as well. By isolating the nanowire bundles into a polymer mold and sandwiching them between metal pads, both mechanical support for the wires and flexibility can be achieved for the overall module.

[0023] Referring to Figure 1, the figure shows exemplary module fabrication steps. The structure in this example is formed by first depositing a thin metal seed layer by physical vapor deposition (PVD) on top of a lift off layer. The seed layer may then be electroplated further until a desired bottom contact thickness is achieved. After the seed layer, a flexible polymer mold can be patterned on top. The polymer can be made of photosensitive SU-8 or other mechanically flexible and stable polymers such as polyethylene terephthalate (PET) or polyimide. Next, aluminum pillars are electroplated up through the mold until each reaches the top; each pillar is subsequently polished smooth. The pillars may then be anodized and chemically etched in order to transform them into isolated AAO templates. Any metal that can lend itself to nanopore formation by anodic oxidation may be used in place of aluminum. Subsequently, thermoelectric nanowires are electroplated through the AAO templates until they reach the top. At this point, it may be desired to polish the entire structure until the polymer/nanowires are completely planarized. The AAO templates may be chemically etched away, exposing only the newly-formed nanowires. A thin PVD metal film may be deposited on top of the structure, covering all of the holes and polymer. The metal may be electroplated to a desired contact thickness and then lithographically patterned and finally etched. Finally, the structure can be released and the bottom contact can be patterned. The final module includes thermoelectric nanowires surrounded by a polymer mold to allow both mechanical support of the wires as well as overall module flexibility.

[0024] In another embodiment, a structure may be fabricated starting with an aluminum sheet or foil in which PDMS is used. An issue with PDMS is that other fabrication techniques disclosed herein may not be compatible with wet processing. Figure 2 illustrates a flow diagram of other exemplary steps for fabricating a flexible, nanowire thermoelectric generator in accordance with embodiments of the present disclosure. Referring to Figure 2, the structure may be formed by first depositing a thin metal seed layer by PVD on top of a high purity aluminum sheet. The seed layer may then be selectively electroplated further by blocking the back aluminum sheet until a desired bottom contact thickness is achieved. The

sheet is then adhesively bonded to a sturdy substrate for ease of future processing. Next, photoresist is spun on the structure to protect the aluminum that may later be etched into the nanotemplate. Exposed Al may then be etched either chemically or by other means to create freestanding Al pillars. Another photolithography step is then needed to protect the seed layer from future processing. The Al pillars may then be transformed into AAO templates by a suitable technique. At this point, thermoelectric nanowires can then be plated through the new AAO structure. Finally, the photoresist may be removed and the entire structure may be spun cast in a polymer mold. The polymer can be SU-8, PDMS, or any suitable material that is flexible and spin-castable. The structure may then be polished smooth to expose the tips of the nanowires. Another layer of PVD and subsequent electroplated metal may be applied to the top of the mold and then patterned. The structure may then be released from the substrate. Finally, the bottom seed layer may be patterned to form the final bottom contacts. The final module is now nanowires in a polymer mold starting from an existing aluminum sheet. The fabrication techniques disclosed herein can produce flexible, large-area, high-performance nanowire thermoelectric generators. The techniques can be compatible with low-temperature requirements of commonly used flexible materials.

[0025] In another aspect, the present disclosure provides a process for fabricating a flexible thermoelectric module (cooler or generator). In one embodiment, the process includes the steps of: providing a back layer having an outer surface and an inner surface; optionally providing an adhesion layer attached to the outer surface of the back layer; providing a flexible layer attached to the adhesion layer and opposite to the back layer, wherein the flexible layer comprises a polymer which is stable at a temperature of at least 200 °C; and forming a plurality of pillars embedded in the flexible layer, wherein each pillar has a first end and a second end, wherein the first end of each pillar extends through the flexible layer in a direction opposite from the adhesion layer, and wherein the second end of each pillar extends through the flexible layer and the adhesion layer and contacts the back layer.

[0026] The present process may further include the steps of: depositing an insulation layer on the flexible layer, wherein the insulation layer is thermally conductive but electrically insulative, and wherein the insulation layer contacts the first ends of the pillars; depositing a base electrode on the insulation layer, wherein the base electrode has a first area and a second area; attaching a first thermoelectric material to the first area of the base electrode; and attaching a second thermoelectric material to the second area of the base

electrode. The present process may further include the steps of: applying a stretchable polymer on the base electrode, wherein the first thermoelectric material and the second thermoelectric material are embedded in the stretchable polymer; attaching a first electrode to the first thermoelectric material; and attaching a second electrode to the second thermoelectric material.

[0027] The back layer may serve as an interface, or part of an interface, between the flexible thermoelectric module and a heat source (such as a region of human skin or a curved surface). Suitably, the back layer includes a metal which is highly thermally conductive, such as gold (Au) or other metals or alloys. For use on a human body, the back layer may include metals that are not harmful to human skin when placed in direct contact. In various embodiments, gold or a combination of gold and at least one other thermally conductive metal is used to form the back layer at an appropriate thickness. The optional adhesion layer provides sufficient adhesion between the flexible layer and the back layer. Suitably, the adhesion layer may include a metal such as titanium (Ti), chromium (Cr), or nickel (Ni).

[0028] The flexible layer provides flexibility for the thermoelectric module, and in various embodiments includes a polymer material that is stable at temperature of up to at least 200 °C, i.e. the polymer does not degrade, deform, lose flexibility, or undergo significant physical changes such that it becomes unusable as a component of the present module. Suitably, the polymer material is stable at a temperature of at least about 200 °C, such as at least about 250 °C, at least about 300 °C, at least about 350 °C, or at least about 400 °C. Suitably, the polymer material is stable at a temperature of at most about 450 °C, such as at most about 400 °C, at most about 350 °C, at most about 300 °C, or at most about 250 °C. Preferably, the polymer material is stable at a temperature between about 200 °C to about 400 °C, such as between about 200 °C to about 300 °C. In some embodiments, the polymer includes polyimide, such as the commercially available photodefinable HD-4110 polyimide (supplied by Hitachi DuPont MicroSystems, Catalog No. MHD4110250). Other photodefinable polymers, which can be etched or cut to provide vacancy (e.g., holes) in its structure, may also be suitable for the present process. For example, the polymer of SU-8 (MicroChem Corp., item number Y131269) may also be used to form the flexible layer. In some embodiments, lithography or plasma etching may be employed to form holes in the flexible layer. Preferably, these polymers are stable at temperatures of up to about 200-300 °C and can be spun and lithographically defined on a surface. Other desirable properties of

the polymer include chemical stability and resistance to metal etchants, plating solutions, solvents, and acids.

[0029] The pillars typically are made of a metal, such as copper, gold, or nickel. Typically, copper is used for the present process to form copper pillars by electroplating, since copper is sufficiently conductive and inexpensive. Suitably, each pillar has a diameter of from about 1 μm to about 500 μm , such as from about 10 μm to about 200 μm or from about 10 μm to about 100 μm . Smaller diameters are preferred. In various embodiments, the pillars have a diameter of about 50 μm . In some embodiments, the first end of each pillar may have a slight overgrowth protruding from flexible layer, and these first ends may have a diameter that is slightly different from the rest of pillar (e.g., a difference of about $\pm 5 \mu\text{m}$). Optionally, the overgrowth of the first ends may be polished so that the first ends of the pillars are flat and flush with the flexible layer. In various embodiments, the pillars are spaced approximately 25 μm apart from one another, which can be adjusted according to the diameter of the pillars.

[0030] The insulation layer may include Al_2O_3 , AlN , or other materials that are thermally conductive but electrically insulative. The insulation layer allows first ends of the pillars to be electrically insulated from the thermoelectric materials. In some embodiments, materials with low thermally conductivity, such as SiO_2 , Si_3N_4 , HfO_2 may also be included in the insulation layer, provided that the insulation later is sufficiently thin. While these latter materials do not have a high level of thermal conductivity, when used in a thin layer they permit sufficient heat transfer while providing electrical insulation.

[0031] The base electrode may include a metal layer having a first area and a second area, where the first and second areas each provides a bonding pad for electrical connections to the thermoelectric materials. In one embodiment, the first area and the second area cover the first ends of the plurality of pillars. Suitably, the base electrode may include a layer of copper, gold, or combinations thereof. In a particular embodiment, the base electrode includes a copper layer with a gold cap on the first area and the second area.

[0032] The thermoelectric materials for the present process typically include N-type and P-type semiconductors. In a particular non-limiting embodiment, cubical semiconductors (other semiconductors having a shape other than cubical), used as thermoelectric “legs,” are soldered onto the base electrode (such as a copper layer) and on top of the first ends of the

plurality of pillars (e.g., copper studs). The soldering temperature typically is about 200-300 °C. In various embodiments, other suitable thermoelectric materials (in appropriate size and shape) can be attached to the base electrode by soldering within this temperature range.

[0033] The stretchable polymer used in the present process at least partially covers the first thermoelectric material, the second thermoelectric material, and the base electrode to provide additional flexibility, support, and a platform upon which to lay the first and second electrodes on top. Suitable stretchable polymers include polydimethylsiloxane (PDMS) and other stretchable polymers having low thermal conductivity. In some embodiments, PDMS polymer may be drop-casted over the thermoelectric legs.

[0034] The first and second electrodes are located at the “cold” (i.e. the lower temperature side, generally the side at which heat is dissipated) surface of the module and are attached to the first and second thermoelectric materials, respectively. Suitably, the material for the cold surface electrodes may be a flexible, electrically-conductive material. For example, a conductive paste may be used as the first and second electrodes. In a particular embodiment, Ag/AgCl is used to form the first and second electrodes. The cold surface electrodes can be arranged in serial.

[0035] In one embodiment, the present process can be used to fabricate a flexible thermoelectric module (cooler or generator). The process utilizes a polyimide substrate with embedded copper pillars to “thermally short” the polyimide, i.e. to transfer heat from one side to the other of the polyimide layer. High thermal conductivity of the pillars through the substrate is important for the semiconductor legs to absorb heat from the heat source (or to dissipate heat). The polyimide substrate is temperature-resistant up to about 400 °C, which enables thermal compression bonding of the semiconductor legs on metal pads formed on the polyimide substrate. While the polyimide can be used with thermally-bonded solid semiconductor legs, other materials such as printable semiconductors can also be used on this substrate, allowing high annealing/curing temperatures, which are often required. The semiconductor legs are enclosed in PDMS, a stretchable silicone, but other materials that are stretchable with low thermal conductivity can be used instead of or in addition to PDMS. The disclosed thermoelectric module employs screen-printed Ag/AgCl metal interconnects but other techniques and metals can be used. The module is constructed on a silicon wafer

and peeled off the wafer after the fabrication is complete. As such, the silicon wafer is only used for mechanical support and other types of wafers (e.g., glass) can also be used.

[0036] The fabrication process begins by coating the Si wafer with PI2611 polyimide by HD Microsystems. This is followed by deposition of a thin (>250 nm) gold layer. The gold layer does not stick to the polyimide permanently, allowing easy peel-off when the fabrication is complete. A layer of Ti (20 - 50 nm) is then deposited on the gold layer. Then, a layer of polyimide (e.g. HD-4110 photodefinable polyimide) is spun on the Ti layer. The Ti layer serves as an adhesion layer between the gold and the HD-4110. Essentially, any metal that provides sufficient adhesion to the polyimide may be suitable in this process. In various embodiments, Cr can also be used to form this layer instead of Ti. Windows are lithographically defined in the polyimide and then filled with copper by electroplating. Many small windows may be formed under a single semiconductor leg in order to maximize the sidewall surface area and to improve adhesion of copper to the polyimide walls. This is followed by the deposition of an thermally conductive but electrically insulative material such as Al₂O₃ or AlN (at a thickness of 100 - 200 nm) on top of the copper pillars. This allows the studs under different legs to be electrically isolated from one another. On top of this layer, metal pads on which the semiconductor legs are bonded are formed. The metal pads serve as a base electrode and provide electrical connections between the thermoelectric legs. In a particular embodiment, the metal pads are made from copper, which is capped with gold to avoid oxidation of copper. Gold is a commonly used material in thermal compression bonding, although other metal combinations may also be used.

[0037] After patterning of the metal pads and interconnects, the semiconductor legs are bonded using a common solder material. This is followed by drop casting of PDMS around the legs. Other materials, which provide stretchability and low thermal conductivity may also be used. The PDMS is planarized to minimize the PDMS thickness on the semiconductor legs. Final plasma etching of the PDMS is used to ensure that the top of the semiconductor legs are exposed for final metallization. The module is finalized by forming metal pads/interconnects (as top electrodes) on the semiconductor legs, which are exposed through the PDMS.

[0038] While the embodiment described above makes use of solid semiconductor legs, the same polyimide substrate with embedded copper studs can be used with other types of semiconductor legs. For example, another photodefinable polyimide or other materials on

this substrate can be used to define windows, which can then be filled with printable semiconductor legs. Examples include organic materials and nanoparticles in liquid materials, such as those disclosed in Bubnova, Olga, et al. (“Optimization of the thermoelectric figure of merit in the conducting polymer poly (3, 4-ethylenedioxythiophene),” *Nature materials* 10.6 (2011): 429-433) and Madan, Deepa, et al. (“Dispenser printed composite thermoelectric thick films for thermoelectric generator applications.” *Journal of Applied Physics* 109.3 (2011): 034904), each of which is incorporated herein by reference in its entirety. Additionally, there may be other applications, which may benefit from a flexible substrate which is thermally conductive. The process can be used to embed copper studs in a very large area without losing the flexibility of the material.

[0039] As a non-limiting example, the present process can be implemented as follows. As shown in Figure 3, PI-2611 non-photodefinable polyimide (layer 2) is spun on top of a silicon wafer (layer 1). The silicon wafer is only used as a smooth starting surface and for mechanical support. Other thermally stable, smooth, mechanically rigid materials such as glass can also be used as an alternative to silicon wafer. A layer of gold (layer 3) is deposited on top of the non-photodefinable polyimide, followed by a layer of titanium (layer 4). The titanium layer is then etched to expose gold below it (as shown by the openings on layer 4). The exposed gold surface will be used as an electrical “seed” layer for electrodeposition. The titanium is used as an adhesion promoter for the deposition of photo definable polyimide. Next, photodefinable HD-4110 polyimide (layer 5) is spun and lithographically defined to open up windows down to the gold seed layer. Copper is then electrodeposited through the holes defined by the polyimide layer 5 to form pillars (depicted as pillars 6 in Figure 3) embedded in the polyimide layer. Each pillar has a first end and a second end. The first ends of these pillars extend through the polyimide layer 5 and away from the gold layer 3, and may contain slight overgrowth creating the caps at the top. The second ends of these pillars extend through the polyimide layer 5 toward the gold layer 3 and are connected with the gold layer 3 at the exposed gold surface (i.e. the “seed” surface) resulting from the etching of titanium layer 4.

[0040] Next, a thin layer of a thermally conductive but electrically isolative material (such as Al_2O_3 or AlN, layer 7) is deposited on top of the first ends of the copper pillars to serve as an insulation layer which electrically insulate the copper pillar. In addition to the top

surface of the first ends of the copper pillars, the insulation layer may also extend to cover a portion of the polyimide layer. A layer of metal (such as copper with a gold cap on top, layer 8) is then deposited over the insulation layer (covering the copper studs) to serve as a base electrode. The base electrode (metal layer 8) creates bonding pads for, and electrical connections between, the thermoelectric materials.

[0041] Thermoelectric materials, such as N- and P-type semiconductors “legs” (labeled as “N” and “P” in Figure 3) are then soldered to the metal pads (layer 8) on top of the copper studs. Other suitable thermoelectric material can also be soldered to the metal pad/copper studs in the conventional 200-300 °C temperature range without any degradation to the structure. PDMS is then drop casted / poured over the semiconductor legs and base electrodes (shown as layer 9 surrounding the “N” and “P” semiconductor legs), which is then planarized into a flat surface and to expose the top surfaces of the semiconductor legs. Plasma etching is used to remove any residue on top of the legs. At this point, the top electrodes 10 are deposited over the semiconductor legs. The top electrodes (layer 10) extend laterally to make electrical connections with adjacent N- and P-type legs of adjoining modules; a single unit (sometime referred to as a thermocouple) is shown in Figure 3 for simplicity, although in practice many such units would be connected in series (electrically) in a larger, complete module (e.g., see Figures 4A, 4D). Typically, Ag/AgCl paste is used to create thick, stable pads which are also sufficiently elastic. Other metals can also be used as top electrodes, provided that the electrode materials are sufficiently flexible. Typically, the thermoelectric module fabricated by the present process contains multiple pairs of N- and P-semiconductors legs, and their top electrodes are arranged in serial fashion.

[0042] The gold layer 3 can be separated from the polyimide layer 2 by wedging a razor blade in between the two layers and “peeling” the module (built on top of the gold layer as described above) off the bottom substrate. This separation step can also be done, for example, before or after installation of the semiconductor legs. Alternatively, the separation of the gold layer 3 from the supporting polyimide layer 2 can be accomplished using a “lift-off” method, i.e. by depositing a sacrificial layer prior to gold deposition that can be etched in a solution that does not etch gold, titanium, polyimide, and other components of the module. The etchant would remove the sacrificial layer, therefore releasing the gold layers 3 and the components attached thereto.

[0043] As a non-limiting example, Figures 4A-4D show a representative module fabricated by the present process. Figure 4A shows the flexibility of the present module containing a flexible polyimide substrate (corresponding to the polyimide layer 5 in Figure 3). Figure 4B shows a top view of a typical arrangement for copper studs embedded in the polyimide layer, the semiconductor leg soldered on top of the copper studs, and the copper/gold interconnect. Figure 4C shows a flexible module after drop casting and planarization of PDMS. Figure 4D shows a flexible module after forming the printed metal electrodes. Figure 4E shows the layered structure of a representative complete module fabricated by the present process, which has the same numbered layers as defined in Figure 3 but does not contain the supporting polyimide (layer 2) or the silicon wafer (layer 1).

[0044] In yet another aspect, the present disclosure provides a flexible thermoelectric module, which includes a thermoelectric material; a base electrode; an insulation layer attached to the base electrode, wherein the insulation layer is thermally conductive but electrically insulative; a flexible layer comprising a polymer which is stable at a temperature of at least 200 °C; a plurality of pillars embedded in the flexible layer; and a back layer; wherein each pillar has a first end and a second end, wherein the first end of each pillar extends through the flexible layer and contacts the insulation layer, and wherein the second end of each pillar extends through the flexible layer and contacts the back layer.

[0045] In one embodiment, the flexible thermoelectric module includes: a first electrode; a second electrode; a base electrode having an outer surface and an inner surface, wherein the outer surface has a first area and a second area; a first thermoelectric material connecting the first electrode and the base electrode at the first area of the base electrode; a second thermoelectric material connecting the second electrode and the base electrode at the second area of the base electrode; an insulation layer attached to the inner surface of the base electrode, wherein the insulation layer is thermally conductive but electrically insulative; a flexible layer attached to the insulation layer and opposite to the inner surface of the base electrode, wherein the flexible layer comprises a polymer which is stable at a temperature of at least 200 °C; an optional adhesion layer attached to the flexible layer and opposite to the insulation layer; a back layer attached to the adhesion layer and opposite to the flexible layer; and a plurality of pillars embedded in the flexible layer, wherein each pillar has a first end and a second end, wherein the first end of each pillar extends through the flexible layer and contacts the insulation layer, and wherein the second end of each pillar extends through the

flexible layer and the adhesion layer and contacts the back layer. In another embodiment, the present module may further include a stretchable polymer. The materials suitable for the first and second electrode, the base electrode, the first and second thermoelectric materials, the insulation layer, the flexible layer, the pillars, the adhesion layer, the back layer, and the stretchable polymer are the same as described above.

[0046] The present module is fully compatible with traditional bulk thermoelectrics and standard thermal bonding techniques. The present module provides an open-platform package, which can accept any bulk thermoelectric material including the state-of-the-art nanocomposites and, in certain embodiments, could be adapted to use the nanowire-based material disclosed above. In a particular embodiment, the present module employs a polyimide substrate with metal interconnects (e.g., as a base electrode) for bonding the thermoelectric legs. The polyimide substrate is made thermally conductive by including copper studs between the metal interconnects and a backside heat spreader (e.g., a metal back layer) to eliminate any thermal losses through the polyimide. Thermoelectric legs can be bonded to this substrate at typical module bonding temperatures, i.e. 200-300 °C. After bonding, for elasticity, the thermoelectric legs are encased in stretchable polydimethylsiloxane (PDMS), which also serves as a base for the top flexible interconnects. The present module can be used as an energy harvester from a heat source, such as a human body. The flexibility and reduced thermal loss of the present module improves its utility and efficiency as a thermoelectric device.

[0047] Various features and advantages of the present invention are set forth in the following claims.

CLAIMS

What is claimed is:

1. A process for fabricating a flexible thermoelectric device, the process comprising:
 - a. providing a back layer having an outer surface and an inner surface;
 - b. optionally attaching an adhesion layer to the outer surface of the back layer;
 - c. attaching a flexible layer to the adhesion layer and opposite the back layer, wherein the flexible layer comprises a polymer which is stable at a temperature of at least about 200 °C;
 - d. forming a plurality of pillars embedded in the flexible layer, wherein each pillar has a first end and a second end, wherein the first end of each pillar extends through the flexible layer in a direction opposite from the adhesion layer, and wherein the second end of each pillar extends through the flexible layer and the adhesion layer and contacts the back layer.

2. The process of claim 1, further comprising:
 - e. depositing an insulation layer on the flexible layer, wherein the insulation layer is thermally conductive but electrically insulative, and wherein the insulation layer contacts the first ends of the pillars;
 - f. depositing a base electrode on the insulation layer, wherein the base electrode has a first area and a second area; and
 - g. attaching a first thermoelectric material to the first area of the base electrode, and attaching a second thermoelectric material to the second area of the base electrode;

3. The process of claim 2, further comprising:
 - h. applying a stretchable polymer on the base electrode, wherein the first thermoelectric material and the second thermoelectric material are embedded in the stretchable polymer;
 - i. attaching a first electrode to the first thermoelectric material; and
 - j. attaching a second electrode to the second thermoelectric material

4. The process of claim 1, wherein the polymer of the flexible layer comprises polyimide.
5. The process of claim 1, wherein the back layer comprises gold.
6. The process of claim 1, wherein the pillars comprises copper, gold, or nickel.
7. The process of claim 1, wherein the adhesion layer comprises titanium, chromium, or nickel.
8. The process of claim 2, wherein the first thermoelectric material comprises an N-type semiconductor and the second thermoelectric material comprises a P-type semiconductor.
9. The process of claim 2, wherein the insulation layer comprise a material selected from the group consisting of Al_2O_3 , AlN , SiO_2 , Si_3N_4 , HfO_2 , and combinations thereof.
10. The process of claim 3, wherein each of the first electrode and the second electrode independently comprises Ag/AgCl .
11. The process of claim 3, wherein the stretchable polymer comprises polydimethylsiloxane.
12. A flexible thermoelectric module fabricated according to the process of any one of claims 1-11.

13. A flexible thermoelectric module, comprising:
- a first electrode;
 - a second electrode;
 - a base electrode having an outer surface and an inner surface, wherein the outer surface has a first area and a second area;
 - a first thermoelectric material connecting the first electrode and the base electrode at the first area of the base electrode;
 - a second thermoelectric material connecting the second electrode and the base electrode at the second area of the base electrode;
 - an insulation layer attached to inner surface of the base electrode, wherein the insulation layer is thermally conductive but electrically insulative;
 - a flexible layer attached to the insulation layer and opposite to the inner surface of the base electrode, wherein the flexible layer comprises a polymer which is stable at a temperature of at least 200 °C;
 - an optional adhesion layer attached to the flexible layer and opposite to the insulation layer;
 - a back layer attached to the adhesion layer and opposite to the flexible layer; and
 - a plurality of pillars embedded in the flexible layer, wherein each pillar has a first end and a second end, wherein the first end of each pillar extends through the flexible layer and contacts the insulation layer, and wherein the second end of each pillar extends through the flexible layer and the adhesion layer and contacts the back layer.

14. A method comprising:
 - depositing a polymer mold pattern on a substrate, the pattern defining a first recess and a second recess that each extend towards a seed layer attached to the substrate;
 - forming a plurality of pillars within each of the first recess and the second recess;
 - growing nanowires between the pillars;
 - attaching a first contact on top of the nanowires, the first contact extending between the nanowires of the first recess and the second recess;
 - removing the seed layer to expose bottoms of the pillars and nanowires of the first recess and the second recess;
 - attaching a second contact on the bottom of the pillars and nanowires within the first recess; and
 - attaching a third contact on the bottom of the pillars and nanowires within the second recess.
15. The method of claim 14, wherein the pillars comprise metal.
16. The method of claim 15, wherein the metal is aluminum.
17. The method of claim 14, further comprising etching away the pillars subsequent to growing the nanowires.
18. The method of claim 14, further comprising electroplating the nanowires.
19. The method of claim 14, further comprising anodizing the conductive pillars.
20. The method of claim 14, further comprising planarizing a top surface of the nanowires subsequent to depositing the nanowires between the conductive pillars.

21. A method comprising:
 - forming pillars on a first area and a second area of seed layer attached to a substrate;
 - growing nanowires between the pillars on the first area;
 - growing nanowires between the pillars on the second area;
 - attaching a first contact on top of the nanowires on the first area of the substrate;
 - attaching a second contact on top of the nanowires on the second area of the substrate; and
 - attaching a third contact on a bottom of the nanowires, the third contact extending between the pillars and nanowires of the first and second areas.
22. The method of claim 21, wherein the pillars comprise metal.
23. The method of claim 22, wherein the metal is aluminum.
24. The method of claim 21, further comprising etching away the pillars subsequent to growing the nanowires.
25. The method of claim 21, further comprising electroplating the nanowires.
26. The method of claim 21, further comprising anodizing the conductive pillars.
27. A thermoelectric nanowire module fabricated by any of the methods of claims 14-26.

Figure 1

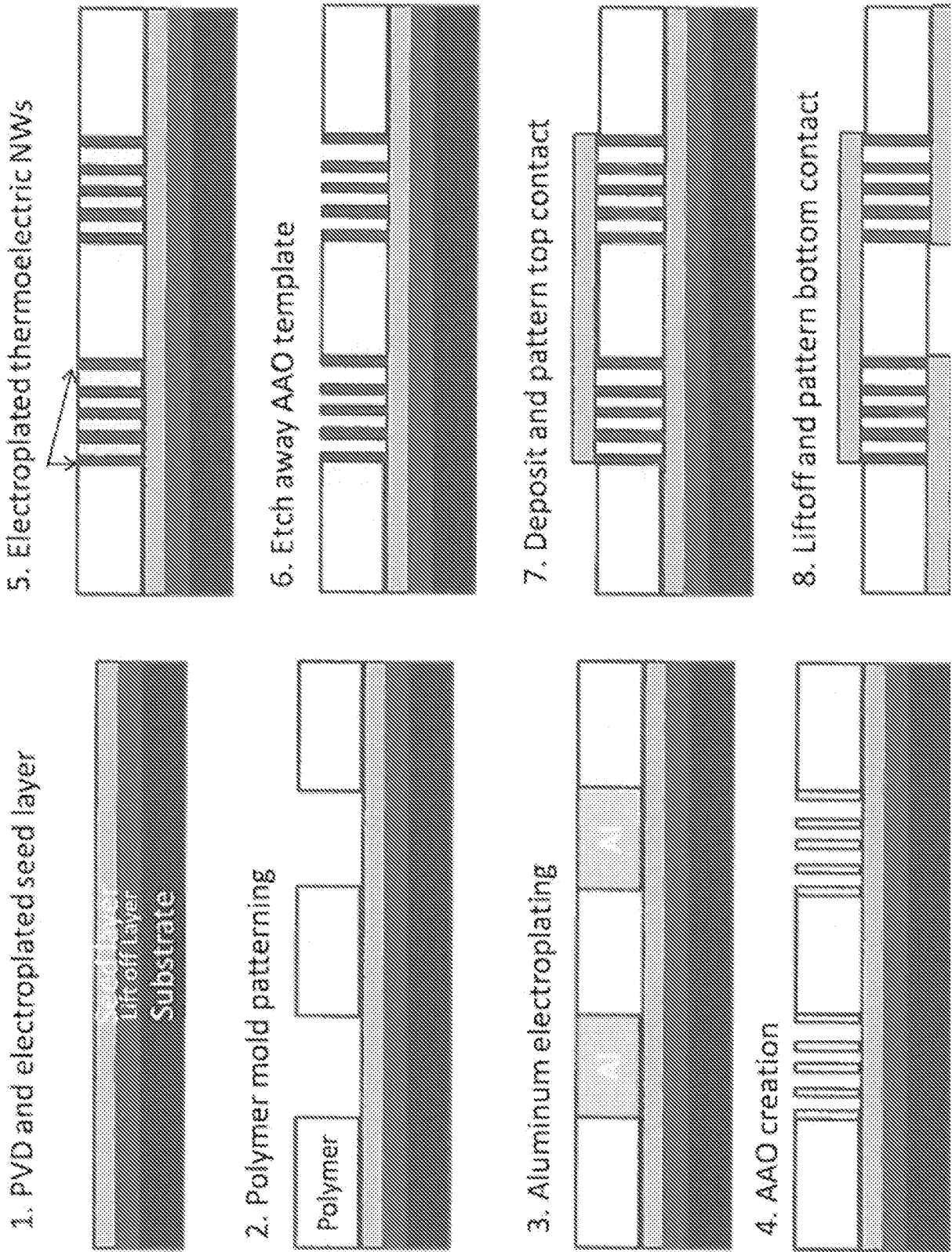
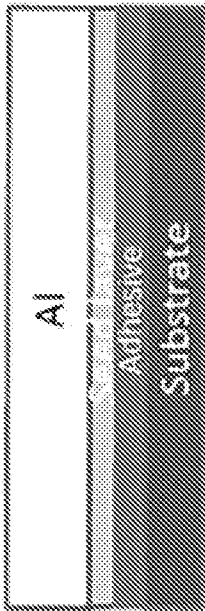
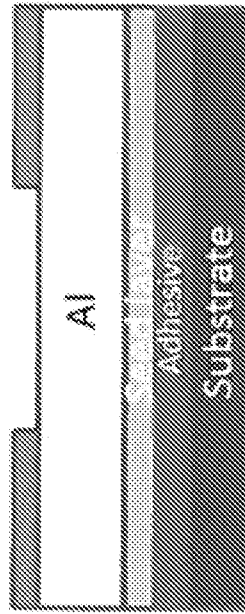


Figure 2

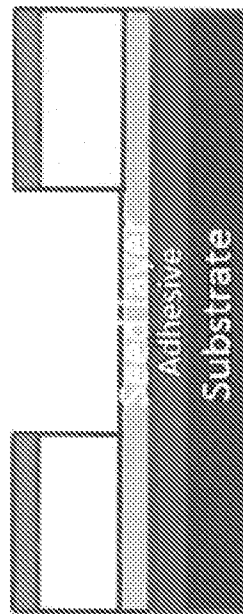
1. PVD Seed on the back of Al sheet and bond to hard substrate



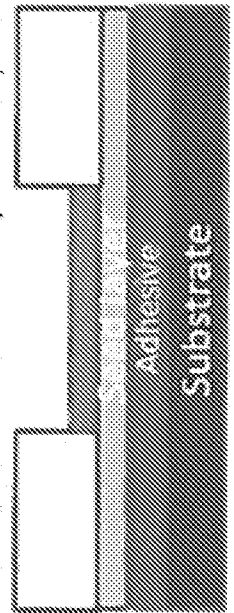
2. Pattern Photoresist on the top of the aluminum foil on areas that will become AAO



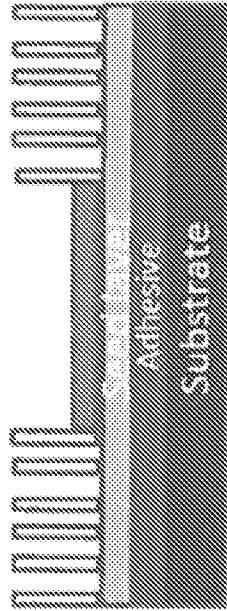
3. Etch away exposed Al



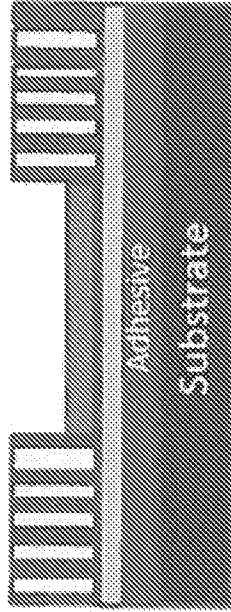
4. Pattern photoresist around newly formed Al pillars



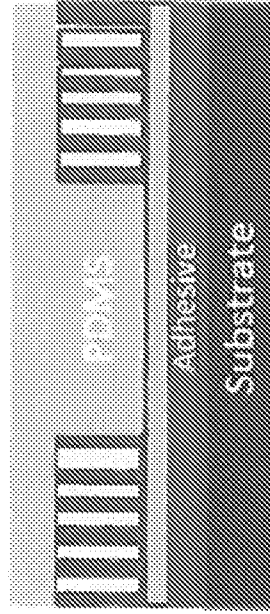
5. Transform AL pillars to AAO templates



6. Electroplate Nanowires through template



6. Remove photo resist and cast structure in PDMS



6. Polish PDMS down to wires and PVD and pattern top contact. Release adhesive layer and pattern bottom contacts

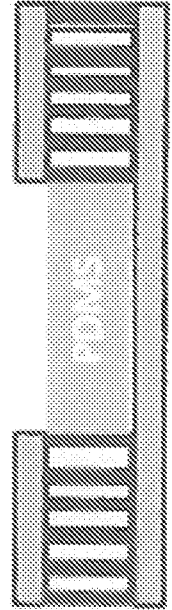


Figure 3

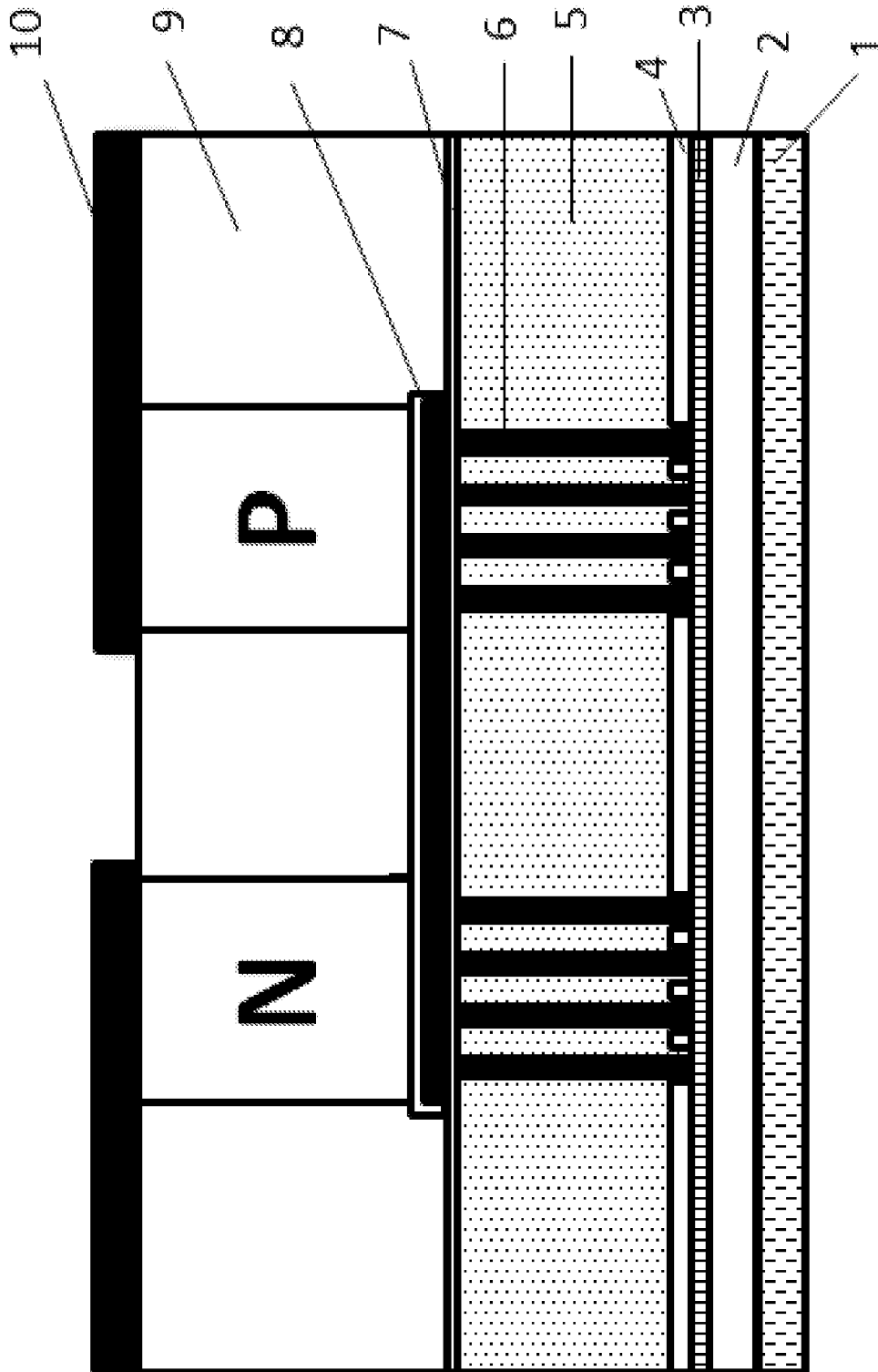
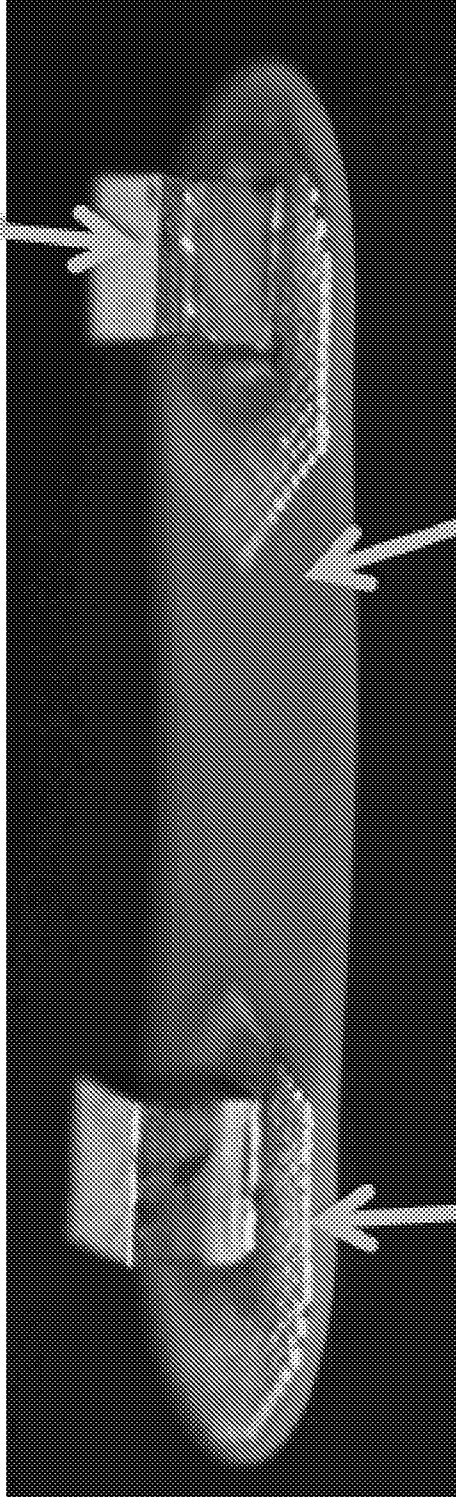


Figure 4A



Figure 4B

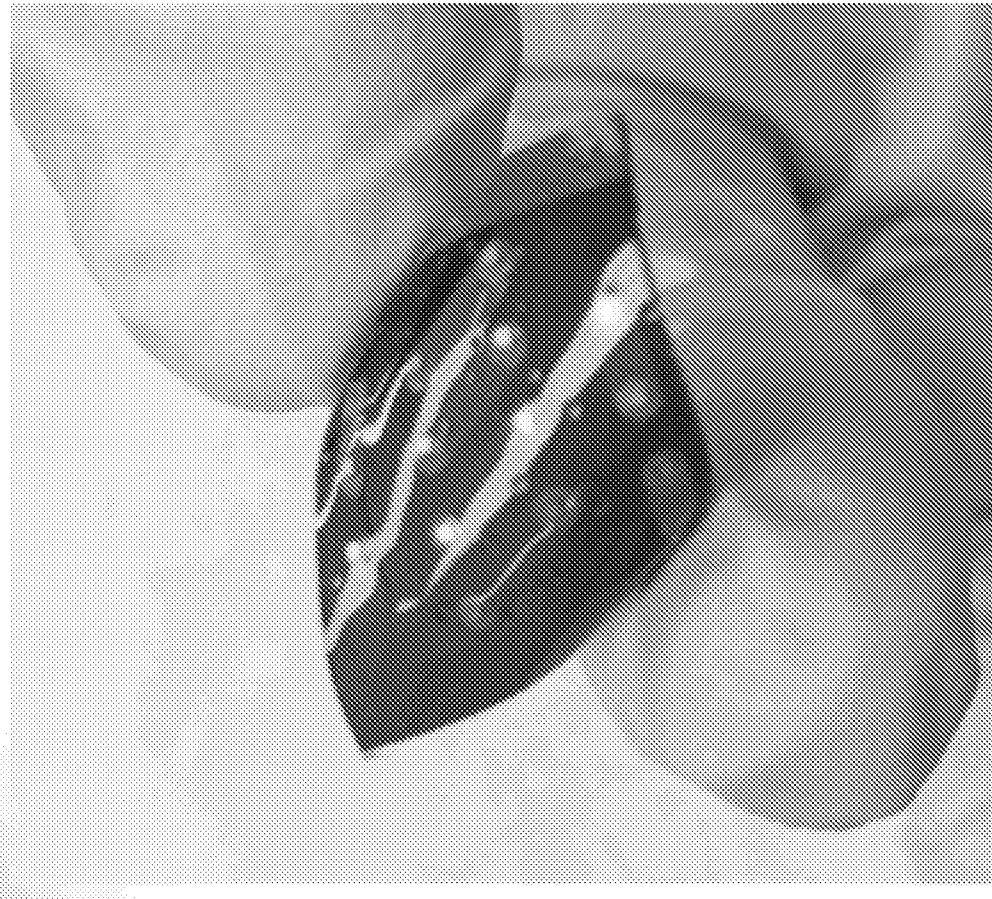
Semiconductor Leg



Copper Studs embedded in polyimide

Copper / Gold Interconnect

Figure 4C



After dropcasting and planarization of PDMS

Figure 4D



After forming the printed metal electrodes

Figure 4E

