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(54) Title: FABRICATION OF POLYMERIC MICROSTRUCTURES

(57) Abstract: A method for fabricating a three-dimensional (3D) polymeric microstructure is disclosed. The method comprises 3D-printing a metallic mold, the metallic mold including a mold cavity corresponding to the 3D polymeric microstructure, polymer casting in the metallic mold by inserting a liquid polymer into the mold cavity, curing the liquid polymer inside the metallic mold, and etching the metallic mold away from the cured polymer wherein the polymeric microstructure comprises a soft polymeric microelectromechanical systems, MEMS, device, and the soft polymeric MEMS device comprises at least one sensor.

Fabrication of polymeric microstructures

Field of the invention

[0001] The present invention relates to a method of fabricating polymeric microstructures. More specifically, the present invention relates to a method of fabricating complex polymeric microstructures using 3D printing.

Background art

[0002] Traditionally, flexible microstructures (e.g. microfluidic channels) have been fabricated using soft lithography which allows for very fine resolution (e.g. standard microfluidic channel width ~ 5 μm); however, this method is beset by problems such as restrictions in fabricating 3D structures, low throughput, and an inherent incompatibility with automated manufacturing.

[0003] More recently, direct 3D printing to fabricate polymeric microstructures in MEMS technology has been attempted; here, the required polymeric structure is 3D-printed layer-by-layer either by: (a) extruding heated polymer through a nozzle which subsequently solidifies after being deposited on the substrate, e.g., fused deposition modeling (FDM); (b) curing a liquid polymer resin using a light source (ultraviolet, laser, etc.), e.g., stereolithography (SLA), digital light processing (DLP), polyjet 3D printing, and 2-photon lithography; or, (c) using a laser beam to selectively fuse powder that is spread by a recoating blade at each layer, e.g., selective laser sintering (SLS). Commercially available polymer 3D printers typically allow minimum feature sizes ranging from ~ 1 mm (FDM), ~ 0.7-1.2 mm (SLS), and ~ 0.3-0.6 mm (SLA); although this resolution is much coarser than that possible with soft lithography, 3D printing is compatible with automated manufacturing, unlike soft lithography.

[0004] However, the 3D printing techniques mentioned above can only build a limited number of polymers typically with Young's moduli in the range of 1.5 – 9.5 GPa, making them unsuitable for printing flexible microstructures made of soft, biocompatible elastomers such as PDMS (Young's modulus ~ 750 kPa) or hydrogels (Young's modulus ~ 50 kPa), owing to their low modulus values and long curing times. Moreover, the 3D printing techniques mentioned above are generally incapable of using multiple materials to print a given part, thus rendering them ineffective for fabricating functionally graded structures that possess different properties (mechanical, optical, thermal, etc.) in different locations.

[0005] Complex 3D soft polymeric microstructures with feature sizes in the range of 15-200 μm are the building blocks of MEMS devices and biomimetic structures, and find varied applications in flexible sensors, wearable electronics, soft robotics, tissue engineering, and so on.

[0006] 3D microstructures such as high-aspect ratio micropillar arrays and complex microfluidic channel networks are too tedious to fabricate using soft lithography; on the other hand, commercial plastic 3D printing techniques either lack the necessary fine resolution or are limited by their inability to print using the desired soft polymer material (e.g. PDMS, hydrogels) at the required fine resolution. Furthermore, plastic 3D printing techniques are unable to print high-aspect ratio structures. For example, SLA processes are limited to aspect ratios below or around 20.

[0007] There is therefore a need to provide a method for fabricating complex polymeric microstructures which is suitable for a variety of polymers, without limitations on the number or choice of polymeric materials. Moreover, a method of fabrication which is repeatable and batch-fabrication-compatible would simply fabrication of a range of technologies, such as MEMS devices, biomimetic structures and the like, often found in wearable electronics, flexible sensors and tissue engineering, *etc*.

Summary of the invention

[0008] The present invention aims to enable the manufacture of complex polymeric microstructures, in an adaptable and repeatable manner.

[0009] Accordingly, in a first aspect of the invention there is provided a method comprising 3D-printing a metallic mold, the metallic mold including a mold cavity corresponding to the 3D polymeric microstructure, polymer casting in the metallic mold by inserting a liquid polymer into the mold cavity, curing the liquid polymer inside the metallic mold, and etching the metallic mold away from the cured polymer.

[0010] The use of a metallic mold may improve the stability of the mold, especially when printing complex microstructures. Thus, a liquid polymer can be inserted and subsequently cured. Additionally, the method may allow for multiple polymers, even polymers with different physical properties such as Young's modulus, to be used. Once the polymer is cured, the metal mold can be etched away, leaving the complex polymeric microstructure.

[0011] Advantageously, the mold cavity may be a thin-shelled cavity with a wall thickness between 15 μm and 140 μm.

[0012] Having a low wall thickness may result in a faster etching process, and this range also ensures that the mold is sufficiently structurally robust to be 3D printed and to be used as a mold.

[0013] Advantageously, prior to etching the metallic mold away and after curing the liquid polymer inside the metallic mold, the method may further comprise polymer casting in the metallic mold by inserting at least one further liquid polymer into the mold cavity, and curing the at least one further liquid polymer inside the metallic mold.

[0014] The use of multiple polymers, such as polymers with different physical properties, may enable the fabrication of certain complex microstructures, in which different regions need to have different properties.

[0015] Advantageously, the metallic mold may comprise at least one of iron, copper, steel, titanium and aluminium alloys.

[0016] These materials may be particularly suitable for 3D printing, and may be etched away.

[0017] Advantageously, the 3D-printed metallic mold containing the cured polymer may be etched in a solvent that at least partially dissolves the metallic mold and releases the polymer microstructure.

[0018] Use of a solvent to at least partially dissolve the metallic mold and release the polymer microstructure may increase the ease of obtaining the polymer microstructure from the sacrificial mold.

[0019] Advantageously, the polymeric microstructure may comprise at least one micropillar with a diameter between 15 µm and 140 µm, an aspect ratio up to 100, and/or a pillar length with a varying cross-section.

[0020] Such a microstructure may be used in the design and fabrication of biologically inspired flow sensors with high signal-to-noise ratios.

[0021] Advantageously, the polymeric microstructure may comprise at least one array of said micropillars.

[0022] Such a microstructure may be used in the design and fabrication of biologically inspired flow sensors which may have improved directional sensitivity, and may be used to create super-hydrophobic surfaces, dry adhesive surfaces, microneedles and the like.

[0023] Advantageously, the polymeric microstructure may comprise an internal microfluidic 3D channel network with minimum feature sizes between 15 µm and 140 µm.

[0024] Advantageously, the polymeric microstructure may comprise internal microfluidic 3D channel networks inside high aspect ratio micropillars, with minimum feature sizes between 15 µm and 140 µm.

[0025] An internal microfluidic 3D channel network may help to increase the surface area of the internal channels when compared to planar 2D channels. This can be advantageous in micro-heat exchangers (enhanced cooling), sensing applications (enhanced signal), microreactors, and the like. The microchannel may be filled with another material, which may improve the adaptability to the microstructure to different use cases.

[0026] Advantageously, the polymeric microstructure may comprise a soft polymeric microelectromechanical systems (MEMS) device.

[0027] Advantageously, the soft polymeric MEMS device may comprise at least one flow sensor comprising at least one high aspect ratio structure.

[0028] The inclusion of a soft polymeric MEMS device, optionally with at least one flow sensor comprising at least one high aspect ratio structure, may enable the microstructure to be used as a flow sensor having a high signal-to-noise ratio.

[0029] Advantageously, the at least one high aspect ratio structure may comprise at least one integrated microchannel having minimum feature sizes between 15 µm and 140 µm for at least one piezoresistive sensing element.

[0030] This could enable the microstructure to be used to sense flow velocity.

[0031] Advantageously, the at least one high aspect ratio structure my comprise at least one of a micropillar and a cantilever.

[0032] Such structures may assist in biomimicry, and may improve the adaptability of the MEMS device.

[0033] Advantageously, the at least one piezoresistive sensing element may comprise at least one of conductive graphene nanoplatelet ink, silver nanoparticle ink, and liquid metal such as a Gallium-based eutectic alloy.

[0034] The use of the above-listed materials may result in a resistance change that can be used to sense flow velocity.

[0035] Advantageously, the polymeric microstructure may comprise biomimetic, polymeric, 3D microstructures and MEMS devices, the biomimetic, polymeric, 3D microstructures and MEMS devices comprising at least one of arrays of variable aspect ratio micropillars and high aspect ratio micropillars with undulating geometries, with minimum feature sizes between 15 µm and 140 µm.

[0036] These components may further improve flow sensing capabilities and may be used to obtain biologically inspired flow sensors with high signal-to-noise ratios.

Brief description of the drawings

[0037] Embodiments of the present invention will be described hereinafter, by way of example only, with reference to the accompanying drawings which are schematic in nature and therefore not necessarily drawn to scale. Furthermore, like reference signs in the drawings relate to like elements.

[0038] In the attached figures,

- Figure 1 depicts a simplified process for fabricating a microstructure according to an embodiment of the present invention;
- Figure 2 depicts a flowchart of a method for fabricating a polymeric microstructure according to an embodiment of the present invention;
- Figure 3 schematically shows (a) a model polymeric microstructure and (b) an associated mold, according to an embodiment of the present invention;
- Figures 4a and 4b depict flowcharts of a method for fabricating a polymeric microstructure according to an embodiment of the present invention;
- Figure 5 depicts an illustrative process schematic for fabricating a multi-material structure; and
- Figure 6 shows examples of complex polymeric microstructures according to an embodiment of the present invention.

Detailed description of embodiments

[0039] Figure 1 depicts a simplified process for fabricating a microstructure according to an embodiment of the present invention.

[0040] In order to fabricate a polymeric microstructure having a particular shape, a mold having a cavity corresponding to that particular shape is designed and 3D-printed, as shown in part (a). This process will be described in greater detail with reference to Figure 2. Once a suitable mold has been 3D-printed, at least one polymer is inserted into the mold, as shown in part (b). The at least one polymer is then cured according to the material(s) used and the desired hardness of the resulting polymeric microstructure. Once the at least one polymer is cured, the mold is etched away. In other words, the mold is sacrificial, and the etching process releases the polymeric microstructure, which is shown in part (c). Each of these steps will now be described in detail with reference to Figure 2.

[0041] Figure 2 depicts a flowchart of a method for fabricating a polymeric microstructure according to an embodiment of the present invention.

[0042] In operation 10 of Figure 2, a computerised model of a mold is generated. Preferably, the model is generated using computer-aided design (CAD) software, such as Solidworks (Dassault

Systemes, France). The mold comprises a 'negative' of the desired polymer structure. For example, if a simple micropillar polymer structure is desired (such as that shown in Fig. 3(a), a mold design is generated in which the cavity (or, in some embodiments, cavities) has the shape of the desired polymer structure. In the present description, the method is described by reference to a CAD model being generated, although any other digital or computerised model or algorithm configured for use with 3D printing may be used.

[0043] The mold may be modelled as a thin-shelled cavity, as illustrated in Figure 3(b). The CAD model may then be converted into a sliced stereolithography (STL) file, for example by using the Magics software (Materialise NV, Belgium) where support structures (usually 'line' supports to facilitate removal) are incorporated. Preferably, the shell of the mold has a wall thickness of between approximately 15 µm and 140 µm. Having a low wall thickness can result in a faster etching process (see operation 50).

[0044] In operation 20 of Figure 2, a metallic mold is 3D-printed based on the generated mold design. For example, the metallic mold may be produced by using any one of powder bed fusion (PBF), binder jetting, bound metal deposition, and micro laser sintering, and the like. The use of a metallic mold enables the fabrication of high aspect ratio microstructures, such as those shown in Figure 6. Metal ensures that molds for high aspect ratio microstructures are sufficiently stable during the 3D printing process.

[0045] For the sake of conciseness, the method will be described with reference to a laser powder bed fusion (LPBF) 3D printing technique, although any other 3D printing technique may be used. In one example, 17-4 PH stainless steel powder with a size distribution of 10 to 45 µm may be used as a raw material, although other materials are also envisaged. For example, any other 3D-printable metal or metallic alloy (e.g. 316L stainless steel, titanium allows such as Ti-6Al-4V, aluminium alloys such as Al-Si10-Mg, copper, iron, etc.) may be used to print a mold. Cheap powders, such as water-atomised pure iron, may be particularly beneficial for reducing costs, as the molds are single-use.

[0046] In the LPBF method, a focused laser beam (with a wavelength of 1 µm, for example) that selectively melts and fuses the powder into the final mold shape, layer-by-layer, where each powder layer is, for example, approximately 30 µm in thickness. In some embodiments where micro-laser sintering is used, the layer thickness may be between 1µm and 5µm.

[0047] After the 3D-printing process, the mold may be removed from a build plate, by sawing off the support structures, for example, and is preferably thoroughly cleaned using acetone, compressed air, and/or the like to remove remnant powder particles inside the mold cavity.

[0048] In operation 30 of Figure 2, a liquid polymer is inserted into the mold cavity. Preferably, a biocompatible thermosetting elastomer, such as polydimethylsiloxane (PDMS), is used as the liquid polymer. PDMS is difficult to 3D-print directly due to its long curing times and low Young's modulus. For example, a liquid PDMS solution may be prepared by thoroughly mixing 1 part curing agent with 10 parts silicone by weight.

[0049] Although the above refers to PDMS, any moldable polymer (thermoset or thermoplastic) may be used instead of, or in addition to, PDMS (for example, hydrogels). Thermosets, such as

silicone, polyurethane, epoxy resin, polyester resin, etc., and thermoplastics, such as acrylic, acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polycarbonate (PC), etc., are particularly suitable moldable polymers. When a thermoplastic polymer is used, it should be heated above its glass transition temperature and then solidified inside the mold. Thermosets, being liquid at room temperature, should be cured at higher temperatures inside the mold. It is advantageous to use polymers that are difficult to 3D-print directly, such as soft polymers.

[0050] In operation 40 of Figure 2, the liquid polymer in the mold cavity is cured. The term "curing" is used to denote any process by which the liquid polymer becomes a solid product. Curing is also referred as solidifying, casting and/or hardening. Once the liquid polymer has been inserted into the metal mold cavity, it may be cured. The curing may be effected by heating the polymer to a high temperature for a period of time. For example, when the chosen polymer is PDMS and after insertion into the metal mold cavity, the liquid PDMS may be degassed in a vacuum chamber to remove air bubbles, drop-cast into the metallic mold, degassed in a vacuum chamber again, and finally cured to form a solid PDMS microstructure inside the mold. The duration and conditions for curing the polymer depend on the desired hardness of the cured polymer. For example, the PDMS may be cured at 120°C for 20 minutes or an hour, or, for a softer cured polymer, PDMS may be cured at 25°C for 48 hours. As a further example, EPO-TEK (RTM) 353ND (an epoxy resin) may be cured for (a) 1 minute at 150°C, (b) 5 minutes at 120°C, (c) 10 minutes at 100°C, or (d) 30 minutes at 80°C. The polyurethane resin Xencast(RTM) PX30, may be cured for 1 hour at 25°C, or for a shorter time and at a higher temperature. The temperature and duration of the curing process can thus be tailored to the desired cured polymer hardness.

[0051] In operation 50 of Figure 2, once the polymer inside the mold cavity is cured, the mold may be removed from the polymeric microstructure. The cured polymer microstructure may be referred to as being "casted". The mold may first be cooled or may be allowed to cool down to room temperature. Preferably, the outer walls of the mold may be lightly ground with sandpaper or a suitable abrasive surface to remove traces of cured polymer adhered to it. The metallic mold may then be etched in a solvent (also referred to as etchant) to at least partially etch the metallic mold away. The choice of solvent may depend on the material of the metallic mold and/or the polymer, as the chosen solvent (etchant) should not interact with or change the properties of the cured polymer. In some cases, for example, an acidic solvent, such as 5 – 10 wt. % $FeCl_3$, 20 – 40 wt. % HCl, balance H_2O, may be used, and for other materials, a basic solvent may be used to dissolve the metal mold.

[0052] Preferably, the metallic mold is completely etched away. However, in some embodiments, the metallic mold is partially etched away and any remaining metallic mold material is removed from the polymer microstructure using any other known means, such as peeling, sanding, chiselling and/or chipping, etc. At least one of electrolytic etching, magnetic stirring and ultrasonic agitation may be used to assist the etching process. Once the metallic mold is etched away and/or removed, the polymeric microstructure is released.

[0053] The type of solvent may be based on the material of the mold, as well as on the type of polymer used for the polymeric microstructure. In particular, in an example where the thin-shelled

metallic mold is stainless steel and the polymer is PDMS, the etchant may be an acidic solvent (5 – 10 wt. % $FeCl_3$, 20 – 40 wt. % HCl, balance H_2O) at 50°C under ultrasonic agitation and/or magnetic stirring for a period of 3 to 4 hours. Once the mold is etched away, the polymer structure may float atop the etchant (solvent). It would also be possible to use a non-acidic solvent, such as sodium hydroxide or potassium hydroxide, although acidic etchants are preferred.

[0054] In some embodiments, the etching process may be achieved through the use of electrolytic etching, which is faster than normal immersive etching with ultrasonic agitation or magnetic stirring. In one example, a stainless steel mold may be etched away using oxalic acid by means of electrolytic etching.

[0055] Once released from the metallic mold, the polymer microstructure may be cleaned, for example ultrasonically. In one example, the released polymer microstructure is cleaned ultrasonically in water for 15 minutes.

[0056] Referring now to Figure 3, an example of a desired polymeric microstructure is shown in (a) and an associated mold design is shown in (b), according to an embodiment of the present invention.

[0057] For the sake of clarity and simplicity, a simple microstructure (a single micropillar) is shown in Figure 3. However, it should be noted that the microstructure may be considerably more complex (see, for example, Figure 5), although the principles remain the same.

[0058] Microstructure 1 is shown in Figure 3(a) as an example of a desired microstructure. Microstructure 1 comprises micropillar 2 having pillar length L and diameter d, and fixture 3 having height H and diameter Dfix. The fixture 3 facilitates the handling of the micropillar structure, which is often delicate. Preferably, the angle of the fixture 3, $\tan^{-1}(2H/D)$, is at least 45° in order to be 3D-printed without the need of a support structure during an SLM process..

[0059] Based on the desired microstructure 1, a corresponding mold 4 is designed as described with reference to operation 10 of Figure 2. Mold 4 may be a thin-shelled mold, preferably having a wall thickness (shown as 'x' in Figure 3(b)) between 15 µm and 140 µm. The wall thickness of the mold should be thick enough to maintain the robustness of the mold structure during the 3D printing process, and thin enough to be etched within reasonable times, such as 3 or 4 hours. For this reason, a wall thickness between 15 µm and 140 µm is preferred. Preferably, the size of mold cavity 5 is of the same dimension as the mold thickness, especially when laser PBF 3D printing is used. For example, in the case of Figure 3(b), the minimum diameter of the cavity would preferably be 30-200 µm.

[0060] As illustrated in Figure 3(b), mold 4 comprises mold cavity 5, which matches the dimensions of the desired microstructure 1 of Figure 3(a). In other words, the shape and size of the desired microstructure 1 has been subtracted from the mold design, resulting in a cavity having the shape of the desired microstructure.

[0061] The mold 4 may be 3D-printed using at least one of iron, copper, steel, titanium and aluminium, and/or any alloys thereof. Preferably, the material used for the mold has a low corrosion resistance. The mold is sacrificial, as it is etched away (or otherwise removed) from a polymeric

microstructure. As such, raw materials such as water-atomised pure iron powder are preferable due to their low cost.

[0062] Figures 4a and 4b depict flowcharts of methods for fabricating a polymeric microstructure according to an embodiment of the present invention. In particular, the flowcharts of Figures 4a and 4b illustrate methods in which multiple polymers may be used, in order to fabricate a microstructure with multiple polymers.

[0063] Referring first to Figure 4a, a method is provided in which a further liquid polymer is used in the fabrication of a polymeric microstructure. The details of operations 10 and 20 of Figure 4a are unchanged from operations 10 and 20 of Figure 2, and so shall not be repeated. Operations 30 and 40 of Figure 4a are also similar to operations 30 and 40 of Figure 2. The method of Figure 4a differs from the method of Figure 2 in that, after a first liquid polymer is inserted into the mold cavity and cured, a second, different liquid polymer is inserted into the mold cavity (operation 42) and cured (44) in a similar manner as the first liquid polymer in operation 40.

[0064] In other words, in operation 30, the mold cavity may be partially or selectively filled with the first liquid polymer. For example, in a complex microstructure, aspects of the microstructure may be filled with different polymers. As a further example, a microstructure may be only partially filled with the first liquid polymer and then further filled with a second (or further) liquid polymer.

[0065] The second liquid polymer may be cured under different conditions or through different means than the first liquid polymer. In some embodiments, the properties of the second liquid polymer differ from those of the first liquid polymer – the second liquid polymer may have a different Young's modulus, malleability, curing time, and/or the like, and may require different conditions in order to solidify. The operation of etching the mold away, provided in operation 50, corresponds to operation 50 of Figure 2 and is not described further.

[0066] Although the method of Figure 4a describes two liquid polymers, it is to be understood that a plurality of liquid polymers (e.g. two or more) may be used in the same way.

[0067] In the method of Figure 4a, the first liquid polymer is inserted and cured prior to the insertion of the second liquid polymer. However, a further embodiment is envisaged in which a plurality of liquid polymers are inserted in the mold cavity, and then a single curing operation occurs. This is illustrated in Figure 4b.

[0068] In Figure 4b, operations 10, 20 and 30 correspond to respective operations 10, 20 and 30 of Figures 2 and 4a, and shall not be described further here. In operation 35, prior to the operation of curing (operation 40), a second liquid polymer, distinct from the first liquid polymer, is inserted into the mold cavity.

[0069] It is further envisaged that the method of Figure 4b is not limited to the use of two liquid polymers, and that any number of liquid polymers may be used.

[0070] In the event that the second liquid polymer has different chemical and physical properties from the first liquid polymer, and may thus require different timing or conditions for curing, the curing operation 40a may correspond to the conditions required to cure the polymer with the most demanding conditions. For example, if the first liquid polymer requires 20 minutes to cure at 120°C

and the second liquid polymer requires 40 minutes to cure at 120°C, then the curing operation 40a will follow the requirements of the second liquid polymer (40 minutes at 120°C).

[0071] In the event that more than two polymers are used within the same microstructure, a combination of the methods of Figures 4a and 4b may be used. For example, a first liquid polymer and a second liquid polymer may be inserted into a mold and cured, as described in Figure 4b, and a third liquid polymer may be inserted additionally after the curing operation of the first and second polymers. A further curing step may then follow after the insertion of the third polymer.

[0072] The metallic mold is then etched away in operation 50, in the manner described with reference to operation 50 of Figure 2.

[0073] As described above and illustrated in Figures 4a and 4b, the process of Figure 2 may be used to fabricate multi-material polymeric microstructures which have different properties (e.g. density, Young's modulus, etc.) in different regions. For example, within a single microstructure, a first region may have a first Young's modulus, whilst another region of the microstructure has a different Young's modulus. Moreover, different regions of a single microstructure may have different hardnesses. An example of this is provided in Figure 5.

[0074] Figure 5 depicts an illustrative process schematic for fabricating a multi-material structure, according to the methods of Figures 4a and 4b. In Figure 5, mold 4 is designed and 3D-printed to fabricate an array of three thin pillars, with an aspect ratio of 50, and a thick base for handling the structure. Each pillar cavity is filled with a different polymer and degassed sequentially.

[0075] Referring now to Figure 5, a metallic mold 4 is provided in part (a). A first polymer is inserted into a first region of the mold 4, as shown in part (b). Optionally, the first polymer may be cured. This may be advantageous if the subsequent polymers require curing times and temperatures that differ considerably from those of the first polymer. Alternatively, the first polymer may be cured at the same time as one or more subsequent polymers.

[0076] A second polymer may then be inserted into a second region of the mold 4, as shown in part (c). The second polymer may optionally be cured at this point, or may be cured at the same time as one or more subsequent polymers.

[0077] As shown in part (d), a third polymer may be inserted into a third region of the mold 4. The third polymer may optionally be cured at this stage, or may be cured at the same time as one or more subsequent polymers. In some embodiments, certain polymers may be used in the microstructure(s) whilst at least one different polymer may be used in a fixture (such as fixture 3). In these cases, it may be preferable to cure any uncured polymers in the microstructure(s) prior to inserting the at least one polymer to be used for the fixture.

[0078] In part (e), a fourth polymer, used in fixture 3, is inserted. Subsequently, a curing operation occurs and any uncured polymers are cured. After all of the polymers have been cured, the mold 4 is etched away as described with reference to Figure 2 to obtain a multi-material microstructure such as that shown in part (f).

[0079] Referring now to Figure 6, several examples of complex microstructures are shown and described.

[0080] Figure 6(a) depicts single microstructure, inspired by a typically high-aspect ratio structure found throughout nature, such as a seal whisker. The micropillar shown in Figure 6(a) is a high-aspect ratio (HAR) micropillar with a HAR of approximately 50, with an undulating elliptical cross-section inspired by the whisker of a harbour seal (*phoca vitulina*). The undulations help the seal whisker minimise or decrease vortex-induced vibrations, and assists in attaining ultra-sensitive flow sensing capabilities. The ability to mimic such structural complexities (such as undulations and/or high-aspect ratios) may be used in the design and fabrication of biologically-inspired soft polymer microelectromechanical systems (MEMS) flow sensors possessing high signal-to-noise ratios. Through the processes described herein, a micropillar having a minimum elliptical cross section of approximately 15 to 140 μm for any desired height is achievable.

[0081] Figure 6(b) depicts an array of micropillars, inspired by stereocilia hair bundles commonly found in nature. The micropillars of Figure 6(b) may be similar to that shown in Figure 6(a). The array of micropillars shown in Figure 6(b) comprises HAR micropillars of varying heights, with a maximum aspect ratio of approximately 22. This array mimics the stereocilia hair bundles found throughout nature, such as in fish, a bull frog saccule, a human inner ear, etc. The ability to fabricate a microstructure having such structural complexity (i.e. an array of micropillars of varying heights) can be used to design and fabricate biologically-inspired soft polymer MEMS flow sensors with high directional sensitivity. Moreover, an array of micropillars such as that of Figure 6(b) may be used more generally to create super-hydrophobic surfaces, dry adhesive surfaces, microneedles and the like. Preferably, the minimum feature sizes are between 15 μm and 140 μm.

[0082] Figure 6(c) depicts an internal microfluidic 3D channel inside a HAR micropillar. More specifically, Figure 6(c) shows a HAR micropillar with an embedded helical microfluidic channel along its length, thus combining two structural complexities (a high aspect ratio micropillar and a 3D microfluidic channel). In one example, a helical microchannel having a minimum dimension of 15 to 140μm and a helical radius of between 50 and 350μm may be obtained within a micropillar with a diameter of approximately 60 to 400μm larger than the helix diameter. In the example shown in Figure 6(c), the helix angle with respect to the horizontal (i.e. $\tan^{-1}[\frac{\text{pitch}}{2*\text{helix diameter}}]$) is greater than 45°.

[0083] Figure 6(d) depicts a flow sensor with embedded sensing elements, inspired by cilia. The flow sensor of Figure 6(d) is a bio-inspired MEMS flow sensor, in the form of a HAR micropillar (such as that of Figure 6(a)) with an embedded, double helical microfluidic channel along a third of its length. As such, this structure also combines multiple structural complexities (namely a HAR micropillar and 3D microfluidic channels). When the microchannel is backfilled with a suitable piezoresistive material, such as graphene nanoplatelet ink, carbon nanotube solution, silver nanoparticle ink or the like, a flow stimulus produces a resistance change due to bending strain that can be used to sense the flow velocity. This sensing principle is inspired by the hair-like cilia structures which are used as ultrasensitive flow or tactile sensors by fish, insects and the like. The ability to embed the sensing elements into the hair-like sensor structure makes the sensor liquid-proof, and can be especially useful in sensing liquid flow, since direct contact between the sensing elements and the liquid is avoided. Moreover, the 3D helical shape of the microchannel increases

the conductive path, and hence net resistance change, upon application of stimulus (flow and/or tactile), thereby improving device sensitivity. In some embodiments, a piezoresistive structure such as the microchannel shown in Figure 6(d) may comprise any flowable (and therefore injectable) piezoresistive material. Preferably, materials with high gauge factors are used in order to attain high sensitivity. One or more liquid metal materials (such as Gallium-based eutectic alloys), carbon-based nanomaterials (such as carbon nanotubes, carbon nanofibers, graphene nanoplatelets, graphene oxide, carbon black, etc.), and/or silver nanoparticle ink may be used.

[0084] Additional microstructures other than those depicted in Figure 6 are also envisaged. For example, a high aspect ratio structure may comprise a micropillar and/or a cantilever, either in addition to or as an alternative to any of the elements described in relation to Figure 6.

[0085] Recently, 3D printing technology has advanced to a stage where the sacrificial molds can be made of non-metal materials, such as sugar, isomalt, acrylonitrile butadiene styrene (ABS), wax, acrylic, polyvinyl alcohol (PVA_, and so on which all dissolve in a suitable solvent or can be removed manually from the cured liquid polymer inside the mold.

[0086] In another embodiment of the present invention, the mold created through 3D printing in operation 20 of Figure 2 may be made of a combination of metallic and polymeric materials. For example, the mold is a composite of metal and polymers. Examples of polymers that could be used for 3D printing are acrylates, epoxides, polyamides, polylactic acid (or PLA), ABS, and polycarbonate. As long as the polymeric material used in the mold is not the same as the liquid polymer material that is inserted into the mold, any polymeric material may be suitable.

[0087] The advantage of the 3D printed mold comprising of a plurality of materials, such as metallic and polymeric materials is that it is then possible to perform the etching process into multiple stages. As each material may be etched away in a different manner, it may be possible to dynamically mold the liquid polymer inside the mold. For example, the polymeric material of the composite mold comprising of metallic and polymeric material may be etched off first, leaving openings in the mold. A second mold, comprising of the same material as the remaining metallic mold with liquid polymer inside its cavity could then be attached to the mold tosurrounding the opening. The liquid polymer is then cured, and the metallic material of both the original mold and the additional mold are then etched away. The result is a polymeric microstructure created through a multi-stage fabrication process.

[0088] In the preceding, a MEMS flow sensor has been described. However, other types of sensors can be provided as well by the described method of fabricating, such as force and tactile sensors. For example, it is possible to fabricate a MEMS force sensor featuring a GNP-infused microchannel embedded in a PDMS dome (diameter = 4 mm), where the force applied on top of the dome is transduced into a resistance change in the strained GNP microchannel. The microchannel (300 μm channel diameter) can be an internal microfluidic channel. It can have a double helical shape connected at the top by a horizontal rectangular (300 μm × 500 μm) microchannel.

[0089] In an alternative embodiment, the force sensor has an internal microfluidic channel in a different 3D shape. What is important is that the channel forms a conductive path for current flow

between two contact pads at the bottom, with no unintended interconnections anywhere along the conductive path, and while increasing, as much as possible, the amount of sensing material inside the PDMS dome, to maximize the length of the conducting path. In an embodiment, the length of the conducting path is at least 1.5 times, 2 times, or at least 3 times, or at least 4 times the length of a representative dimension of the sensor or the PDMS dome (e.g. of the width, diameter, or height of the sensor or PDMS dome). A double helical channel is one way of achieving this, but other ways exist too, for example two straight microchannels meeting at the top (e.g. an inverted V).

[0090] Such microchannel structures in sensors are difficult to fabricate using conventional methods. It should be noted that the measurements provided here are merely indicative of a typical example. Depending on the application, other measurements are possible. A wide variety of sensor shapes, sizes, and functionalities that can be achieved using the described method of fabrication. Advantageously, the embedding of a (GNP) piezoresistor inside a PDMS structure results in a naturally waterproof design, eliminating the need for any post-fabrication packaging.

[0091] The MEMS force sensor as described above was tested against a controlled load applied using a universal microtribometer (UMT-3, Bruker, USA). The double helical shape of the 3D strain gauge allowed us to maximize the length of the piezoresistor within a small (4 mm diameter) PDMS dome for enhanced sensitivity. The sensor was subjected to a compressive force (0 – 1.8 N in steps of 0.2 N) applied for 30 seconds through a cylindrical pin (10 mm diameter): the load was linearly increased to its maximum value in 5 seconds and then maintained at this value for 25 seconds before it was released. The application of the normal load strained the PDMS dome and the embedded GNP piezoresistor, thus inducing a change in resistance that was monitored using a Wheatstone bridge circuit at a sampling frequency of 10 Hz. The sensor showed a saturation in its output after a force of around 1 N (Fig. 6b), and displayed a resolution of at least 0.2 N.

[0092] Such a MEMS force sensor is suitable for many applications, including for example integration in an electric shaver, where the sensor can be used to warn a user when the amount of pressure applied by the shaver on the skin could lead to skin irritation. This is an alternative to measuring skin-cutter distance, which is very difficult and expensive to do in a shaver. In an embodiment, the MEMS force sensor is integrated into the middle between a plurality of rotary cutters of the electric shaver, so that the sensor directly pressed against the skin during shaving and measures the normal force. A dome-shaped MEMS sensor is ideally suited for this application since it satisfies the requirements of size (4 mm dome small enough to fit in the centre of the rotary cutters), flexibility (elastomeric PDMS), biocompatibility (PDMS structure), and force detection range (0 – 2 N). For shavers with a different configuration of cutters, another place for the sensor can be found. What is important is that it is in a position to measure the normal force against the skin during shaving.

[0093] Both the described flow sensor and the force sensor can use a piezoresistive sensing principle. In that case, the polymeric microstructure may comprise a piezoresistive sensing element. Other sensing principles are possible as well.

[0094] In the foregoing description of the figures, the invention has been described with reference to specific embodiments thereof. It will, however, be evident that various modifications and changes may be made thereto without departing from the scope of the invention as summarised in the attached claims.

[0095] In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed, but that the invention will include all embodiments falling within the scope of the appended claims.

[0096] In particular, combinations of specific features of various aspects of the invention may be made. An aspect of the invention may be further advantageously enhanced by adding a feature that was described in relation to another aspect of the invention.

[0097] It is to be understood that the invention is limited by the annexed claims and its technical equivalents only. In this document and in its claims, the verb “to comprise” and its conjugations are used in their non-limiting sense to mean that items following the word are included, without excluding items not specifically mentioned. In addition, reference to an element by the indefinite article “a” or “an” does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there be one and only one of the elements. The indefinite article “a” or “an” thus usually means “at least one”.

[0098] It will be appreciated that the present invention has been described with reference to a number of non-limiting exemplary embodiments and modifications can made to the above-described embodiments without departing from the scope of the invention. Moreover, features from the above-described embodiments can be combined with other embodiments described herein.

Claims

1. A method for fabricating a three-dimensional, 3D, polymeric microstructure comprising the following steps:

3D-printing a metallic mold, the metallic mold including a mold cavity corresponding to the 3D polymeric microstructure,

polymer casting in the metallic mold by inserting a liquid polymer into the mold cavity,

curing the liquid polymer inside the metallic mold, and

etching the metallic mold away from the cured polymer, wherein the polymeric microstructure comprises a soft polymeric microelectromechanical systems, MEMS, device, and the soft polymeric MEMS device comprises at least one sensor.

2. The method of claim 1, wherein the sensor is a flow sensor comprising at least one high aspect ratio structure, the at least one high aspect ratio structure preferably comprising at least one of a micropillar and a cantilever.

3. The method of claim 1, wherein the sensor is a force sensor comprising a microchannel which forms a conductive path for current flow between two contact pads at a side of the force sensor, the microchannel for example having a shape of a connected pair of double helical microchannels or two microchannels in the form of an inverted V.

4. The method according to any of the preceding claims, wherein the mold cavity is a thin-shelled cavity with a wall thickness between 15 µm and 140 µm.

5. The method according to any of the preceding claims, further comprising:

prior to etching the metallic mold away and after curing the liquid polymer inside the metallic mold, polymer casting in the metallic mold by inserting at least one further liquid polymer into the mold cavity, and curing the at least one further liquid polymer inside the metallic mold.

6. The method according to any of the preceding claims, wherein the metallic mold comprises at least one of iron, copper, steel, titanium and aluminum alloys.

7. The method according to any of the preceding claims, wherein the 3D-printed metallic mold containing the cured polymer is etched in a solvent that at least partially dissolves the metallic mold and releases the polymer microstructure.

8. The method according to any of the preceding claims, wherein the polymeric microstructure comprises at least one micropillar with a diameter between 15 µm and 140 µm, an aspect ratio up to 100, and/or a pillar length with a varying cross-section.

9. The method according to any of the preceding claims, wherein the polymeric microstructure comprises at least one array of said micropillars.

10. The method according to any one of the preceding claims, wherein the polymeric microstructure comprises an internal microfluidic 3D channel network with minimum feature sizes between 15 µm and 140 µm.

11. The method according to any one of the preceding claims, wherein the polymeric microstructure comprises internal microfluidic 3D channel networks inside high aspect ratio micropillars, with minimum feature sizes between 15 µm and 140 µm.

12. The method of any of the preceding claims, wherein the at least one high aspect ratio structure comprises at least one integrated microchannel having minimum feature sizes between 15 µm and 140 µm for at least one piezoresistive sensing element.

13. The method of claim 12, wherein the at least one piezoresistive sensing element comprises at least one of conductive graphene nanoplatelet ink, silver nanoparticle ink, and liquid metal such as a Gallium-based eutectic alloy.

14. The method according to any one of the preceding claims, wherein the polymeric microstructure comprises biomimetic, polymeric, 3D microstructures and MEMS devices, the biomimetic, polymeric, 3D microstructures and MEMS devices comprising at least one of arrays of variable aspect ratio micropillars and high aspect ratio micropillars with undulating geometries, with minimum feature sizes between 15 µm and 140 µm.

15. A three-dimensional, 3D, polymeric microstructure obtained by a method according to any one of claims 1 to 14.

Fig. 1A

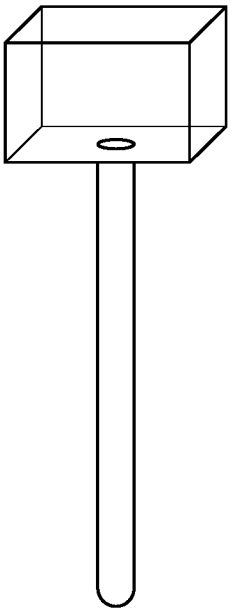


Fig. 1B

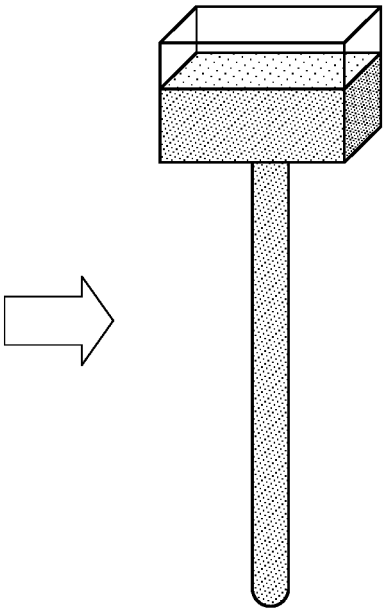


Fig. 1C

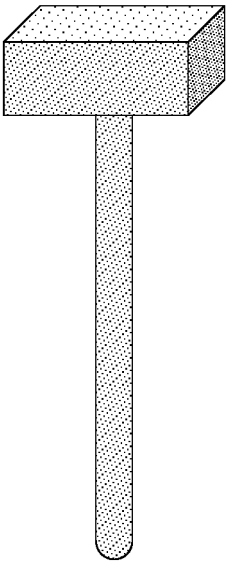
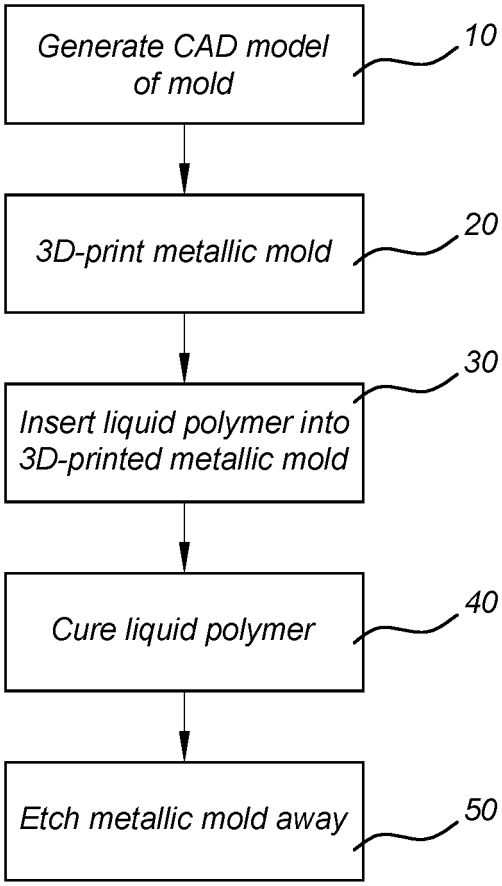


Fig. 2



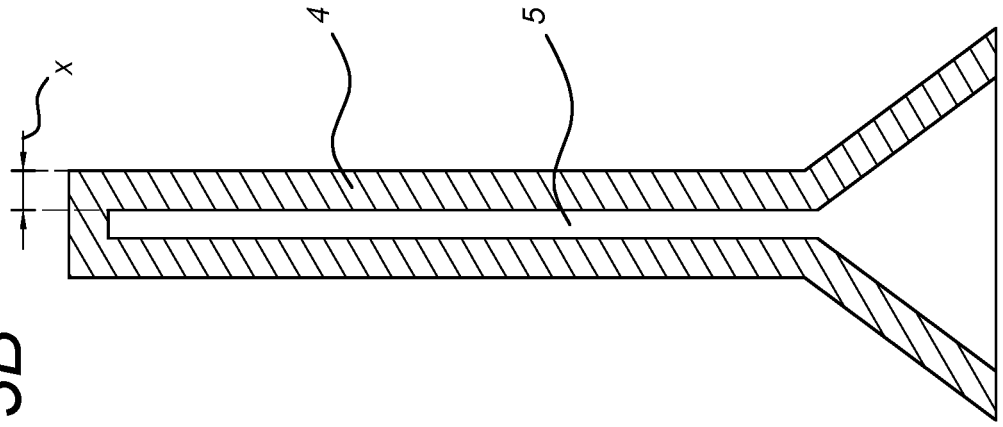


Fig. 3B

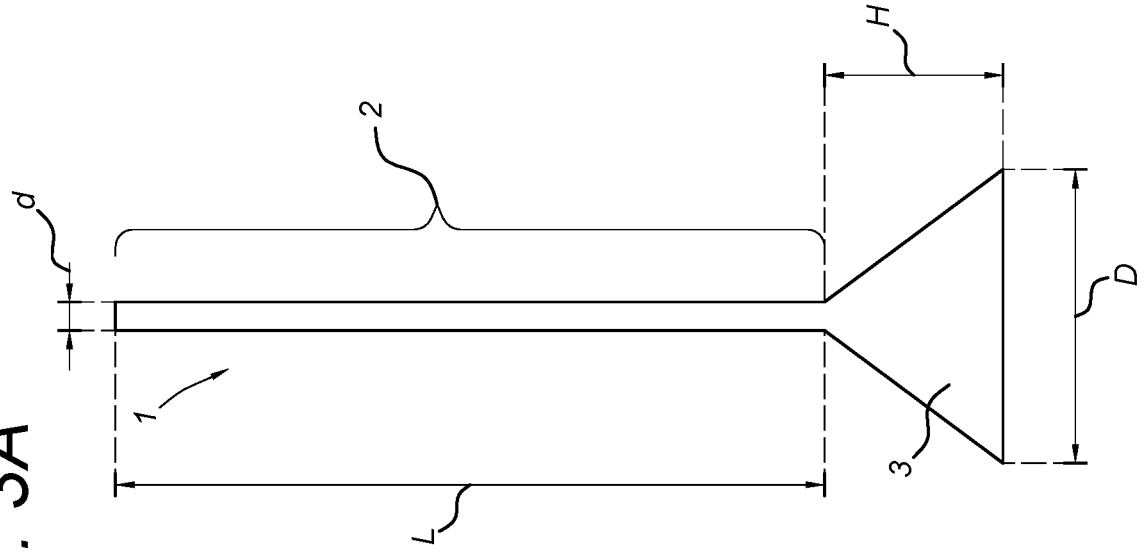


Fig. 3A

Fig. 4A

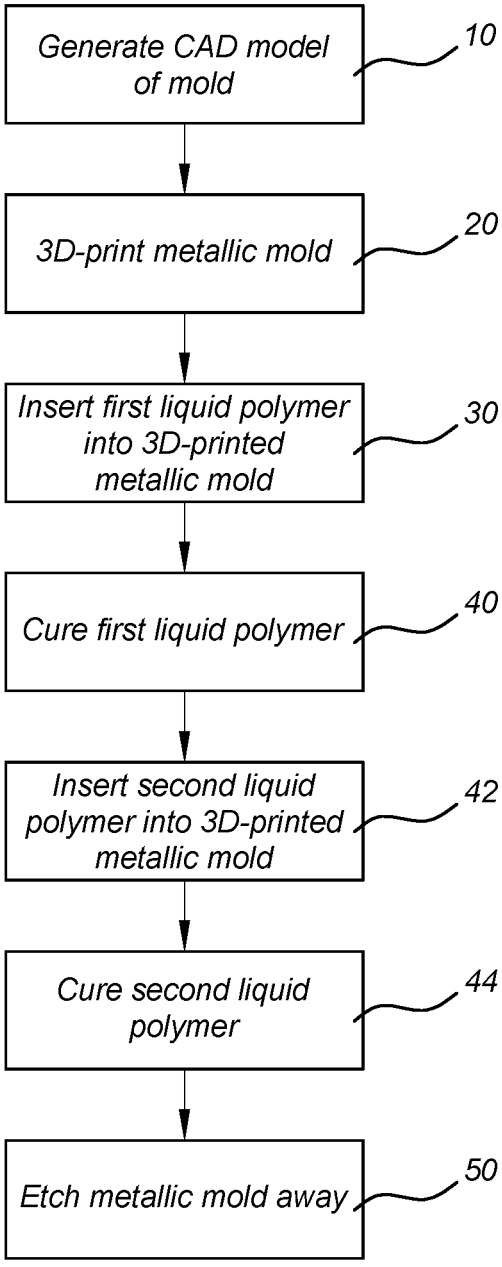

Generate CAD model of mold
10
3D-print metallic mold
20
Insert first liquid polymer into 3D-printed metallic mold
30
Cure first liquid polymer
40
Insert second liquid polymer into 3D-printed metallic mold
42
Cure second liquid polymer
44
Etch metallic mold away
50

Fig. 4B

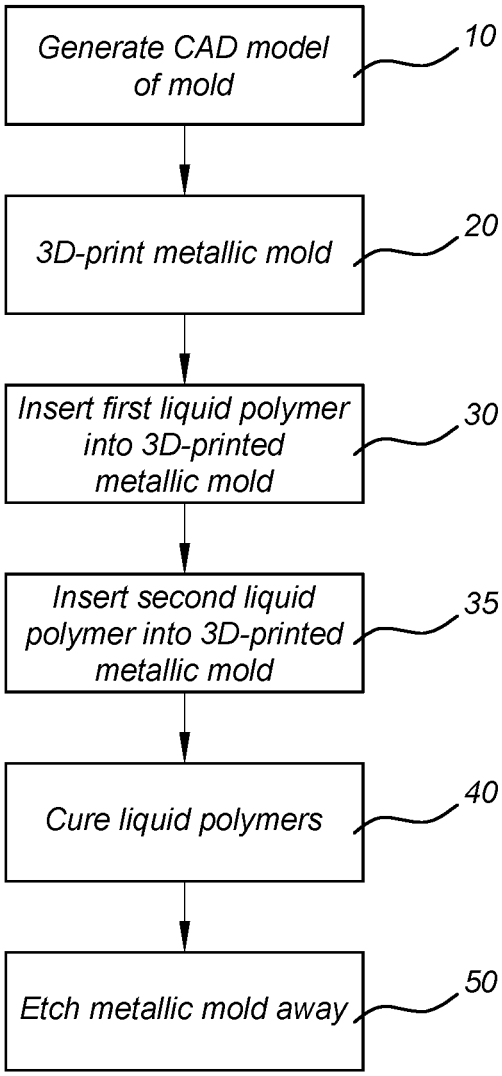

Generate CAD model of mold
10
3D-print metallic mold
20
Insert first liquid polymer into 3D-printed metallic mold
30
Insert second liquid polymer into 3D-printed metallic mold
35
Cure liquid polymers
40
Etch metallic mold away
50

Fig. 5A

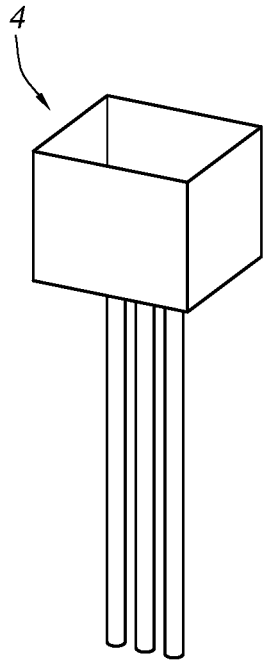


Fig. 5B

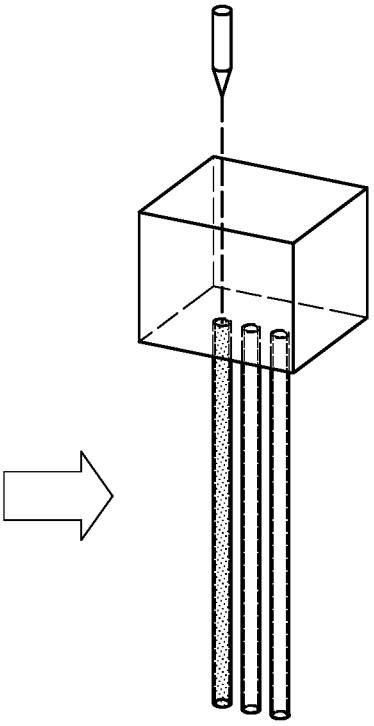


Fig. 5C

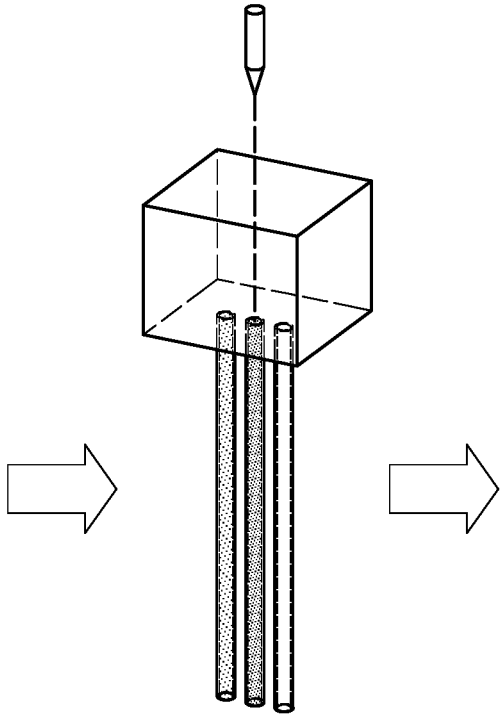


Fig. 5D

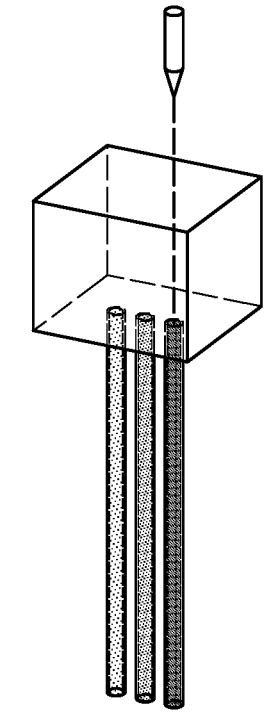


Fig. 5E

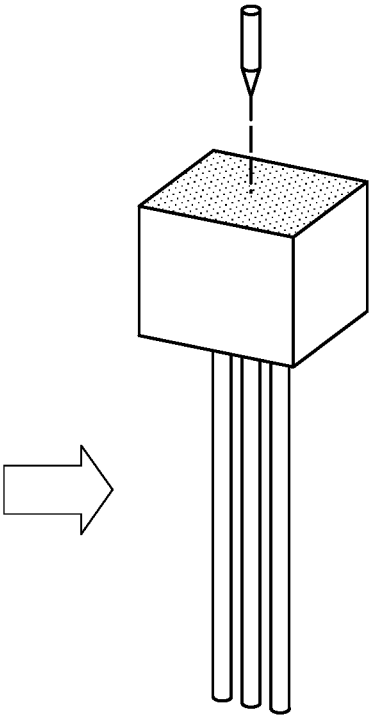
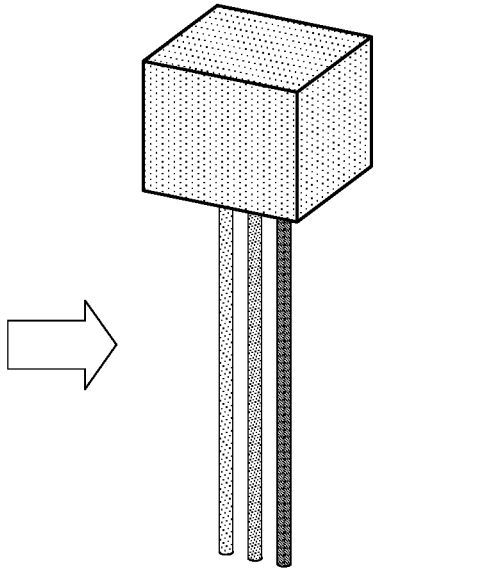


Fig. 5F



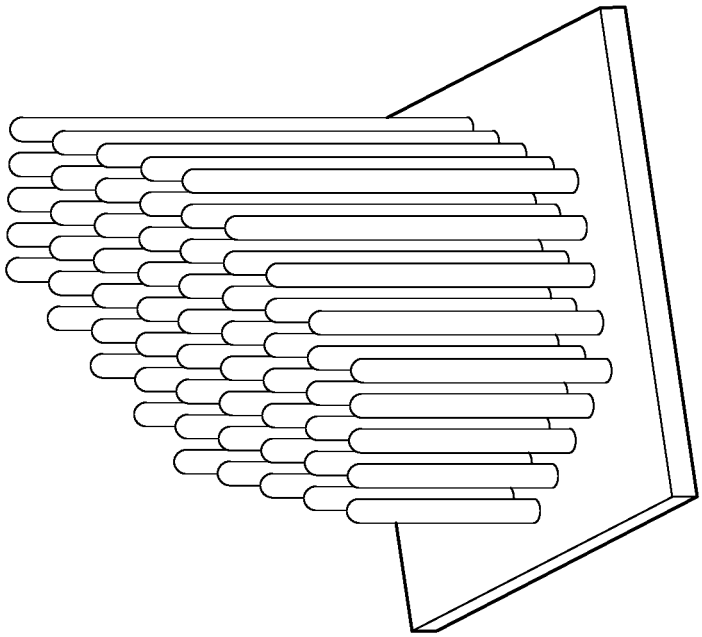


Fig. 6B

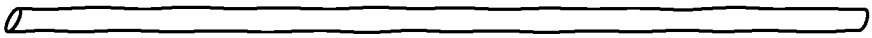


Fig. 6A

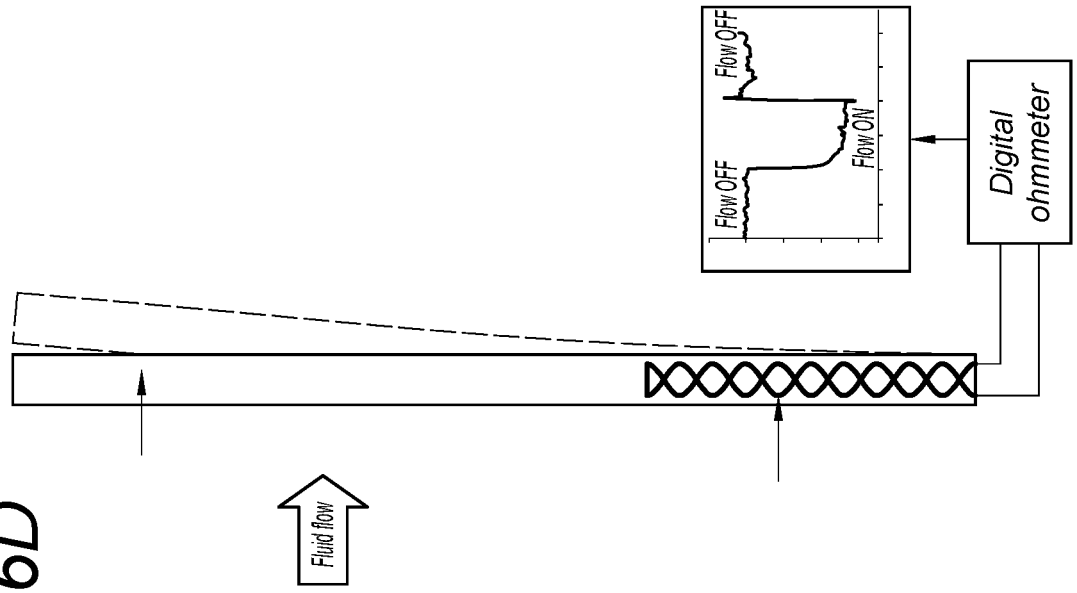


Fig. 6D

Fig. 6C

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/082304

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29C39/36 B29C33/38 B29C33/52 B29C64/153 B29C64/40
B22F3/00 B22F5/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B29C B29K B33Y B29L A61B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 371 605 A2 (CSEM CT SUISSE ELECTRONIQUE [CH]) 17 December 2003 (2003-12-17)	1,2, 4-11,15
A	paragraphs [0001], [0005], [0025]; claims 1,3,5	3,12-14

X	US 2003/006534 A1 (TABOAS JUAN M [US] ET AL) 9 January 2003 (2003-01-09)	1,2, 4-11,15
A	paragraph [0156]; claims 1,5,6,8,9	3,12-14

A	CN 109 523 887 A (UNIV BEIJING TECHNOLOGY) 26 March 2019 (2019-03-26) paragraphs [0005], [0007] - [0012]; claim 1	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 November 2020	08/12/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Ferrer Santos, A

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2019/112521 A1 (AGENCY SCIENCE TECH & RES [SG]) 13 June 2019 (2019-06-13) page 16, lines 1-19; claims 1-4,15,17; figure 2A	1-15
A	US 2019/077054 A1 (JESSEN JON [DK] ET AL) 14 March 2019 (2019-03-14) paragraphs [0290] - [0292], [0372]; claim 35	1-15
A	WO 02/098624 A1 (MIKRO SYSTEMS INC [US]; APPLEBY MICHAEL P [US] ET AL.) 12 December 2002 (2002-12-12) paragraphs [0040], [0112], [0213]; claim 1,	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2020/082304

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