

(51) International Patent Classification:
B29C 33/40 (2006.01)(21) International Application Number:
PCT/US2009/043306(22) International Filing Date:
8 May 2009 (08.05.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/153,028 17 February 2009 (17.02.2009) US(71) Applicant (for all designated States except US): **THE BOARD OF TRUSTEES OF THE UNIVERSITY OF ILLINOIS** [US/US]; 352 Henry Administration Building, 506 South Wright Street, Urbana, Illinois 61801 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KING, William P.** [US/US]; 1608 Crabapple Lane, Champaign, Illinois 61822 (US). **CANNON, Andrew H.** [US/US]; 2905 Weybourne Way, Columbia, South Carolina 29223 (US).(74) Agents: **GIANOLA, Adam J.** et al.; Greenlee, Winner And Sullivan, P.c., 4875 Pearl East Circle, Suite 200, Boulder, CO 80301 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHODS FOR FABRICATING MICROSTRUCTURES

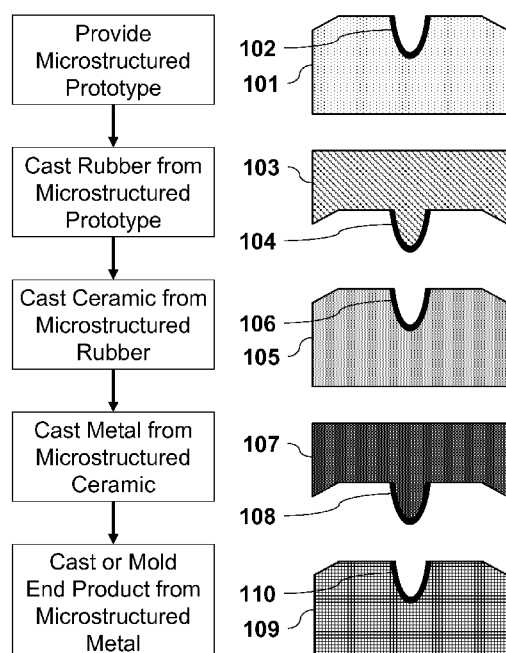


Figure 1

(57) Abstract: Described herein are casting and molding methods useful for making microstructured objects. By including a plurality of microfeatures on the surface of an object, other characteristics may be imparted to the object, such as increased hydrophobicity. Some of the casting and molding methods described herein further allow for manufacture of objects having both microfeatures and macro features, for example microfeatures on or within macro features or selected macro feature regions.

WO 2010/096072 A1



Published:

— *with international search report (Art. 21(3))*

METHODS FOR FABRICATING MICROSTRUCTURES

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application 61/153,028, filed on February 17, 2009, which is hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] This invention is in the field of casting/molding methods. This invention relates generally to methods of making molded or cast microstructured objects.

[0003] Casting and molding methods have long been utilized for producing and replicating objects. In general, the negative of an object is produced in a casting or molding process; that is, recessed features are replicated as raised features and vice versa. As such, at least two steps are generally required for replication of an object or features via casting or molding. First, a mold or form of an object is created around or on the master object, creating a negative of the master. For a casting method, the mold or form is filled with an end product material, creating a negative of the mold or form, which results in an end product generally resembling the master. In a molding method, the mold or form is stamped onto the end product material and the features of the master are replicated into the end product. Alternatively, the negative of the desired end product can be fabricated directly and used in a casting, molding or stamping process.

[0004] Only recently, however, have casting and molding methods been applied to microstructured objects. A limited number of U.S. Patents and Patent Application Publications disclose cast or molded microstructured objects. For example, U.S. Patent Application Publication US 2006/0162896 discloses methods for forming microstructured metallic surfaces via single use wax molds. U.S. Patent No. 5,735,985 discloses a method for high pressure compression molding of ceramic micro scale articles, for example a micro molded integrated ceramic light reflector. U.S. Patent No. 7,237,337 discloses a heat dissipating apparatus having a microstructured capillary layer formed by injection molding or

printing. U.S. Patent No. 7,410,606 discloses casting methods for microstructured objects utilizing a mold fabricated from multiple thin layers stacked to form the desired micro mold.

SUMMARY OF THE INVENTION

[0005] Described herein are casting and molding methods useful for making microstructured objects. By including a plurality of microfeatures on the surface of an object, other characteristics may be imparted to the object, such as increased hydrophobicity. Some of the casting and molding methods described herein further allow for manufacture of objects having both microfeatures and macro features, for example microfeatures on or within macro features or selected macro feature regions.

[0006] In one embodiment, a method for making a microstructured end product comprises the steps of fabricating a microstructured prototype; casting a rubber from the microstructured prototype, thereby making a microstructured rubber; casting a ceramic from the microstructured rubber, thereby making a microstructured ceramic; casting a metal from the microstructured ceramic, thereby making a microstructured metal; and casting or molding an end product material from the microstructured metal, thereby making a microstructured end product. For some embodiments, the microstructured prototype comprises a first set of features having dimensions selected over the range of 10 nm to 100 μm and a second set of features having dimensions of 100 μm and larger, for example, selected over the range of 100 μm to 1 m, 1 mm to 1 m, 1 cm to 1 m, or 5 cm to 1 m. In embodiments, a pitch of the microfeatures is selected over the range of 10 nm to 100 μm .

[0007] For some embodiments, the microstructured prototype comprises a plurality of micro features, for example features having dimensions selected over the range of 10 nm to 100 μm , and one or more macro features, for example features having dimensions 100 μm and larger, such as selected over the range of 100 μm to 1 m. Optionally, at least a portion of the microfeatures are positioned on a curved surface of the microstructured prototype. In a specific embodiment, at least a portion of the microfeatures are located on and/or within

the macro scale features. In a more specific embodiment, 80% to 100% of a surface area of the macro scale features is covered by the preselected pattern of microfeatures.

[0008] In embodiments, the features of the microstructured prototype are replicated in the rubber with high fidelity, for example with a replication fidelity selected over the range of 50% to 100%. An optional step of this method includes providing a release agent to the surface of the microstructured prototype before casting, for example a release agent selected from the group consisting of: napfin, paraffin wax, polysiloxanes, synthetic waxes, mineral oil, Teflon, fluoropolymers, silanes, thiols, and any combination of these. These and other release agents known to those skilled in the art may aid in separation of the cast rubber and the prototype from one another.

[0009] In a specific embodiment, a microstructured prototype comprises microfeatures having a preselected pattern. In some embodiments, the preselected pattern of microfeatures is transferred and/or replicated in a casting or molding process. In specific embodiments, the preselected pattern is transferred and/or replicated in every step of a multiple step casting and/or molding process, for example in a rubber casting step, a ceramic casting step, a metal casting step and/or an end product molding or casting step.

[0010] In an exemplary embodiment, the preselected pattern is a regular array of microfeatures. In another embodiment, the preselected pattern includes regions where the microfeatures have a first pitch and regions where the microfeatures have a second pitch, for example greater than the first pitch. As used herein, the term pitch refers to the spacing between adjacent microfeatures.

[0011] In one embodiment, a preselected pattern of microfeatures includes a region of microfeatures having a first cross sectional shape and a region of microfeatures having a second cross sectional shape, for example different from the first cross sectional shape. In one embodiment, a preselected pattern of microfeatures includes a region of microfeatures having multiple cross sectional shapes. In an embodiment, a preselected pattern of microfeatures refers to two or more arrays of microfeatures of two or more cross-sectional shapes. In a

specific embodiment, the two or more arrays can be positioned side by side; that is, where the two arrays do not overlap. In another specific embodiment, the two or more arrays are positioned to overlap, and microfeatures having the two or more cross sectional shapes are interspersed within the overlapping arrays.

[0012] In an embodiment, a preselected pattern of microfeatures includes multiple dimensions of microfeatures, for example a bimodal or multimodal distribution of dimensions. In an exemplary embodiment, a preselected pattern of microfeatures includes a first group of microfeatures having dimensions selected from 10 nm to 1 μ m and a second group of microfeatures having dimensions selected from 1 μ m to 100 μ m. In a specific embodiment, the sizes, shapes and positions of the microfeatures are preselected with micrometer-scale or nanometer-scale accuracy and/or precision. In a specific embodiment, each of the microfeatures in a preselected pattern have identical dimensions. In another embodiment, at least a portion of microfeatures in a preselected pattern have dimensions which differ. In embodiments, at least a portion of microfeatures in a preselected pattern have height/depth : width aspect ratios selected over the range of 1 : 2 to 7 : 1.

[0013] In some embodiments, the preselected pattern of microfeatures is engineered to impart specific physical characteristics to an object. For example, an ordered array of microfeatures can impart superhydrophobicity to the surface of an object. Physical characteristics which can be adjusted and imparted by a preselected pattern of microfeatures include, but are not limited to: hydrophobicity; hydrophilicity; self-cleaning ability; hydro and/or aerodynamic drag coefficients; optical effects such as prismatic effects, specific colors and directional dependent color changes; tactile effects; grip; and surface friction coefficients.

[0014] In general, the methods described herein can be utilized for making microstructured objects including molds, prototypes, primary objects, master objects, and end products. A method of this aspect for making a microstructured object comprises the steps of fabricating a microstructured prototype; and casting a rubber from the microstructured prototype, thereby making a microstructured

rubber having rubber microfeatures. In some embodiments, the microstructured prototype is reusable and is used for casting multiple microstructured rubber objects. For example, after one microstructured rubber object is cast and separated from the microstructured prototype, the microstructured prototype is used again for casting an additional microstructured rubber object.

[0015] A further casting method additionally comprises the step of casting a ceramic from the microstructured rubber, thereby making a microstructured ceramic comprising ceramic microfeatures. In some embodiments, the microstructured rubber is reusable and is used for casting multiple microstructured ceramic objects. For example, after one microstructured ceramic is cast and separated from the microstructured rubber, the microstructured rubber is used again for casting an additional microstructured ceramic object. In an embodiment, the microstructured rubber comprises a plurality of microfeatures and/or one or more macro features. Optionally, at least a portion of the rubber microfeatures are positioned on a curved surface of the microstructured rubber. In a specific embodiment, at least a portion of the microfeatures are located on or within the macro scale features. In embodiments, the features of the microstructured rubber are replicated in the ceramic with high fidelity, for example with a replication fidelity selected over the range of 50% to 100%. Optionally, a debonding agent is provided to the surface of the microstructured rubber before casting, for example a debonding agent selected from the group consisting of: water, soap, paraffin wax, polysiloxanes, synthetic waxes, mineral oil, Teflon, fluoropolymers, silanes, thiols, and any combination of these. These and other debonding agents known to those skilled in the art may aid in separation of the cast ceramic and the rubber from one another.

[0016] A further casting method additionally comprises the step of casting a metal from the microstructured ceramic, thereby making a microstructured metal comprising metal microfeatures. In some embodiments, the microstructured ceramic is reusable and is used for casting multiple microstructured metal objects. For example, after one microstructured metal is cast and separated from the microstructured ceramic, the microstructured ceramic is used again for casting an additional microstructured metal object. In an embodiment, the

microstructured ceramic comprises a plurality of microfeatures and/or one or more macro features. Optionally, at least a portion of the ceramic microfeatures are positioned on a curved surface of the microstructured ceramic. In a specific embodiment, at least a portion of the microfeatures are located on or within the macro scale features. In embodiments, the features of the microstructured ceramic are replicated in the metal with high fidelity, for example with a replication fidelity selected over the range of 50% to 100%.

[0017] Yet a further casting method additionally comprises the step of casting or molding an end product material from the microstructured metal, thereby making a microstructured end product comprising end product material microfeatures. In some embodiments, the microstructured metal is reusable and is used for casting or molding multiple microstructured end products. For example, after one microstructured end product is cast or molded and separated from the microstructured metal, the microstructured metal is used again for casting an additional microstructured end product. In an embodiment, the microstructured metal comprises a plurality of microfeatures and/or one or more macro features. Optionally, at least a portion of the metal microfeatures are positioned on a curved surface of the microstructured metal. In a specific embodiment, at least a portion of the microfeatures are located on or within the macro scale features. In embodiments, the features of the microstructured metal are replicated in the end product with high fidelity, for example with a replication fidelity selected over the range of 50% to 100%. For some embodiments, the end product comprises a plurality of microfeatures and/or one or more macro features. Optionally, at least a portion of the end product material microfeatures are positioned on a curved surface of the microstructured end product.

[0018] For some embodiments, the features of a cast microstructured object include an additional layer of roughness, for example a roughness inherent to the casting material itself and/or comprising features smaller in size than the features being cast. In one embodiment, the additional layer of roughness corresponds to the size of particles which make up a ceramic casting material. In an exemplary embodiment, the cast material comprises particles having sizes smaller than the features of the object being cast. In specific embodiments, the casting material

comprises spherical particles having diameters selected from 1 nm to 100 μm . In a preferred embodiment, the particles of the casting material have sizes less than one-tenth the size of the features being cast. When a cast object includes an additional layer of roughness, in an embodiment, the additional layer of roughness is transferred during a subsequent casting process to additional cast objects. For example, when a microstructured ceramic includes an additional layer of roughness, the roughness is replicated in a microstructured metal cast from the microstructured ceramic. In a further embodiment, a microstructured metal having an additional layer of roughness will transfer the additional layer of roughness to an end product cast to or molded from the microstructured metal.

[0019] In embodiments, a useful microstructured object comprises a plurality of microfeatures, for example features including, but not limited to: holes, pillars, steps, ridges, curved regions, raised regions, recessed regions, other standard geometric shapes known to those skilled in the art of microfabrication and any combination of these. Optionally at least a portion of the microfeatures are positioned on a curved surface of the microstructured object. In specific embodiments, the plurality of microfeatures have dimensions selected over the range of 10 nm to 100 μm , for example heights, widths and/or lengths. Useful cross-sectional shapes for the microfeatures include, but are not limited to: circles, ellipses, triangles, squares, rectangles, polygons, stars, hexagons, letters, numbers, mathematical symbols, other geometric shapes known to those skilled in the art of microfabrication and any combination of these.

[0020] In an embodiment, a useful microstructured object comprises one or more macro scale features, for example features including, but not limited to: channels, grooves, bumps, ridges, recessed regions, raised regions, curved regions and any combination of these or other useful macro scale features. In a specific embodiment, the macro scale features have dimensions of 100 μm and larger, for example, selected over the range of 100 μm to 1 m, 1 mm to 1 m, 1 cm to 1 m, or 5 cm to 1 m.

[0021] Also provided herein are methods for fabricating a microstructured prototype. In a specific method, fabricating a microstructured prototype

comprises providing a prototype; and attaching a microstructured polymer to at least a portion of the surface of the prototype. For some embodiments, the microstructured polymer includes a preselected pattern of microfeatures. For example, the microstructured polymer may comprise a lithographically patterned flexible polymer and/or a pattern made using methods including, but not limited to micropatterning techniques such as photolithography, photoablation, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these. In a specific embodiment, the attaching step comprises flexing at least a portion of the microstructured polymer and inserting and/or attaching at least a portion of the microstructured polymer into and/or onto a macro scale feature of the prototype. In an embodiment, a flexible polymer is a flexible elastomer.

[0022] In a specific embodiment of this aspect, fabricating a microstructured prototype comprises the steps of providing a semiconductor wafer; patterning the semiconductor wafer with a preselected pattern of microfeatures; molding an uncured flexible polymer to the patterned semiconductor wafer; curing the polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures; removing the microstructured flexible polymer from the patterned semiconductor wafer; providing a prototype having one or more macro scale features; and deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the prototype. In a specific embodiment, a prototype is a large-area prototype. For some embodiments, multiple microstructured flexible polymer sections are required to cover one or more macro scale features of a large-area prototype. In an embodiment, a flexible polymer is a flexible elastomer.

[0023] In another embodiment of this aspect, fabricating a microstructured prototype comprises providing a prototype; depositing uncured polymer onto at least a portion of the surface of the prototype; attaching a microstructured polymer to at least a portion of the surface of a macro mold; bringing the macro mold and microstructured polymer into contact with the prototype and the uncured polymer; applying heat and pressure to cure the uncured polymer;

releasing the macro mold and microstructured polymer from the prototype and cured polymer. For some embodiments, the microstructured polymer includes a preselected pattern of microfeatures. In a specific embodiment, the microstructured polymer comprises a lithographically patterned flexible polymer. In a specific embodiment, the attaching step comprises flexing at least a portion of the microstructured polymer and inserting and/or attaching at least a portion of the microstructured polymer into and/or onto a macro scale feature of the macro mold.

[0024] In a specific embodiment of this aspect, fabricating a microstructured prototype comprises the steps of providing a semiconductor wafer; patterning the semiconductor wafer with a preselected pattern of microfeatures; molding an uncured first polymer to the patterned semiconductor wafer; curing the first polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures; removing the microstructured flexible polymer from the patterned semiconductor wafer; providing a macro mold having one or more macro scale features; deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the macro mold; providing a prototype having one or more macro scale features; depositing an uncured second polymer onto at least a portion of a surface of the one or more macro scale features of the prototype; bringing the macro mold and microstructured flexible polymer into contact with the prototype and the uncured second polymer; curing the uncured second polymer, thereby making a microstructured second polymer having the preselected pattern of microfeatures; and releasing the macro mold and microstructured flexible polymer from the prototype and microstructured second polymer.

[0025] In another embodiment, fabricating a microstructured prototype comprises providing a prototype and patterning the prototype with a preselected pattern of microfeatures. Useful methods for patterning the prototype with a preselected pattern of microfeatures include, but are not limited to: drilling; milling; ion milling; machining; electro discharge machining; electroplating; ink jet printing; electrohydrodynamic ink jet printing; plasma etching; chemical etching;

photolithography; x-ray lithography; electron beam lithography; soft lithography; embossing; stamping molding; forging; etching with a plasma, gas or liquid; probe microscopy; atomic force microscopy; nano-indentation microscopy; chemical vapor deposition; physical vapor deposition; evaporation; electrospinning; and weaving microfibers or strands onto or into the surface. These and other patterning methods may further be combined with the above methods which utilize polymers; for example, the polymers and/or prototype may be patterned directly using any of the above methods.

[0026] In embodiments where a semiconductor wafer is patterned, methods known to those of skill in the art may be utilized. For certain embodiments, a semiconductor wafer includes a layer of photoresist. As used herein, a patterned semiconductor wafer refers to a semiconductor wafer having a pattern imparted directly into the semiconductor material, a semiconductor wafer having unpatterned semiconductor material and a patterned overlayer, and/or a semiconductor wafer having patterned semiconductor material and a patterned overlayer. Specific patterning methods include, but are not limited to photolithography, photoablation, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography and nano-imprint lithography. Semiconductor wafer patterning methods also include etching methods and methods useful for patterning overlayers, for example photoresist layers.

[0027] Without wishing to be bound by any particular theory, there can be discussion herein of beliefs or understandings of underlying principles relating to the invention. It is recognized that regardless of the ultimate correctness of any mechanistic explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] Figure 1 provides an overview of a method of making a microstructured object.

[0029] Figure 2 shows detail of a microstructured prototype with an expanded view of surface microfeatures.

[0030] Figure 3 shows a rubber cast to a microstructured prototype.

[0031] Figure 4 shows detail of a microstructured rubber with an expanded view of surface microfeatures.

[0032] Figure 5 shows an image of a microstructured rubber with a magnified image of rubber microfeatures.

[0033] Figure 6 shows a ceramic cast to a microstructured rubber.

[0034] Figure 7 shows detail of a microstructured ceramic with an expanded view of surface microfeatures.

[0035] Figure 8 shows an image of a microstructured ceramic with a magnified image of ceramic microfeatures.

[0036] Figure 9 shows a metal cast to a microstructured ceramic.

[0037] Figure 10 shows detail of a microstructured metal with an expanded view of surface microfeatures.

[0038] Figure 11 shows an image of a microstructured metal with a magnified image of metal microfeatures.

[0039] Figure 12 shows an end product cast or molded by microstructured metal.

[0040] Figure 13 shows detail of a microstructured end product with an expanded view of surface microfeatures.

[0041] Figure 14 shows a magnified image of end product microfeatures.

[0042] Figure 15 shows magnified images of a variety of shapes of end product microfeatures.

[0043] Figure 16 shows a microstructured flexible polymer for attachment to a prototype.

[0044] Figure 17 shows an assembled microstructured prototype.

[0045] Figure 18 shows an image of a microstructured prototype with a magnified image of flexible polymer microfeatures.

[0046] Figure 19 shows a microstructured flexible polymer for attachment to a macro mold.

[0047] Figure 20 shows an uncured polymer attached to a prototype.

[0048] Figure 21 shows a macro mold with an attached microstructured flexible polymer molding an uncured polymer attached to a prototype.

[0049] Figure 22 shows a prototype with a cured microstructured polymer molded by a macro mold with an attached microstructured flexible polymer.

[0050] Figure 23 shows an image of a directly molded microstructured prototype with a magnified image of cured polymer microfeatures.

[0051] Figure 24 provides an overview of a method of patterning a flexible polymer.

[0052] Figure 25 shows details of attachment of a microstructured flexible polymer to a structure.

[0053] Figure 26 provides an image of a microstructured aluminum object.

DETAILED DESCRIPTION OF THE INVENTION

[0054] In general the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of the invention.

[0055] “Microstructured object” refers to an object having a plurality of microfeatures. Specific microstructured objects include microstructured prototypes, microstructured rubbers, microstructured ceramics, microstructured metals and microstructured end products.

[0056] “Preselected pattern” refers to an arrangement of objects in an organized, designed or engineered fashion. For example, a preselected pattern of microfeatures can refer to an ordered array of microfeatures. In an embodiment, a preselected pattern is not a random and/or statistical pattern.

[0057] “Casting” refers to a manufacturing process in which a liquid material or a slurry is poured or otherwise provided into, onto and/or around a mold or other primary object, for example for replicating features of the mold or primary object to the cast material. Casting methods typically include a cooling or curing process to allow the cast material and/or precursor material to set and/or become solid or rigid. Some casting methods also include a final sintering, firing or baking step to cure a “green” or not finally cured object. For some casting methods, features of the mold or primary object are incorporated in the cast material as it sets. In specific embodiments, materials such as rubber, ceramic and/or metal are cast from molds or primary objects which are compatible with the liquid or slurry material; that is, the molds or primary objects do not deform, melt, and/or are not damaged when brought into contact with the liquid or slurry material.

[0058] “Molding” or “stamping” refers to a manufacturing process in which a material is shaped or forced to take a pattern using a rigid mold or other primary object. Molding methods typically include placing the mold or primary object in contact with the material to be molded and applying a force to the mold, primary object and/or material to be molded. For some molding methods, features of the mold or primary object are replicated in the material to be molded during the molding process. In a specific embodiment, an end product, such as rubber, is molded from a patterned metal object.

[0059] “Release agent” refers to a substance provided to the surface of a mold or primary object from which a rubber is to be cast to enhance and/or assist in the removal of the cast rubber from the mold or primary object. Specific release agents include materials selected from the group consisting of: napfin, paraffin wax, polysiloxanes, synthetic waxes, mineral oil, Teflon, fluoropolymers, silanes,

thiols, other release agents known to those skilled in the art, and any combination of these. Some release agents are also useful as debonding agents.

[0060] “Debonding agent” refers to a substance provided to the surface of a mold or primary object from which a ceramic is to be cast to enhance and/or assist in the removal of the cast ceramic from the mold or primary object.

Specific debonding agents include materials selected from the group consisting of: water, soap, paraffin wax, polysiloxanes, synthetic waxes, mineral oil, Teflon, fluoropolymers, silanes, thiols, other debonding agents known to those skilled in the art, and any combination of these. Some debonding agents are also useful as release agents.

[0061] “End product” refers to an object formed at the finish of a sequence of manufacturing steps. Some end products are suitable for use in a subsequent manufacturing process. Other end products, however, require additional processing, for example painting or other finalizing procedures. Some end products reach their final form at the finish of the sequence of manufacturing steps and are thus suitable for sale or for their intended use. Specific end products include, but are not limited to: moldable objects; sporting goods, such as grips, baseball bats, golf clubs, footballs, basketballs; cooking utensils; kitchenware; bathroom items such as toilets, sinks, tiles, bath tubs, shower curtains; handheld controllers, such as for gaming or equipment operation; bottles; computer keyboards; computer mice; jewelry; shoes; belts; helmets; pipes, including both inner and outer surfaces; candles; glass jars and jar lids; candy; turbine blades; pump rotors; heat sinks; insignia; windows; hoses; coolers; tires; tire treads; wheels; and sheets of polymer.

[0062] “Prototype” refers to an object which serves as the basis for subsequent molding or casting processes. In an exemplary embodiment, a prototype is constructed to resemble or include the features of a final cast or molded object or end product.

[0063] “Flexible” refers to a property of an object which is deformable in a reversible manner such that the object or material does not undergo damage when deformed, such as damage characteristic of fracturing, breaking, or

inelastically deforming. Flexible polymers are useful with the methods described herein. Specific flexible polymers include, but are not limited to: rubber (including natural rubber, styrene-butadiene, polybutadiene, neoprene, ethylene-propylene, butyl, nitrile, silicones), acrylic, nylon, polycarbonate, polyester, polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyolefin, elastomers and other flexible polymers known to those of skill in the art. In certain embodiments, flexible objects or materials can undergo strain levels selected over the range of 1% to 1300%, 10% to 1300%, or 100% to 1300% without resulting in mechanical failure (e.g., breaking, fracturing or inelastically deforming). In some embodiments, flexible objects or materials can be deformed to a radius of curvature selected over the range of 100 μm to 3 m without resulting in without resulting in mechanical failure (e.g., breaking, fracturing or inelastically deforming).

[0064] “Macro mold” refers to an object mold for shaping or molding an object in a molding, casting or contact process. In some embodiments, a macro mold is used to simultaneously shape an object on a macro scale, for example where features are larger than 1 mm, such as 1 mm to 1 m, 1 cm to 1 m, or 5 cm to 1 m, and impart microfeatures to the surface of the object.

[0065] “Primary object” refers to the object used in a casting or molding process from which the cast or molded object takes its shape, pattern and/or features. In a specific embodiment, a primary object refers to a prototype or master object; however, a primary object can also refer to any object from which the cast or molded object takes its shape, pattern and/or features during a casting or molding process.

[0066] “Cast object” refers to the object which is formed during a casting process and is made of a cured and/or cooled liquid, slurry and/or precursor material.

[0067] “Microfeatures” and “microstructures” refers to features, on the surface of an object or mold, having an average width, depth, length and/or thickness of 100 μm or less or selected over the range of 10 nm to 100 μm , for example 10 nm to 10 μm or 10 nm to 1 μm . In certain embodiments, microfeatures are located on

and/or within at least a portion of larger scale features (e.g., macro scale features) of an object, covering at least a portion of the surface area of the larger scale features are with microfeatures. In some embodiments, microfeatures include relief features. In some embodiments, microfeatures include recessed features.

[0068] “Macro scale features” refers to features, on the surface of an object or mold, having an average width, depth, length and/or thickness of 100 μm or greater, for example 1 mm or greater, 5 mm or greater, 1 cm or greater, 5 cm or greater or selected over the range of 100 μm to 1 m, 1 mm to 1 m, 1 cm to 1 m or 5 cm to 1 m. In some embodiments, macro scale features include relief features. In some embodiments, macro scale features include recessed features.

[0069] “Fidelity” refers to the quality of a cast or molded object; fidelity can also refer to the ability of features to be replicated in a cast or molded object during a casting or molding process. “High fidelity” specifically refers to the situation where a majority of the features of the mold or primary object are replicated in the molding or casting process to the cast or molded objects, for example 50% to 100% of the features, 75% to 100% of the features, 90% to 100% of the features or 100% of the features.

[0070] “Replication” and “replicate” refer to the situation where features are transferred and/or recreated during casting and/or molding processes. Replicated features generally resemble the original features they are cast or molded from except that the replicated features represent the negative of the original features; that is where the original features are raised features, the replicated features are recessed features and where the original features are recessed features, the replicated features are raised features. In a specific embodiment, micropillars in a master object are replicated as microholes in a cast object and microholes in the master object are replicated as micropillars in the cast object.

[0071] “Polymer” refers to a macromolecule composed of repeating structural units connected by covalent chemical bonds or the polymerization product of one or more monomers, often characterized by a high molecular weight. The term

polymer includes homopolymers, or polymers consisting essentially of a single repeating monomer subunit. The term "polymer" also includes copolymers, or polymers consisting essentially of two or more monomer subunits, such as random, block, alternating, segmented, graft, tapered and other copolymers. Polymers useable in the present invention may be organic polymers or inorganic polymers and may be in amorphous, semi-amorphous, crystalline or partially crystalline states. Cross linked polymers having linked monomer chains are particularly useful for some applications of the present invention. Polymers useable in the methods, devices and device components of the present invention include, but are not limited to, plastics, elastomers, thermoplastic elastomers, elastoplastics, thermostats, thermoplastics and acrylates. Exemplary polymers include, but are not limited to, acetal polymers, biodegradable polymers, cellulosic polymers, fluoropolymers, nylons, polyacrylonitrile polymers, polyamide-imide polymers, polyimides, polyarylates, polybenzimidazole, polybutylene, polycarbonate, polyesters, polyetherimide, polyethylene, polyethylene copolymers and modified polyethylenes, polyketones, poly(methyl methacrylate), polymethylpentene, polyphenylene oxides and polyphenylene sulfides, polyphthalamide, polypropylene, polyurethanes, styrenic resins, sulfone based resins, vinyl-based resins, rubber (including natural rubber, styrene-butadiene, polybutadiene, neoprene, ethylene-propylene, butyl, nitrile, silicones), acrylic, nylon, polycarbonate, polyester, polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyolefin or any combinations of these. Exemplary elastomers include, but are not limited to silicon containing polymers such as polysiloxanes including poly(dimethyl siloxane) (i.e. PDMS and h-PDMS), poly(methyl siloxane), partially alkylated poly(methyl siloxane), poly(alkyl methyl siloxane) and poly(phenyl methyl siloxane), silicon modified elastomers, thermoplastic elastomers, styrenic materials, olefinic materials, polyolefin, polyurethane thermoplastic elastomers, polyamides, synthetic rubbers, polyisobutylene, poly(styrene-butadiene-styrene), polyurethanes, polychloroprene and silicones. In an embodiment, a flexible polymer is a flexible elastomer.

[0072] “Ceramic” refers to an inorganic, nonmetallic material which is cured in a heating and/or drying process. As used herein, the term ceramic includes green and finally cured ceramic materials. In embodiments, some ceramics and ceramic precursors undergo a final curing step (e.g., sintering, firing or baking) before undergoing further processing or use. Specific ceramics include, but are not limited to: porcelain; crystalline ceramics; glass ceramics; zeolites; earthenware; plaster; oxides such as alumina and zirconia; non-oxides such as carbides, borides, nitrides and silicides; composite ceramics such as particulate reinforced ceramics and combinations of oxides and non-oxides. Specific ceramic precursors include clays, ceramic powders and slurries, such as slurries comprising water and another ceramic precursor or a ceramic powder. In some embodiments, ceramic precursors include organic components which are reacted away (e.g., by combustion) or otherwise incorporated or removed during the curing process. In specific embodiments, ceramics are useful for casting metals, as certain ceramic materials are capable of withstanding the conditions (e.g., temperatures) associated with molten metals; that is, certain ceramics do not undergo damage, breakage or deformations when brought into contact with molten or liquid metallic materials. In an embodiment, a ceramic is capable of withstanding high temperatures (e.g., above 500 °C) without undergoing damage.

[0073] Methods are described herein for the production of microstructured objects. Specific methods are useful with one another, for example they can be performed in series for the manufacture of a sequence of microstructured objects. The microstructured objects made by the methods described herein include regions of microfeatures which can give the object a variety of useful properties. For example, the microfeatures can impart an increased hydrophobicity to an object and/or can give an object a self-cleaning ability. The microfeatures can also impart optical effects to an object, for example giving an object a prismatic effect, a specific color, or a directional dependent color change or color flop (e.g. the object appears a specific color when viewed from one angle and another color when viewed from another direction).

[0074] The microfeatures can also impart an increase of surface friction or grip to an object, and/or can give an object a specific tactile sensation such as feeling

fuzzy, rough or squishy when touched. The microfeatures can also be located on a specific area or over the entire surface area of an object. For example, these embodiments can be useful for decreasing drag caused by turbulence of an object moving through a fluid (e.g., similar to the dimpling on a golf ball).

[0075] In a specific embodiment, the microfeatures can modify the heat transfer characteristics of an object, for example by changing the surface area of an object, changing how the surface interacts with fluids, or changing the behavior of nucleation sites. In a specific embodiment, the microfeatures can result in a decreased heat transfer by conduction, for example when the microfeatures have a high aspect ratio only the tops of the microfeatures will be in contact with another object for conductive heat transfer while the voids between surface features will not transfer heat well.

[0076] Microstructures can also be electrically conductive, for example metal microstructures or microstructures comprised of an electrically conductive polymer. These types of electrically conductive microstructures are useful, for example, as an array of electrical leads for electronic devices. The electrically conductive microstructures, for example, can be embossed directly onto the surface of an object.

[0077] In one aspect, microstructured tires are a specifically useful end product. Microstructured tires have increased hydrophobicity on specific patterns compared to other tires. A microstructured tire refers to a tire having a plurality of microfeatures on at least a portion of the surface of a tire. In a specific embodiment, a microstructured tire refers to a tire having microstructures on the tread portion of an automobile tire. Microstructuring of other regions of a tire is also useful, for example microstructured sidewalls or other regions of a tire may have reduced drag, increasing overall performance.

[0078] Figure 1 provides an overview of an exemplary method for making a microstructured object. First, a microstructured prototype **101** having a region of microfeatures **102** on a curved surface of microstructured prototype **101** is provided. Next, a rubber is cast to the microstructured prototype **101**, making a microstructured rubber **103**. The prototype microfeatures **102** are replicated in

the casting process as rubber microfeatures **104** on a curved surface of microstructured rubber **103**. Next, a ceramic is cast to the microstructured rubber **103**, making a microstructured ceramic **105**. The rubber microfeatures **104** are replicated in the casting process as ceramic microfeatures **106** on a curved surface of microstructured ceramic **105**. Next, a metal is cast to the microstructured ceramic **105**, making a microstructured metal **107**. The ceramic microfeatures **106** are replicated in the casting process as metal microfeatures **108** on a curved surface of microstructured metal **107**. Finally an end product is cast to or molded from the microstructured metal **107**, making a microstructured end product **109**. The metal microfeatures **108** are replicated in the casting or molding process as end product microfeatures **110** on a curved surface of microstructured end product **109**.

[0079] Figure 2 depicts further detail of a microstructured prototype **201** embodiment showing an expanded view of microfeatures **202**. In this embodiment, the microfeatures **202** are micropillars; that is they are cylindrically shaped structures extending from the surface of the prototype. For some embodiments, however, the microfeatures can include holes, pillars, steps, ridges, curved regions, recessed regions, raised regions, and any combination of these employing any cross-sectional shape including circles, ellipses, triangles, squares, rectangles, polygons, stars, hexagons, letters, numbers, mathematical symbols and any combination of these.

[0080] Figure 3 shows a rubber **303** cast to a microstructured prototype **301**. Microstructured prototype **301** can be used multiple times to cast rubber with high casting fidelity. Figure 4 depicts further detail of a microstructured rubber **403** embodiment showing an expanded view of microfeatures **404**. In this embodiment, the microfeatures **404** are holes which represent the negative of micropillars such as shown in Figure 2. Figure 5 shows an image of a microstructured rubber **503** cast from a microstructured prototype, with an expanded image of rubber microfeatures **504** replicated with high fidelity during the casting process. The bar in the expanded image represents a distance of 50 μm .

[0081] Figure 6 shows a ceramic **605** cast to a microstructured rubber **603**. Microstructured rubber **603** can be used multiple times to cast ceramic with high casting fidelity. Figure 7 depicts further detail of a microstructured ceramic **705** embodiment showing an expanded view of microfeatures **706**. In this embodiment, the microfeatures **706** are pillars, similar to those shown in Figure 2, which represent the negative of holes such as shown in Figure 4. Figure 8 shows an image of a microstructured ceramic **805** cast from a microstructured rubber, with an expanded image of ceramic microfeatures **806** replicated with high fidelity during the casting process. The bar in the expanded image represents a distance of 300 μm .

[0082] Figure 9 shows a metal **907** cast to a microstructured ceramic **905**. Figure 10 depicts further detail of a microstructured metal **1007** embodiment showing an expanded view of microfeatures **1008**. In this embodiment, the microfeatures **1008** are holes, similar to those shown in Figure 4, which represent the negative of pillars such as shown in Figures 2 and 7. Figure 11 shows an image of a microstructured metal **1107** cast from a microstructured ceramic, with an expanded image of metal microfeatures **1108** replicated with high fidelity during the casting process. The bar in the expanded image represents a distance of 200 μm .

[0083] Figure 12 shows an end product **1209** cast to or molded from a microstructured metal **1207**. Figure 13 depicts further detail of a microstructured end product **1309** embodiment showing an expanded view of microfeatures **1310**. In this embodiment, the microfeatures **1310** are pillars, similar to those shown in Figures 2 and 7, which represent the negative of holes such as shown in Figures 4 and 10. Figure 14 shows an image of microfeatures replicated with high fidelity during the casting or molding process. The bar in the figure represents a distance of 60 μm . Figure 15 shows images of additional microfeature embodiments having cross sectional shapes of circles, ellipses, triangles and squares. The ellipse and triangle embodiments show that there can be a variety of orientations of the cross sectional shapes.

[0084] As described above, multiple embodiments are contemplated for providing a microstructured prototype. In a specific embodiment, a microstructured flexible polymer is attached to the surface of a prototype. The microstructured flexible polymer can be patterned using methods including, but not limited to drilling; milling; ion milling; machining; electro discharge machining; electroplating; ink jet printing; electrohydrodynamic ink jet printing; plasma etching; chemical etching; lithographic patterning techniques such as photolithography, x-ray lithography, electron beam lithography, soft lithography; embossing; stamping; molding; forging; etching with a plasma, gas or liquid; probe microscopy; atomic force microscopy; nano-indentation microscopy; chemical vapor deposition; physical vapor deposition; evaporation; electrospinning; or weaving microfibers or strands onto or into the surface. Figure 16 shows an embodiment where a microstructured polymer **1602** having a plurality of micro pillars is inserted into a groove of a prototype **1601**. Figure 17 shows the resulting microstructured prototype **1701**. Figure 18 shows an image of a prototype **1801** embodiment having a microstructured flexible polymer inserted into a groove. Figure 18 also shows an expanded view image of a microstructured flexible polymer showing micro pillar type microfeatures **1802**. The bar in the expanded image represents a distance of 100 μm .

[0085] In another embodiment, microstructures are molded directly onto the prototype. One method of achieving this comprises providing a microstructured flexible polymer **1911** as shown in Figure 19 and attaching to the surface of a macro mold **1912**. Next, an uncured polymer **2013** is placed into the desired position for microstructures on a prototype **2001**, as shown in Figure 20. As shown in Figure 21, macro mold **2112** and microstructured polymer **2111** are brought into contact with prototype **2101** and uncured polymer **2113** where heat and pressure are applied to cure the uncured polymer. Figure 22 depicts the resulting microstructured prototype **2201** having microfeatures **2202**. Figure 23 shows an image of a microstructured prototype having microfeatures directly molded onto the prototype **2301**. Figure 23 also shows an expanded view image of the microstructured prototype showing microfeatures **2302** replicated with high

fidelity in the molding process. The bar in the expanded view image represents a distance of 150 μm .

[0086] The invention may be further understood by the following non-limiting examples.

EXAMPLE 1: MICROCASTING PROCESS CHAIN AND PROCESS DETAILS

[0087] This example describes a method of casting microstructures into the curved surfaces of three different material classes: rubber, ceramic, and metal. Figure 1 illustrates the micromolding casting process chain. The microcasting process chain begins with a prototype that has microstructures incorporated into its curved surface. Rubber is cast to the curved surface of the microstructured prototype, ceramic is cast to the curved surface of the microstructured rubber, metal is cast to the curved surface of the microstructured ceramic, and the microstructured metal molds or casts the curved surface of the end product. The microstructures replicate through all steps in the process chain. While this example describes the microstructured prototype with micropillars, this process is not limited to micropillars. The microstructured prototype could have microholes or other geometry types that would replicate through all steps in the process chain.

[0088] Two methods are described in this example for microstructuring the prototype: Insertion of microstructured polymer and direct molding of microstructures. Figures 16 and 17 explain the insertion route. The insertion route begins with flexible microstructured polymer **1611** and a prototype **1601** that has cm-scale grooves. Flexible microstructured polymer is inserted and adhered into the cm-scale grooves of the Prototype, resulting in a microstructured prototype **1701**. Figure 18 shows a picture of a microstructured prototype **1801** with microstructures **1802** inserted and adhered inside the cm-scale grooves. Figures 19, 20 and 21 explain the direct molding route. Flexible polymer **1911** with microholes adheres to a macro mold **1912** to create a microstructured mold. Uncured polymer **2013** is deposited in the cm-scale grooves of the prototype **2001**, and the microstructured mold **2112** presses and heats the prototype **2101** and uncured polymer **2113**, curing the deposited

polymer. The Microstructured mold releases the prototype resulting in a microstructured prototype **2201**. Figure 23 shows a picture of a microstructured prototype **2301** with microstructures **2302** direct molded inside the cm-scale grooves of the prototype. The curved surface of the microstructured prototype has a conformal covering of microstructures in both the insertion and direct molding routes.

[0089] Figures 2, 3 and 4 explain the microstructured prototype-to-rubber casting step. If desired, a release agent is sprayed onto the microstructured prototype mold **201** to ease demolding rubber from the microstructured prototype. One release agent that has been used is by Ciba Specialty Chemicals and is composed of napfin, paraffin wax, polysiloxanes, synthetic waxes, and mineral oil. When rubber **303** is cast from the microstructured prototype **201/301**, the microstructures **202** from the microstructured prototype **201/301** replicate into the microstructured rubber. A vacuum of 22 in Hg assisted the casting of rubber **303** into the microstructured prototype **201/301**. In this example, microholes **404** are cast into the microstructured rubber **403** from micropillars **202** in the microstructured prototype **201/301**. Figure 5 shows a picture of microstructures **504** replicated in rubber. A comparison of the microholes in the microstructured rubber to the micropillars of the microstructured prototype shows that the microstructured rubber was cast from the microstructured prototype with high fidelity.

[0090] Figures 4, 6 and 7 explain the microstructured Rubber-to-Ceramic casting step. One ceramic that has been used was Rantyre Investment from Ransom and Randolph which is a water based plaster. Any plaster similar to dental plaster is also suitable. If desired, a debonding agent is sprayed onto the microstructured rubber mold **403** to help the ceramic demold from the microstructured rubber mold. One debonding agent that has been used is simple soap in water. When the ceramic **605** is cast from microstructured rubber **403/603**, the microstructured rubber surface replicates into the ceramic **605**. The ceramic was vibrated at atmospheric pressure for approximately 30 seconds to remove gas bubbles from the ceramic before it hardened. In this example, micropillars **706** are cast into the microstructured ceramic **705** by the microholes

404 from the microstructured rubber **403/603**. Figure 8 shows a picture of microstructures **806** replicated in ceramic. A comparison of the micropillars in the microstructured ceramic to the microholes of the microstructured rubber shows that the microstructured ceramic cast to the microstructured rubber with high fidelity. The microstructured ceramic was then cured, for example at 150 °C for 12 hours, before casting metal to it.

[0091] Figures 7, 9 and 10 explain the microstructured ceramic-to-metal casting step. When the metal **907** is cast to microstructured ceramic **905**, the microstructured ceramic surface replicates into the metal. In this example, metal microholes **1008** are cast from micropillars **706** in the microstructured ceramic **705/905**. Figure 11 shows a picture of microstructures **1108** replicated in metal. A comparison of the microholes in the microstructured metal to the micropillars of the Microstructured Ceramic shows that the microstructured metal cast to the microstructured ceramic with high fidelity.

[0092] Figures 12 and 13 explain the microstructured metal-to-end product casting or molding step. When the microstructured metal **1207** casts or molds the end product **1209**, the microstructured metal surface replicates into the end product. In this example, microholes **1008** from the microstructured metal **1007/1207** molded micropillars **1310** into the microstructured end product **1309**. Figure 14 shows a picture of microstructured end product, reduced to practice. While molding created this specific end product, casting methods can also be used.

[0093] Figure 15 shows a variety of shapes that have been micromolded into the end product. 10-50 μm wide circles, ellipses, triangles, and squares have been micromolded into the end product with heights ranging from 35-70 μm . Microstructures with an aspect ratio of 7:1 (height:width) have been molded into the end product. The circles and ellipses show that this process can be used to produce round microstructures in the end product. The triangles and squares show that this process can be used to produce sharp-corned straight-edged microstructures in the end product.

EXAMPLE 2: FABRICATION METHOD FOR TAILORED MICROMETER-SCALE AND NANOMETER-SCALE STRUCTURES

[0094] Figure 24 shows a technique for fabricating Lithographically Defined Arrays of Micro/Nanostructures (LDAMN). The technique begins with a substrate **2414** topped with a photosensitive polymer or resist **2415** sensitive to light or particles. By shining light **2416** through a stencil mask **2417** onto the resist, micrometer-scale or nanometer-scale structures can be formed in the resist. Other kinds of electromagnetic waves, energy beams, or particles can also be used to form these microstructures or nanostructures. The structures can be arrayed into patterns or not, but their key characteristic is that the manufacturing process controls their size, shape, and position with micrometer-scale or nanometer-scale accuracy and precision.

[0095] The resist having tailored microstructures or nanostructures can be used as a mold at this stage. The substrate can also be treated (for example with a chemical etch) to modify the microstructures. Furthermore, the surface can be coated with an agent to ease or improve subsequent molding steps.

[0096] Uncured polymer can be molded into the microstructures and cured by heat, time, UV light or other curing methods. When the cured polymer **2418** is removed from the substrate-resist mold, the structures from the mold are transferred into the polymer, and are also mechanically flexible.

[0097] Figure 25 shows the process of integrating the polymer having tailored microstructure or nanostructures into millimeter-scale or centimeter-scale grooves. The process begins with the flexible polymer sheet **2518** having the microstructures and a structure **2519** suitable for receiving the flexible polymer sheet. Adhesive **2520** is applied to the cm-scale grooves of the receiving structure, and the flexible polymer sheet is inserted into the cm-scale grooves. Once the adhesive cures, the flexible polymer sheet is securely bonded to the structure. The combined structure is now suitable for subsequent molding and/or casting steps.

EXAMPLE 3: REUSABILITY OF MICROSTRUCTURED OBJECTS AND HETEROGENEITY OF MICROFEATURES

[0098] A microstructured prototype having a preselected pattern of microfeatures was fabricated. The preselected pattern included two regions of different microfeature shapes. The first region included micropillars 100 μm tall with 100 μm wide triangular cross-sectional shapes. The second region included micropillars 100 μm tall with 100 μm wide circular cross-sectional shapes.

[0099] A rubber was cast to the microstructured prototype to create a first microstructured rubber object. The microstructured rubber object thus produced included the two regions of different microfeature shapes formed from the casting of those of the microstructured prototype. The first region formed microholes 100 μm deep with 100 μm wide triangular cross-sectional shapes in the microstructured rubber. The second region formed microholes 100 μm deep with 100 μm wide circular cross-sectional shapes in the microstructured rubber.

[0100] Once the first microstructured rubber was removed from the microstructured prototype, rubber was again cast to the microstructured prototype to create a second microstructured rubber object having microfeatures matching those of the first microstructured rubber object.

[0101] A ceramic was cast to the second microstructured rubber object to create a first microstructured ceramic object. The microstructured ceramic object thus produced included the two regions of different microfeature shapes formed from the casting of those of the microstructured rubber. The first region formed micropillars 100 μm tall with 100 μm wide triangular cross-sectional shapes in the microstructured ceramic. The second region formed micropillars 100 μm tall with 100 μm wide circular cross-sectional shapes in the microstructured ceramic.

[0102] Once the first microstructured ceramic was removed from the second microstructured rubber object, ceramic was again cast to the second microstructured rubber object to create a second microstructured ceramic object having microfeatures matching those of the first microstructured ceramic object.

[0103] Finally, aluminum was cast to the second microstructured ceramic object to create a microstructured aluminum object **2600**. The microstructured aluminum object thus produced included the two regions of different microfeature shapes formed from the casting of those of the second microstructured ceramic object. A photograph of the microstructured aluminum object **2600** is shown in Figure 26. The first region **2601** formed microholes **2602** 100 μm deep with 100 μm wide triangular cross-sectional shapes in the microstructured rubber. The second region **2603** formed microholes **2604** 100 μm deep with 100 μm wide circular cross-sectional shapes in the microstructured rubber.

[0104] The microstructured prototype included curved regions which were transferred during the multiple casting steps to the microstructured aluminum. In Figure 26, this curvature can be observed near the bottom portion **2605** of the photograph, where the photograph becomes out of focus due to the shallow depth of field of the camera.

REFERENCES

- [0105]** U.S. Patent Application Publication No. US 2006/0162896.
- [0106]** U.S. Patent No. 5,735,985.
- [0107]** U.S. Patent No. 6,502,622.
- [0108]** U.S. Patent No. 7,237,337.
- [0109]** U.S. Patent No. 6,511,622.
- [0110]** U.S. Patent No. 7,410,606.
- [0111]** Schmitz, Grohn and Buhrig-Polaczek, Advanced Engineering Materials 2007, 9, No. 4, pp. 265-270.
- [0112]** Baumeister, Okolo and Rogner, Microsyst. Technol. (2008) 14: 1647-1655.
- [0113]** Baumeister, Ruprecht and Hausselt, Microsyst. Technol. (2004) 10: 261-264.

- [0114]** Rath, Baumeister and Hausselt, *Microsyst. Technol.* (2006) 12: 258-266.
- [0115]** Baumeister, Rath and Hausselt, *Microsyst. Technol.* (2006) 12: 773-777.
- [0116]** Baumeister, Okolo, Rogner, Ruprecht, Kerscher, Schulze Haußelt and Lohe, *Microsyst. Technol.* (2008) 14: 1813-1821.
- [0117]** Baumeister, Ruprecht and Hausselt, *Microsyst. Technol.* (2004) 10: 484-488.
- [0118]** Baumeister, Mueller, Ruprecht and Hausselt, *Microsyst. Technol.* (2002) 8: 105-108.
- [0119]** Barbieri, Wagner and Hoffman, *Langmuir* (2007) 23: 1723-1734.
- [0120]** Hua, Sun, Gaur, Meitl, Bilhaut, Rotkina, Wang, Geil, Shim, Rogers and Shim, *Nano Lett.* (2004) 4: 2467-2471.
- [0121]** Auger, Schilardi, Caretti, Sanchez, Benitez, Albella, Gago, Fonticelli, Vasquez, Salvarezza and Azzaroni, *Small* (2005) 1: 300-309.
- [0122]** Wang, Liang, Liang and Chou, *Nano Lett.* (2008) 8: 1986-1990.
- [0123]** Bico, Thiele, Quere, *Colloids and Surfaces A* (2002), 206: 41-46.
- [0124]** Lee, Yoon and Kim, *J. Phys. Chem. Solids* (2008), 69: 2131-2136.
- [0125]** Kumar, Tang and Schroers, *Nature* (2009), 457: 868-872.
- [0126]** Guo, *Advanced Materials* (2007), 19: 495-513.

STATEMENTS REGARDING INCORPORATION BY REFERENCE AND VARIATIONS

[0127] All references throughout this application, for example patent documents including issued or granted patents or equivalents, patent application publications, and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not

inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

[0128] U.S. provisional patent application entitled "Methods for Fabricating Microstructures," filed February 17, 2009 and having inventors William P. King and Andrew H. Cannon and serial number 61/153,028, is herein incorporated by reference in its entirety to the extent not inconsistent with the present description.

[0129] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art, in some cases as of their filing date, and it is intended that this information can be employed herein, if needed, to exclude (for example, to disclaim) specific embodiments that are in the prior art. For example, when a compound is claimed, it should be understood that compounds known in the prior art, including certain compounds disclosed in the references disclosed herein (particularly in referenced patent documents), are not intended to be included in the claim.

[0130] When a group of substituents is disclosed herein, it is understood that all individual members of those groups and all subgroups and classes that can be formed using the substituents are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure.

[0131] Every formulation or combination of components described or exemplified can be used to practice the invention, unless otherwise stated. Specific names of materials are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same material differently. One of ordinary skill in the art will appreciate that methods, device elements, starting materials, and synthetic methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such methods, device elements,

starting materials, and synthetic methods are intended to be included in this invention. Whenever a range is given in the specification, for example, a temperature range, a time range, or a composition range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure.

[0132] As used herein, “comprising” is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. Any recitation herein of the term “comprising”, particularly in a description of components of a composition or in a description of elements of a device, is understood to encompass those compositions and methods consisting essentially of and consisting of the recited components or elements. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0133] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

CLAIMS

We claim:

1. A method for making a microstructured end product, the method comprising the steps of:
 - fabricating a microstructured prototype comprising microfeatures having a preselected pattern;
 - casting a rubber from the microstructured prototype, thereby making a microstructured rubber comprising rubber microfeatures having the preselected pattern;
 - casting a ceramic from the microstructured rubber, thereby making a microstructured ceramic comprising ceramic microfeatures having the preselected pattern;
 - casting a metal from the microstructured ceramic, thereby making a microstructured metal comprising metal microfeatures having the preselected pattern; and
 - casting or molding an end product material from the microstructured metal, thereby making a microstructured end product comprising end product material microfeatures having the preselected pattern.
2. The method of claim 1, wherein the microfeatures have dimensions selected over the range of 10 nm to 100 μm and the microstructured prototype further comprises a second set of features having dimensions selected over the range of 100 μm to 1 m.
3. The method of claim 2, wherein at least a portion of the microfeatures are located on and/or within the second set of features
4. The method of claim 3, wherein 80% to 100% of a surface area of the second set of features is covered by the preselected pattern of microfeatures.

5. The method of claim 1, wherein the preselected pattern of microfeatures is made using a method selected from the group consisting of photolithography, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these.
6. The method of claim 1, wherein a pitch of the microfeatures is selected over the range of 10 nm to 100 μm .
7. The method of claim 1, wherein each of the microfeatures in the preselected pattern have identical dimensions.
8. The method of claim 1, wherein at least a portion of the microfeatures in the preselected pattern have dimensions which differ.
9. The method of claim 1, wherein an aspect ratio of at least a portion of the microfeatures is selected over the range of 1:2 to 7:1.
10. The method of claim 1, wherein at least a portion of the microfeatures are positioned on a curved surface of the microstructured prototype, at least a portion of the rubber microfeatures are positioned on a curved surface of the microstructured rubber, at least a portion of the ceramic microfeatures are positioned on a curved surface of the microstructured ceramic, at least a portion of the metal microfeatures are positioned on a curved surface of the microstructured metal, and at least a portion of the end product material microfeatures are positioned on a curved surface of the microstructured end product.
11. The method of claim 1, wherein the end product material is tire rubber, thereby making a microstructured tire.
12. The method of claim 1, wherein the preselected pattern of microfeatures is replicated with high fidelity in each casting and/or molding step.
13. The method of claim 11 wherein the replication fidelity is selected over the range of 50% to 100%.

14. The method of claim 1, wherein the step of fabricating a microstructured prototype comprises:

providing a semiconductor wafer;

patterning the semiconductor wafer with a preselected pattern of microfeatures;

molding an uncured flexible polymer to the patterned semiconductor wafer;

curing the polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;

removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a prototype having one or more macro scale features; and

deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the prototype.

15. The method of claim 1, wherein the step of fabricating a microstructured prototype comprises:

providing a semiconductor wafer;

patterning the semiconductor wafer with a preselected pattern of microfeatures;

molding an uncured first polymer to the patterned semiconductor wafer;

curing the first polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;

removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a macro mold having one or more macro scale features;

deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the macro mold;

providing a prototype having one or more macro scale features;

depositing an uncured second polymer onto at least a portion of a surface of the one or more macro scale features of the prototype;

bringing the macro mold and microstructured flexible polymer into contact with the prototype and the uncured second polymer;

curing the uncured second polymer, thereby making a microstructured second polymer having the preselected pattern of microfeatures; and

releasing the macro mold and microstructured flexible polymer from the prototype and microstructured second polymer.

16. The method of claim 14 or 15, wherein in the deforming step at least a portion of the microstructured polymer is deformed to radius of curvature selected over the range of 100 μm to 3 m.

17. The method of claim 14 or 15, wherein in the deforming step at least a portion of the microstructured polymer is deformed to a strain level selected over the range of 1% to 1300%.

18. The method of claim 14 or 15, wherein the patterning step comprises patterning the semiconductor wafer using a method selected from the group consisting of photolithography, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these.

19. A method for making a microstructured object, the method comprising the steps of:

fabricating a microstructured prototype comprising one or more microfeatures having a preselected pattern and dimensions selected over the range of 10 nm to 100 μm and one or more macro scale features having dimensions selected over the range of 100 μm to 1 m; and

casting a rubber from the microstructured prototype, thereby making a microstructured rubber comprising rubber microfeatures having the preselected pattern.

20. The method of claim 19, wherein at least a portion of the microfeatures are located on or within the macro scale features.

21. The method of claim 20, wherein 80% to 100% of a surface area of the macro scale features is covered by the preselected pattern of microfeatures.

22. The method of claim 19, wherein the preselected pattern of microfeatures is made using a method selected from the group consisting of photolithography, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these.

23. The method of claim 19, wherein a pitch of the microfeatures is selected over the range of 10 nm to 100 μm .

24. The method of claim 19, wherein each of the microfeatures in the preselected pattern have identical dimensions.

25. The method of claim 19, wherein at least a portion of the microfeatures in the preselected pattern have dimensions which differ.

26. The method of claim 19, wherein an aspect ratio of at least a portion of the microfeatures is selected over the range of 1:2 to 7:1.

27. The method of claim 19, further comprising the step of providing a release agent to the surface of the microstructured prototype.

28. The method of claim 27, wherein the release agent is selected from the group consisting of: napfin, paraffin wax, polysiloxanes, synthetic waxes, mineral oil, Teflon, fluoropolymers, silanes, thiols, and any combination of these.

29. The method of claim 19, further comprising the step of:

casting a rubber from the microstructured prototype, thereby making a second microstructured rubber comprising rubber microfeatures having the preselected pattern.

30. The method of claim 19, further comprising the step of:

casting a ceramic from the microstructured rubber, thereby making a microstructured ceramic comprising ceramic microfeatures having the preselected pattern.

31. The method of claim 30, further comprising the step of: providing a debonding agent to the surface of the microstructured rubber.

32. The method of claim 31, wherein the debonding agent is selected from the group consisting of: water, soap, paraffin wax, polysiloxanes, synthetic waxes, mineral oil, Teflon, fluoropolymers, silanes, thiols, and any combination of these.

33. The method of claim 30, further comprising the step of:

casting a ceramic from the microstructured rubber, thereby making a second microstructured ceramic comprising ceramic microfeatures having the preselected pattern.

34. The method of claim 30, further comprising the step of:

casting a metal from the microstructured ceramic, thereby making a microstructured metal having metal microfeatures having the preselected pattern.

35. The method of claim 34, further comprising the step of:

casting or molding an end product material from the microstructured metal, thereby making a microstructured end product comprising end product material microfeatures having the preselected pattern.

36. The method of claim 19, wherein the step of fabricating a microstructured prototype comprises:

providing a semiconductor wafer;

patterning the semiconductor wafer with a preselected pattern of microfeatures;

molding an uncured flexible polymer to the patterned semiconductor wafer;

curing the polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;

removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a prototype having one or more macro scale features; and

deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the prototype.

37. The method of claim 19, wherein the step of fabricating a microstructured prototype comprises:

providing a semiconductor wafer;

patterning the semiconductor wafer with a preselected pattern of microfeatures;

molding an uncured first polymer to the patterned semiconductor wafer;

curing the first polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;

removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a macro mold having one or more macro scale features;

deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the macro mold;

providing a prototype having one or more macro scale features;

depositing an uncured second polymer onto at least a portion of a surface of the one or more macro scale features of the prototype;

bringing the macro mold and microstructured flexible polymer into contact with the prototype and the uncured second polymer;

curing the uncured second polymer, thereby making a microstructured second polymer having the preselected pattern of microfeatures; and

releasing the macro mold and microstructured flexible polymer from the prototype and microstructured second polymer.

38. The method of claim 36 or 37, wherein in the deforming step at least a portion of the microstructured polymer is deformed to radius of curvature selected over the range of 100 μm to 3 m.

39. The method of claim 36 or 37, wherein in the deforming step at least a portion of the microstructured polymer is deformed to a strain level selected over the range of 1% to 1300%.
40. The method of claim 36 or 37, wherein the patterning step comprises patterning the semiconductor wafer using a method selected from the group consisting of photolithography, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these.
41. The method of claim 19, wherein the one or more microfeatures are selected from the group consisting of holes, pillars, steps, ridges, curved regions and any combination of these.
42. The method of claim 19, wherein the microfeatures of the microstructured prototype are replicated in the rubber with high fidelity.
43. The method of claim 42, further comprising the step of: casting a ceramic from the microstructured rubber, thereby making a microstructured ceramic and wherein the microfeatures of the microstructured rubber are replicated in the ceramic with high fidelity.
44. The method of claim 43, further comprising the step of: casting a metal from the microstructured ceramic, thereby making a microstructured metal and wherein the microfeatures of the microstructured ceramic are replicated in the metal with high fidelity.
45. The method of claim 44, further comprising the step of casting or molding an end product material from the microstructured metal, thereby making a microstructured end product and wherein the microfeatures of the microstructured metal are replicated in the end product with high fidelity.
46. The method of claim 42, 43, 44 or 45, wherein the replication fidelity is selected over the range of 50% to 100%.

47. The method of claim 19, wherein at least a portion of the microfeatures are positioned on a curved surface of the microstructured prototype.
48. The method of claim 19, 29 or 42, wherein at least a portion of the rubber microfeatures are positioned on a curved surface of the microstructured rubber.
49. The method of claim 30, 33 or 43, wherein at least a portion of the ceramic microfeatures are positioned on a curved surface of the microstructured ceramic.
50. The method of claim 34 or 44, wherein at least a portion of the metal microfeatures are positioned on a curved surface of the microstructured metal.
51. The method of claim 35 or 45, wherein at least a portion of the end product material microfeatures are positioned on a curved surface of the microstructured end product.
52. The method of claim 20, wherein the plurality of microfeatures have cross-sectional shapes selected from the group consisting of circle, ellipse, triangle, square, rectangle, polygon, stars, hexagons, letters, numbers, mathematical symbols and any combination of these.
53. The method of claim 20, wherein the macro scale features are selected from the group consisting of: channels, grooves, bumps, ridges, recessed regions, raised regions, curved regions and any combination of these.
54. A method for making a microstructured tire, the method comprising the steps of:
- fabricating a microstructured prototype having a preselected pattern of microfeatures;
- casting a rubber from the microstructured prototype, thereby making a microstructured rubber comprising rubber microfeatures having the preselected pattern;

casting a ceramic from the microstructured rubber, thereby making a microstructured ceramic comprising ceramic microfeatures having the preselected pattern;

casting a metal from the microstructured ceramic, thereby making a microstructured metal comprising metal microfeatures having the preselected pattern; and

casting or molding tire rubber from the microstructured metal, thereby making a microstructured tire comprising tire rubber microfeatures having the preselected pattern.

55. The method of claim 54, wherein the microstructured tire includes one or more macro scale features.

56. The method of claim 55, wherein at least a portion of the microfeatures are located on or within the one or more macro scale features.

57. The method of claim 56, wherein 80% to 100% of a surface area of the second set of features is covered by the preselected pattern of microfeatures.

58. The method of claim 55, wherein the macro scale features have dimensions selected over the range of 1 mm to 1 m.

59. The method of claim 54, wherein at least a portion of the microfeatures are positioned on a curved surface of the microstructured prototype.

60. The method of claim 54, wherein the microfeatures have dimensions selected over the range of 10 nm to 100 μm .

61. The method of claim 54, wherein the preselected pattern of microfeatures is made using a method selected from the group consisting of photolithography, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these.

62. The method of claim 54, wherein the preselected pattern of microfeatures is replicated in each casting and/or molding step with a replication fidelity selected over the range of 50 to 100%.
63. The method of claim 54, wherein a pitch of the microfeatures is selected over the range of 10 nm to 100 μm .
64. The method of claim 54, wherein each of the microfeatures in the preselected pattern have identical dimensions.
65. The method of claim 54, wherein at least a portion of the microfeatures in the preselected pattern have dimensions which differ.
66. The method of claim 54, wherein an aspect ratio of at least a portion of the microfeatures is selected over the range of 1:2 to 7:1.
67. The method of claim 54, wherein the microstructured tire comprises a plurality of microfeatures on the tread portion of an automobile tire.
68. The method of claim 54, wherein the microstructured tire comprises a plurality of microfeatures on the sidewall portion of an automobile tire.
69. The method of claim 54, wherein the step of fabricating a microstructured prototype comprises:
- providing a semiconductor wafer;
 - patterning the semiconductor wafer with a preselected pattern of microfeatures;
 - molding an uncured flexible polymer to the patterned semiconductor wafer;
 - curing the polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;
 - removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a prototype having one or more macro scale features; and

deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the prototype.

70. The method of claim 54, wherein the step of fabricating a microstructured prototype comprises:

providing a semiconductor wafer;

patterning the semiconductor wafer with a preselected pattern of microfeatures;

molding an uncured first polymer to the patterned semiconductor wafer;

curing the first polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;

removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a macro mold having one or more macro scale features;

deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the macro mold;

providing a prototype having one or more macro scale features;

depositing an uncured second polymer onto at least a portion of a surface of the one or more macro scale features of the prototype;

bringing the macro mold and microstructured flexible polymer into contact with the prototype and the uncured second polymer;

curing the uncured second polymer, thereby making a microstructured second polymer having the preselected pattern of microfeatures; and

releasing the macro mold and microstructured flexible polymer from the prototype and microstructured second polymer.

71. The method of claim 69 or 70, wherein 80% to 100% of a surface area of the one or more macro scale features is covered by the preselected pattern of microfeatures.

72. The method of claim 69 or 70, wherein at least a portion of the microstructured polymer is deformed to a radius of curvature selected over the range of 100 μm to 3 m.

73. The method of claim 69 or 70, wherein at least a portion of the microstructured polymer is deformed to a strain level selected over the range of 1% to 1300%.

74. The method of claim 69 or 70, wherein the patterning step comprises patterning the semiconductor wafer using a method selected from the group consisting of photolithography, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these.

75. The method of claim 54, wherein at least a portion of the microfeatures are positioned on a curved surface of the microstructured prototype, at least a portion of the rubber microfeatures are positioned on a curved surface of the microstructured rubber, at least a portion of the ceramic microfeatures are positioned on a curved surface of the microstructured ceramic, at least a portion of the metal microfeatures are positioned on a curved surface of the microstructured metal, and at least a portion of the tire rubber microfeatures are positioned on a curved surface of the microstructured tire.

76. The method of claim 1, 30, 33, 43 or 54, wherein the microstructured ceramic includes an additional layer of roughness comprising features

smaller in size than the ceramic microfeatures having the preselected pattern.

77. The method of claim 77, wherein the additional layer of roughness is replicated in further casting or molding steps.

78. A method of making a microstructured object, the method comprising the steps of:

providing a semiconductor wafer;

patterning the semiconductor wafer with a preselected pattern of microfeatures;

molding an uncured flexible polymer to the patterned semiconductor wafer;

curing the polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;

removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a large-area prototype having one or more macro scale features;

deforming at least a portion of the microstructured flexible polymer so as to conform the deformed microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the large-area prototype; and

casting or molding a material to the prototype and microstructured polymer, thereby replicating the preselected pattern of microfeatures in at least a portion of a cast or molded object.

79. A method of making a microstructured object, the method comprising the steps of:

providing a semiconductor wafer;

patterning the semiconductor wafer with a preselected pattern of microfeatures;

molding an uncured first polymer to the patterned semiconductor wafer;

curing the first polymer, thereby forming a microstructured flexible polymer having the preselected pattern of microfeatures;

removing the microstructured flexible polymer from the patterned semiconductor wafer;

providing a macro mold having one or more macro scale features;

deforming at least a portion of the microstructured flexible polymer so as to conform the microstructured flexible polymer to at least a portion of the surface of the one or more macro scale features of the macro mold;

providing a large-area prototype having one or more macro scale features;

depositing an uncured second polymer onto at least a portion of a surface of the one or more macro scale features of the prototype;

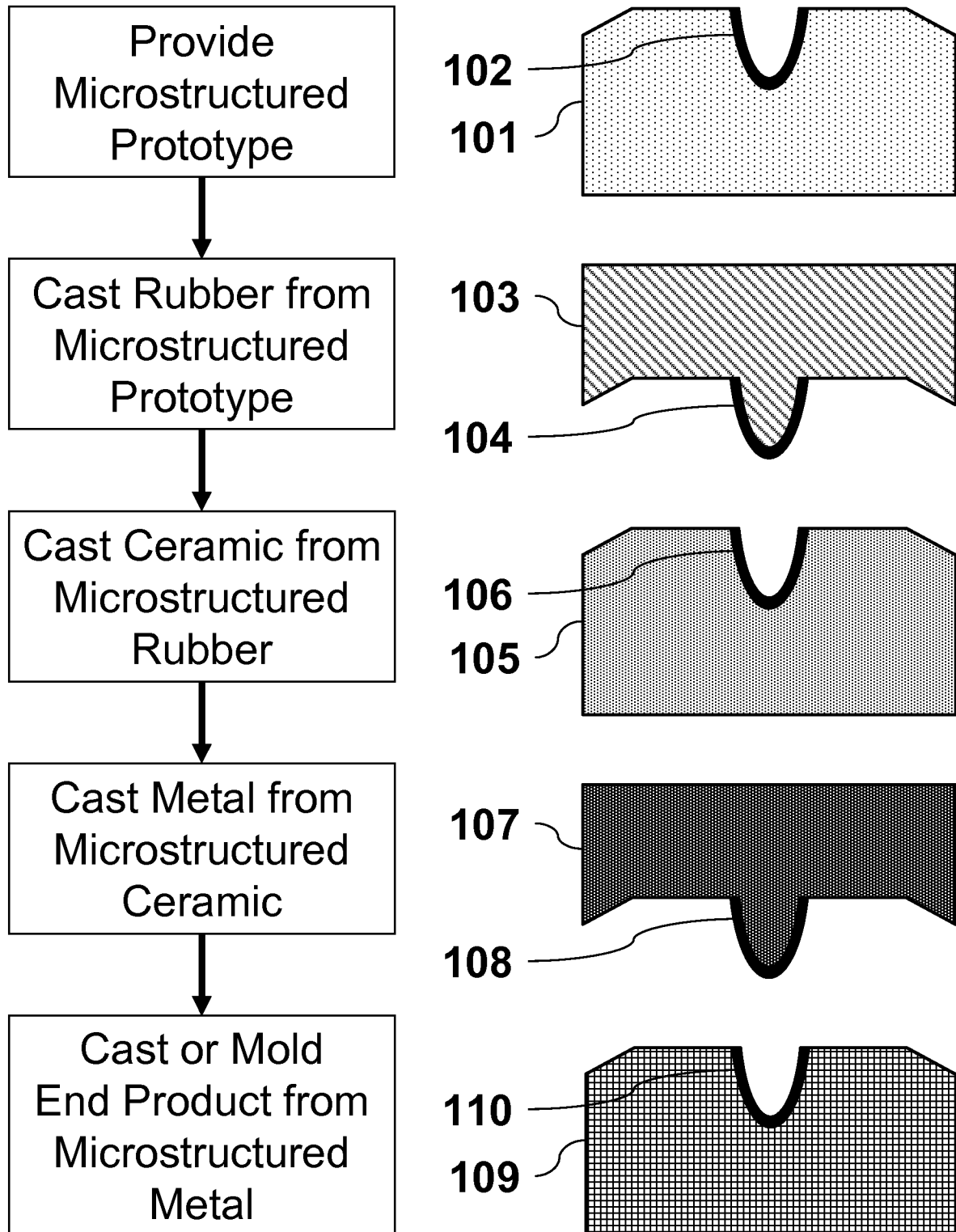
bringing the macro mold and microstructured flexible polymer into contact with the prototype and the uncured second polymer;

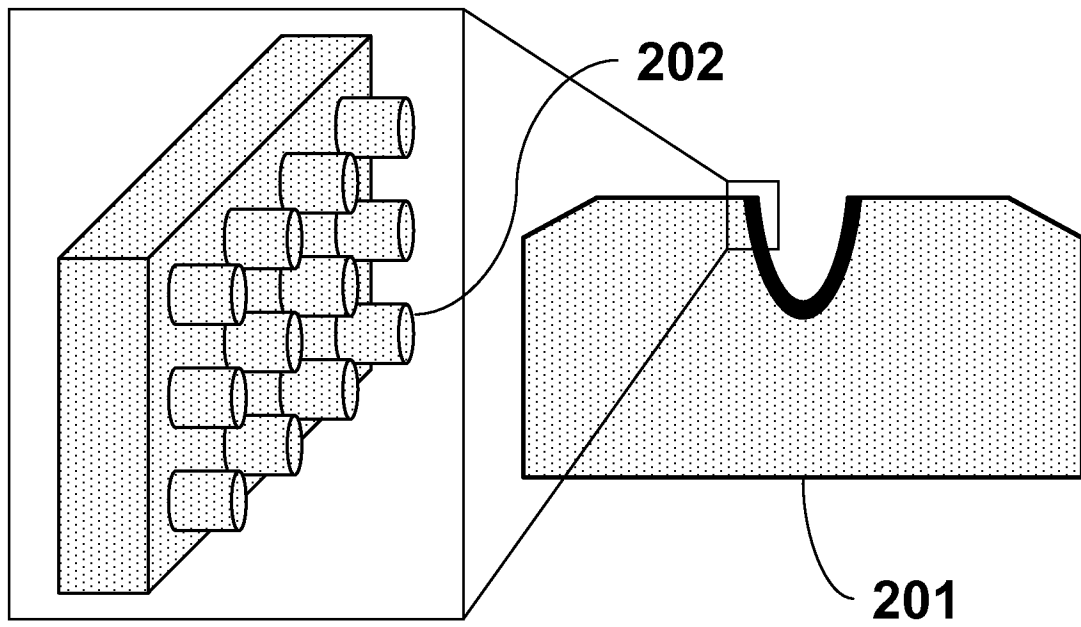
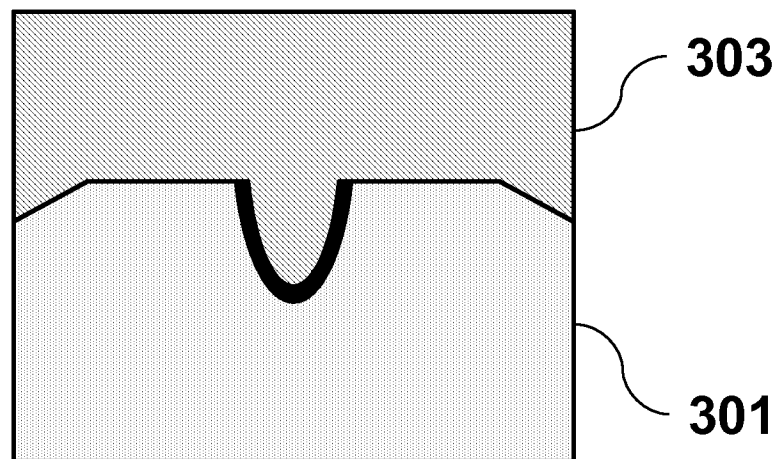
curing the uncured second polymer, thereby making a microstructured second polymer having the preselected pattern of microfeatures;

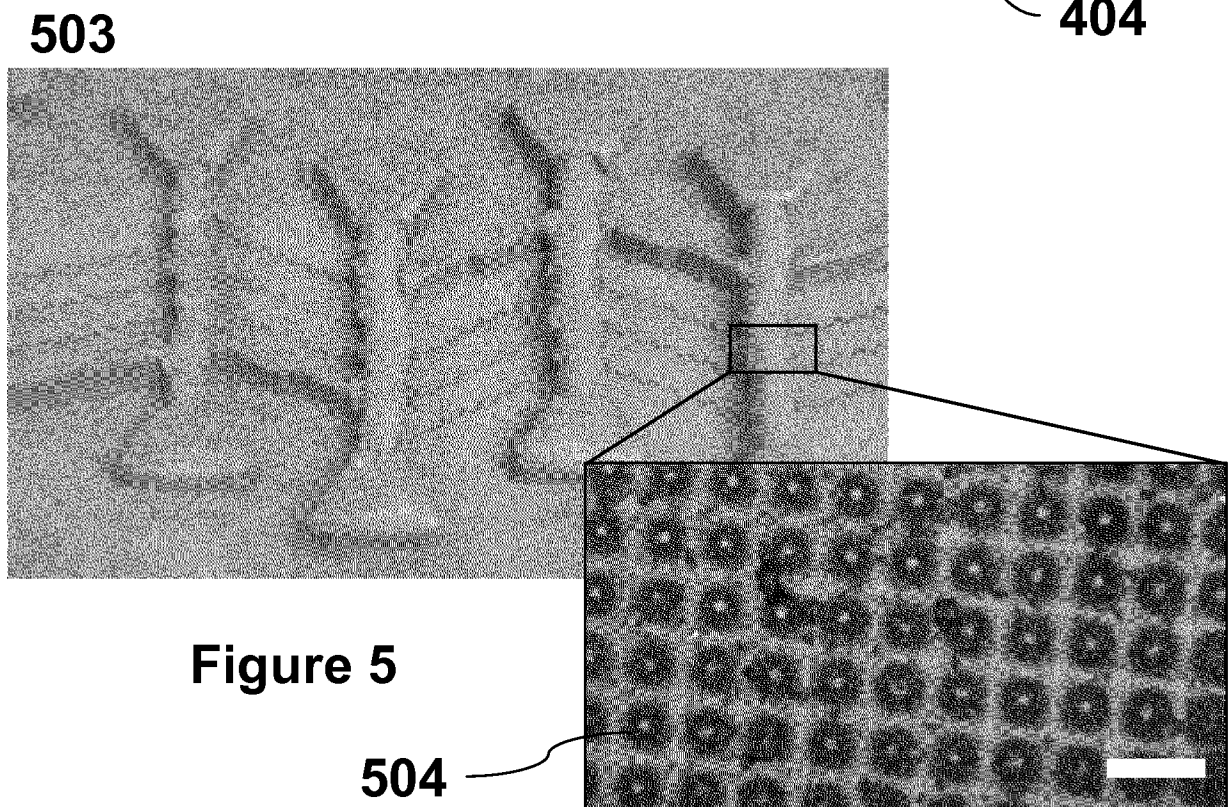
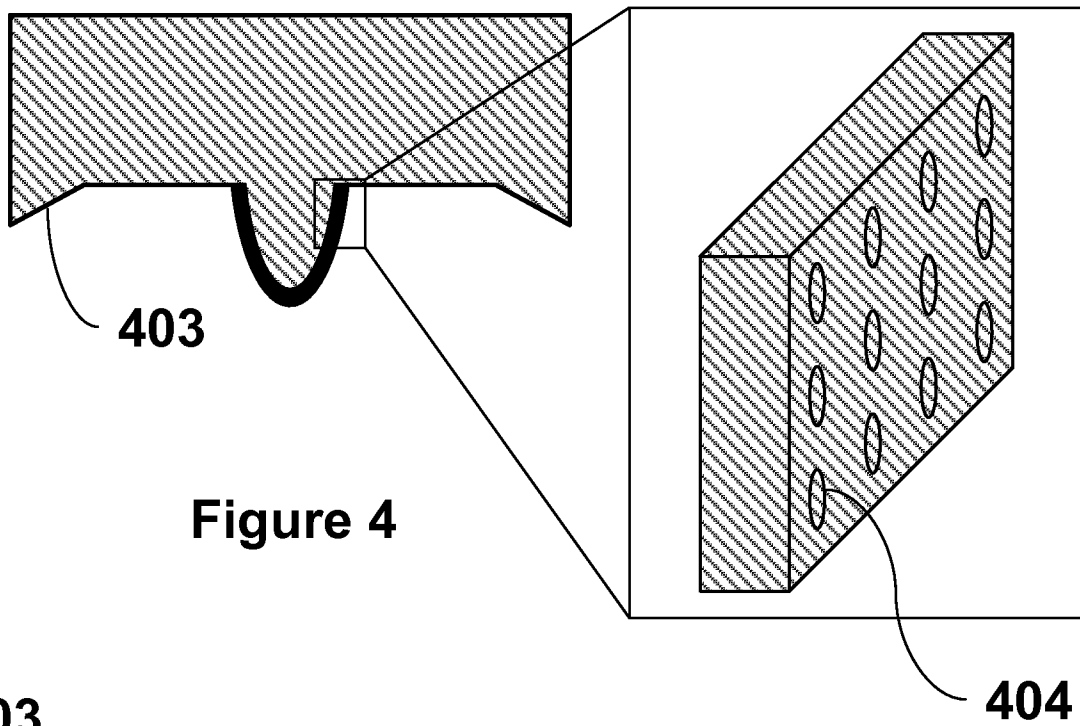
releasing the macro mold and microstructured flexible polymer from the prototype and microstructured second polymer; and

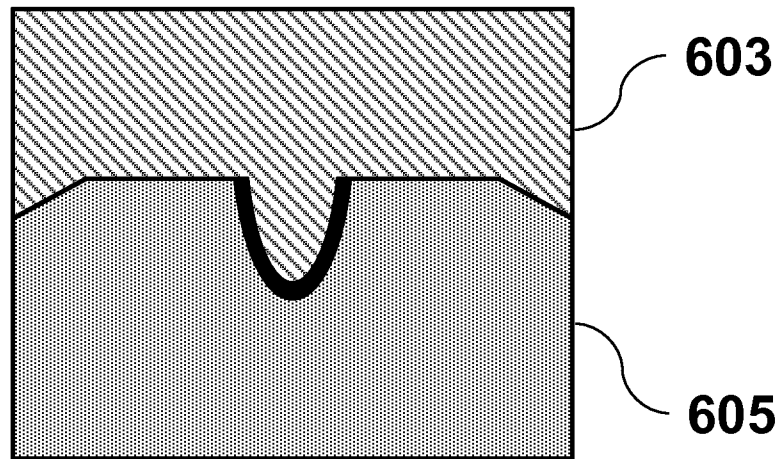
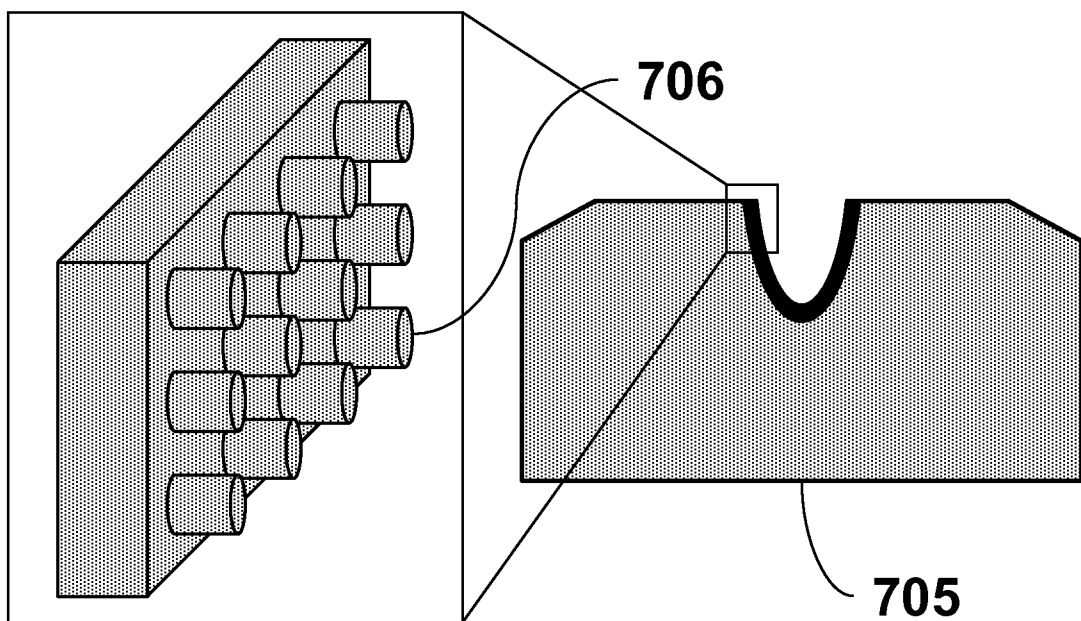
casting or molding a material to the prototype and microstructured second polymer, thereby replicating the preselected pattern of microfeatures in at least a portion of a cast or molded object.

80. The method of claim 78 or 79, wherein 80% to 100% of a surface area of the one or more macro scale features is covered by the preselected pattern of microfeatures.
81. The method of claim 78 or 79, wherein in the deforming step at least a portion of the microstructured polymer is deformed to a radius of curvature selected over the range of 100 μm to 3 m.
82. The method of claim 78 or 79, wherein in the deforming step at least a portion of the microstructured polymer is deformed to a strain level selected over the range of 1% to 1300%.
83. The method of claim 78 or 79, wherein the patterning step comprises patterning the semiconductor wafer using a method selected from the group consisting of photolithography, laser ablation, laser patterning, laser machining, x-ray lithography, e-beam lithography, nano-imprint lithography and any combination of these.
84. The method of claim 78 or 79, wherein the cast or molded material is selected from the group consisting of: rubber, polymer, ceramic and metal.
85. The method of claim 78 or 79, further comprising additional casting and/or molding steps.

**Figure 1**

**Figure 2****Figure 3**



**Figure 6****Figure 7**

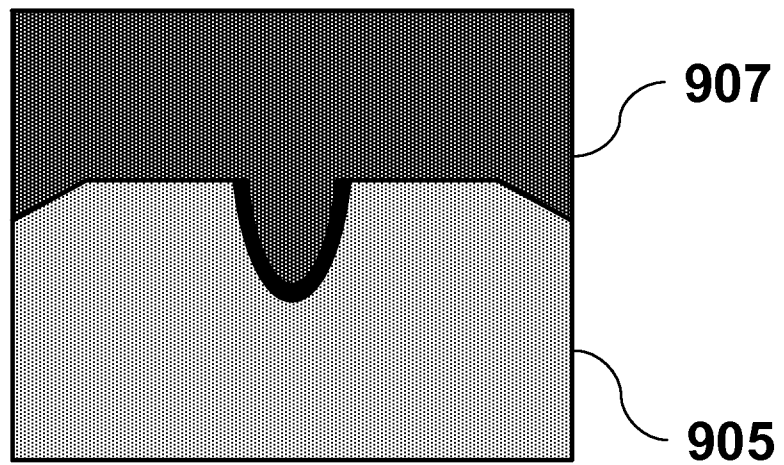
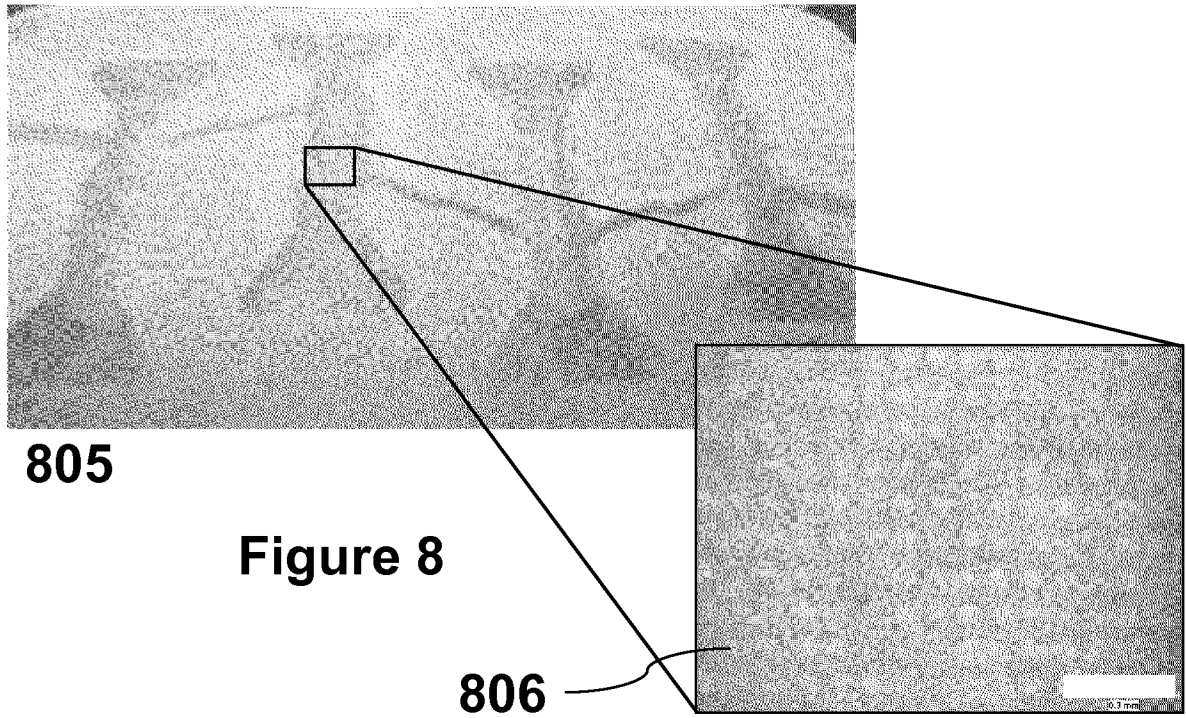
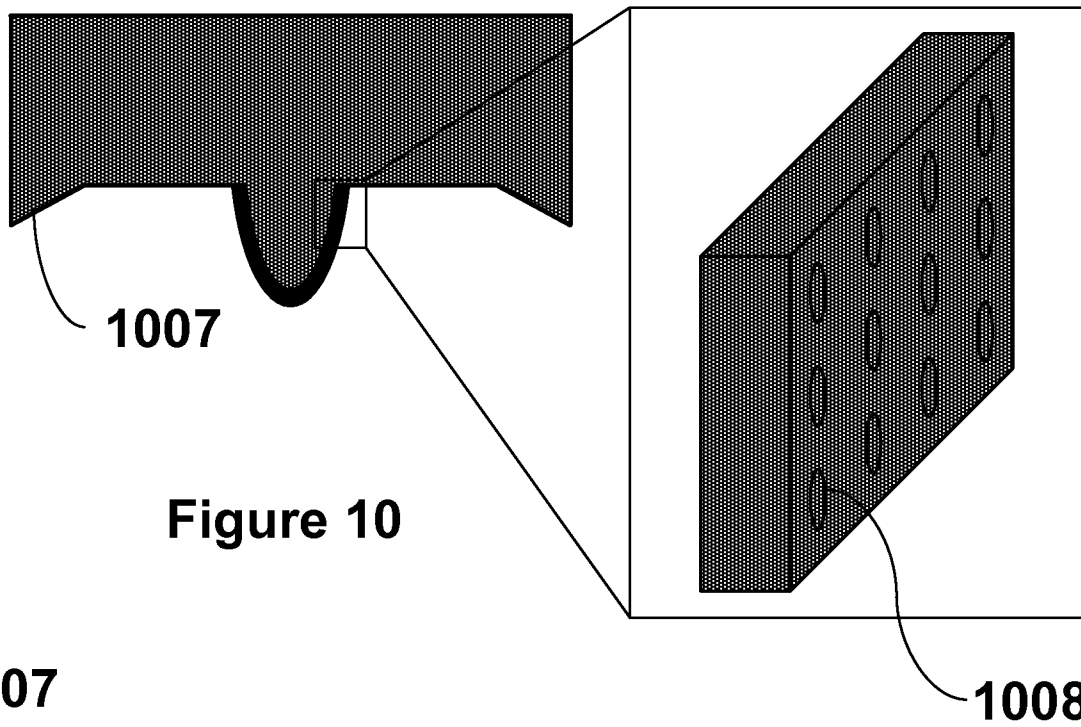


Figure 9



1107

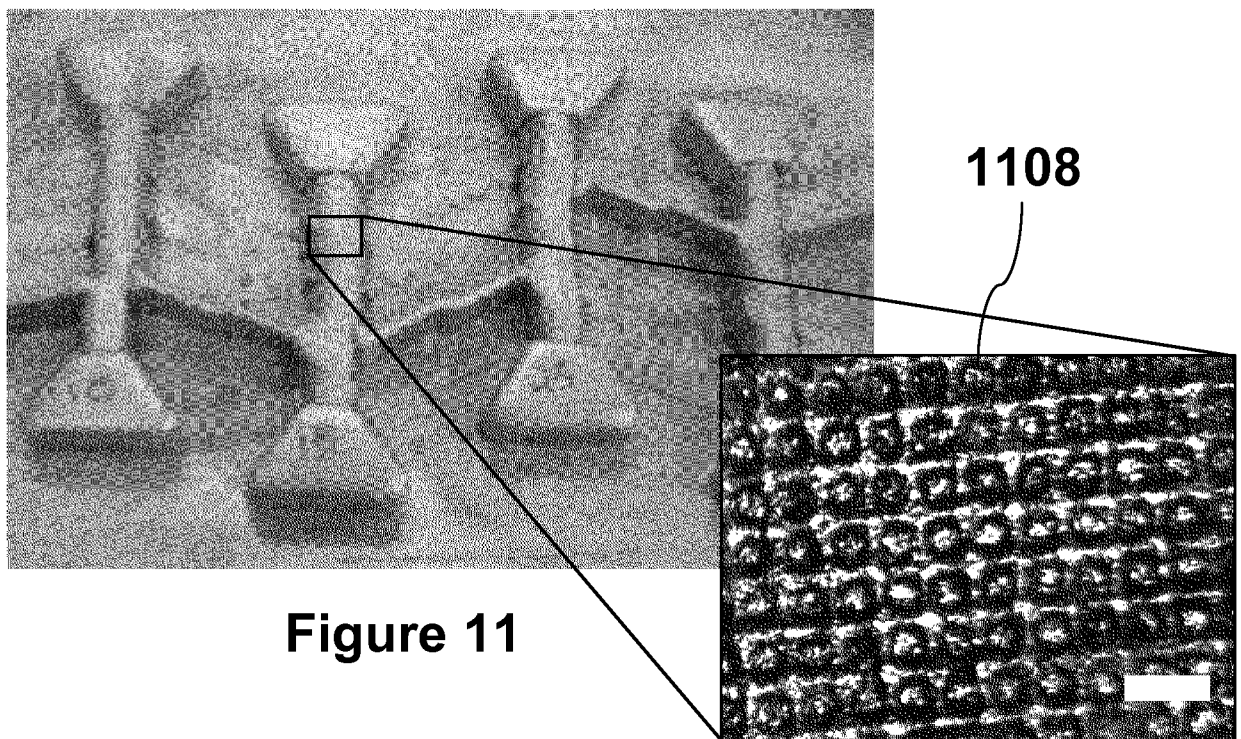


Figure 11

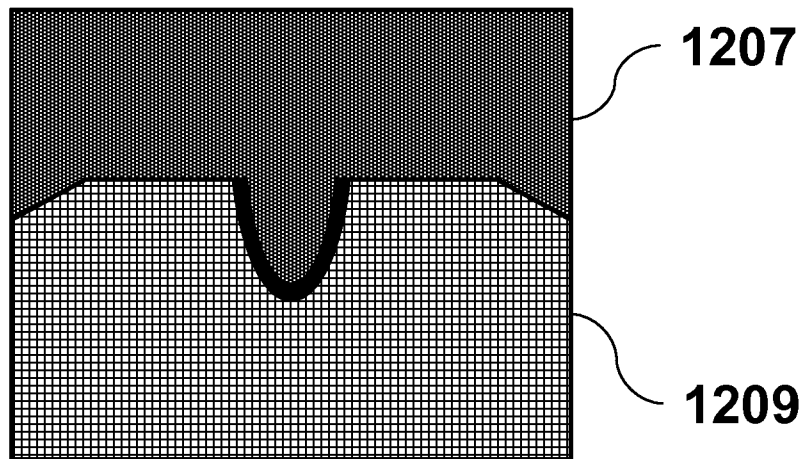


Figure 12

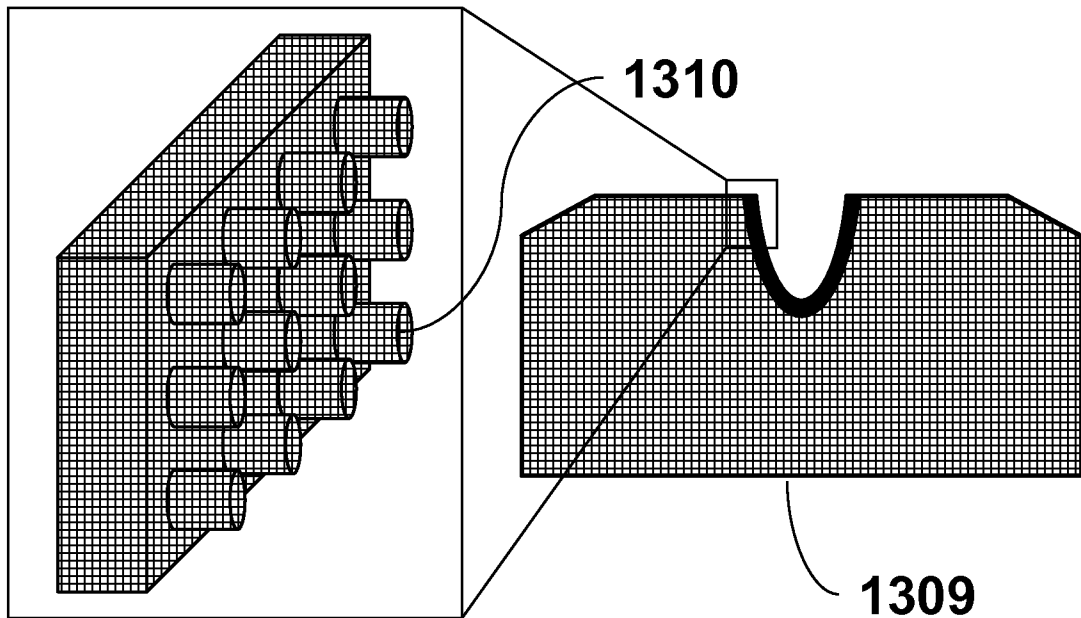


Figure 13

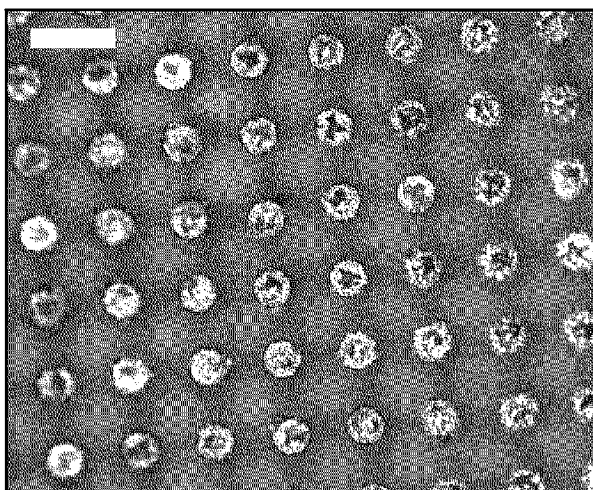


Figure 14

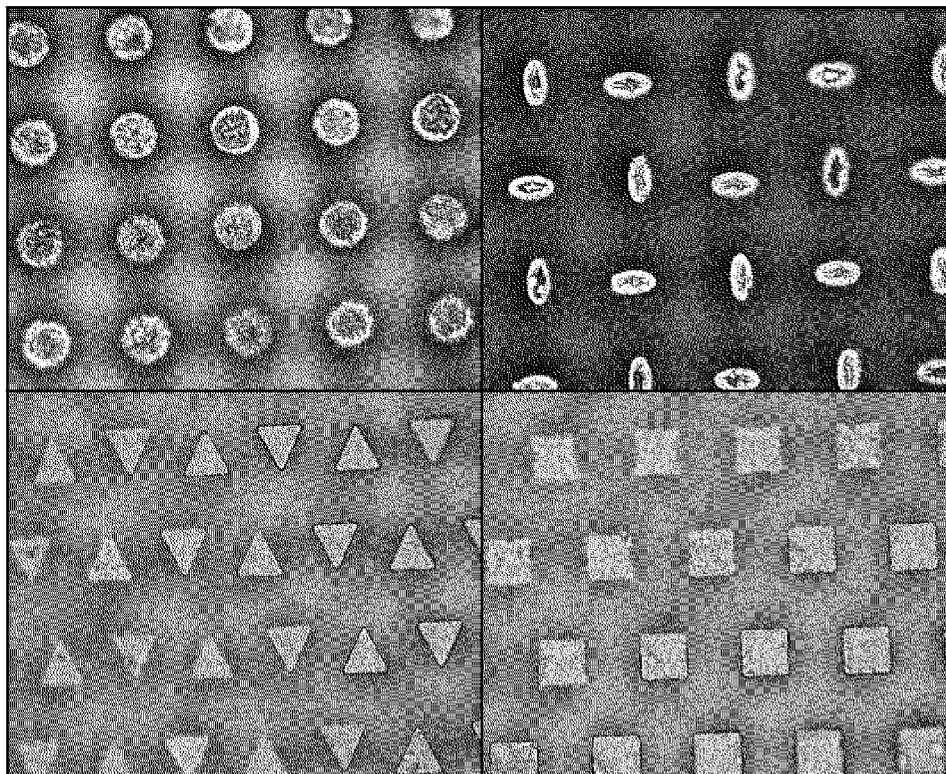


Figure 15

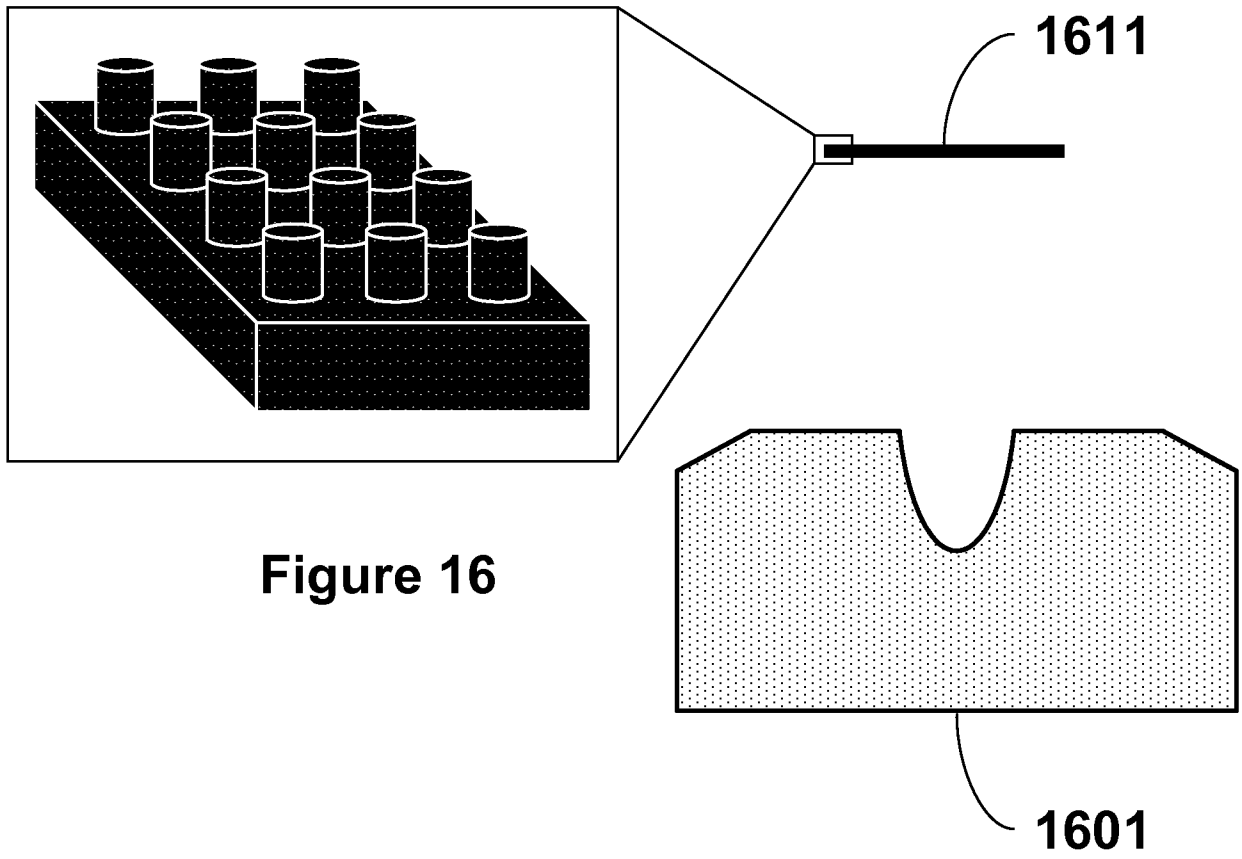


Figure 16

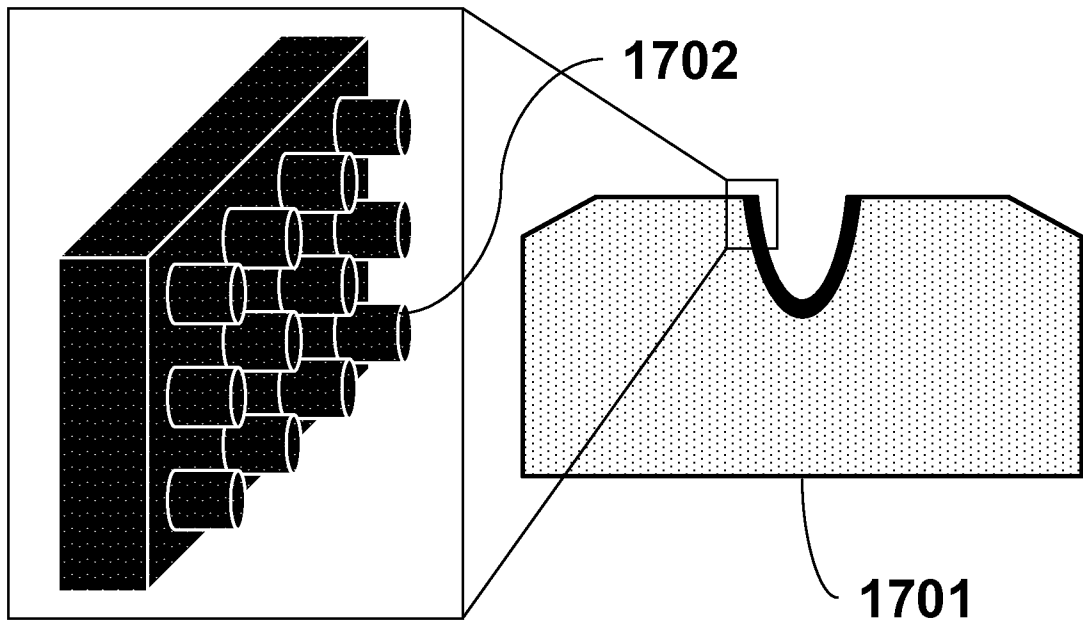
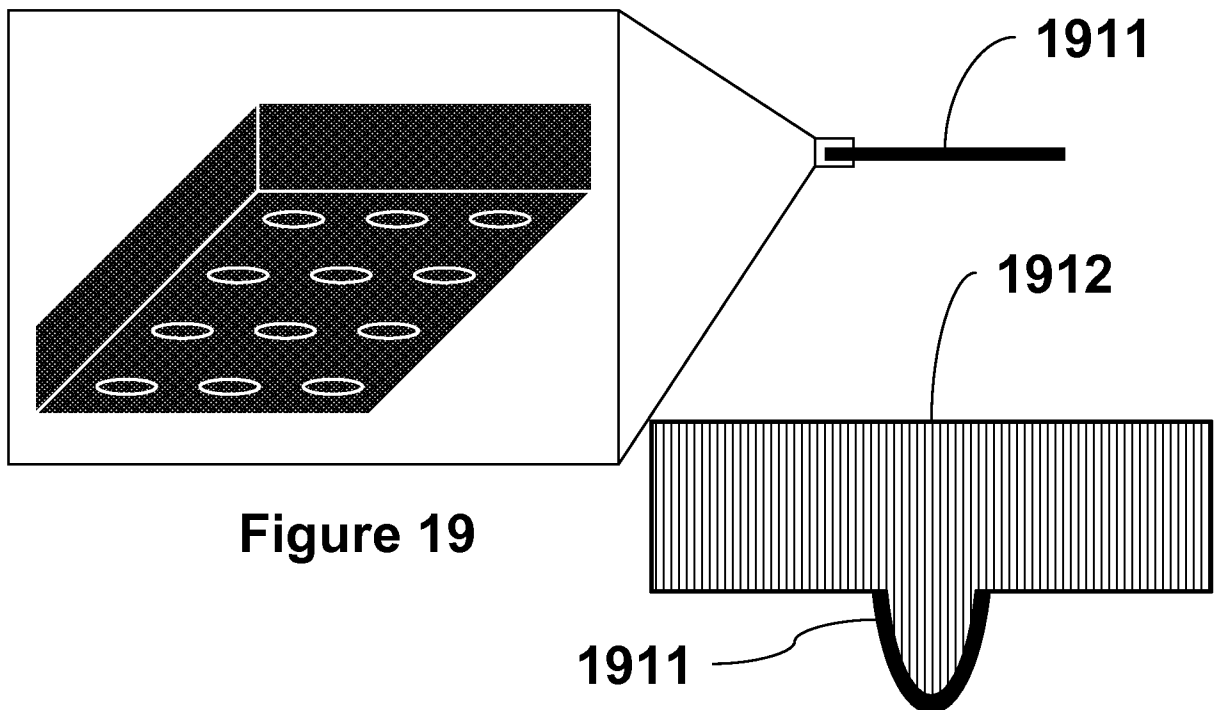
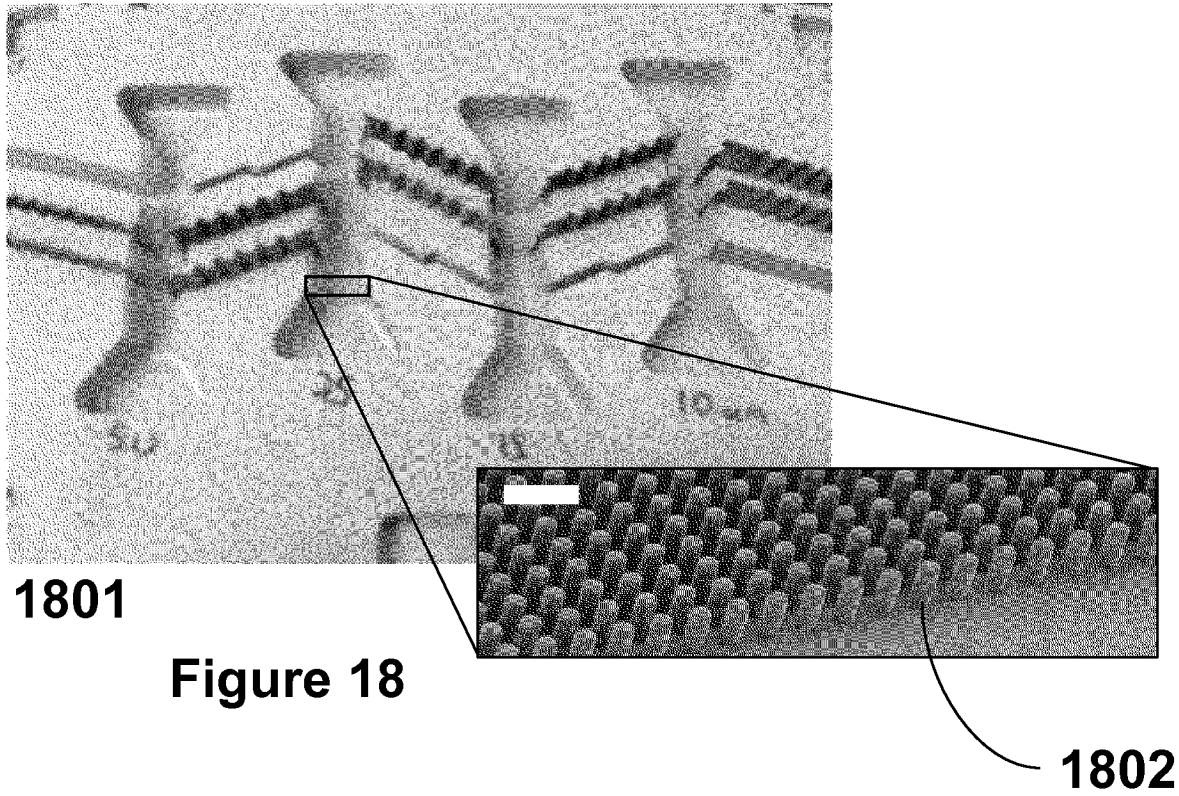


Figure 17



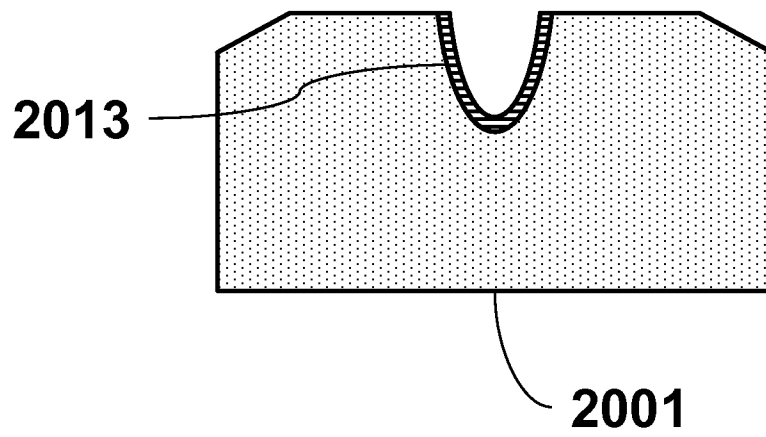


Figure 20

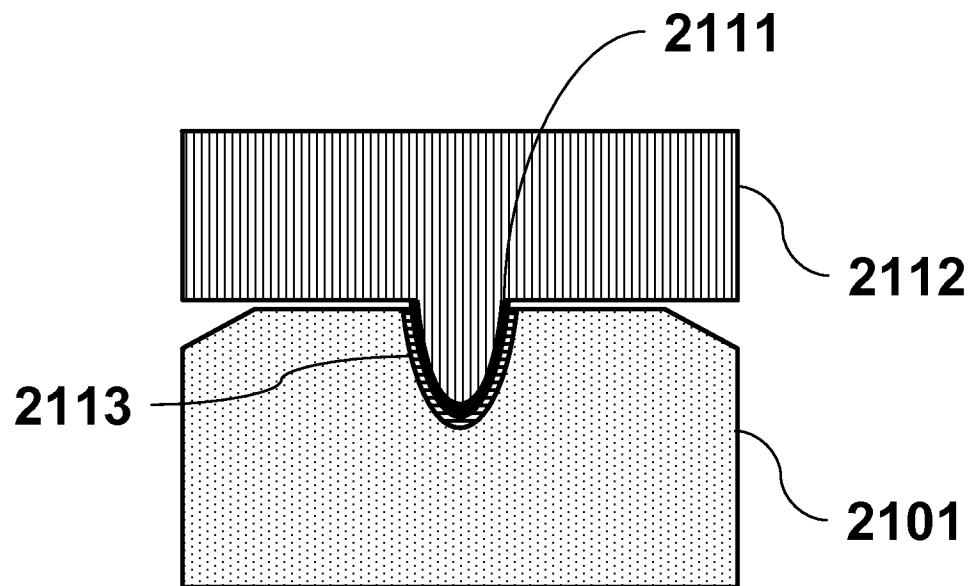
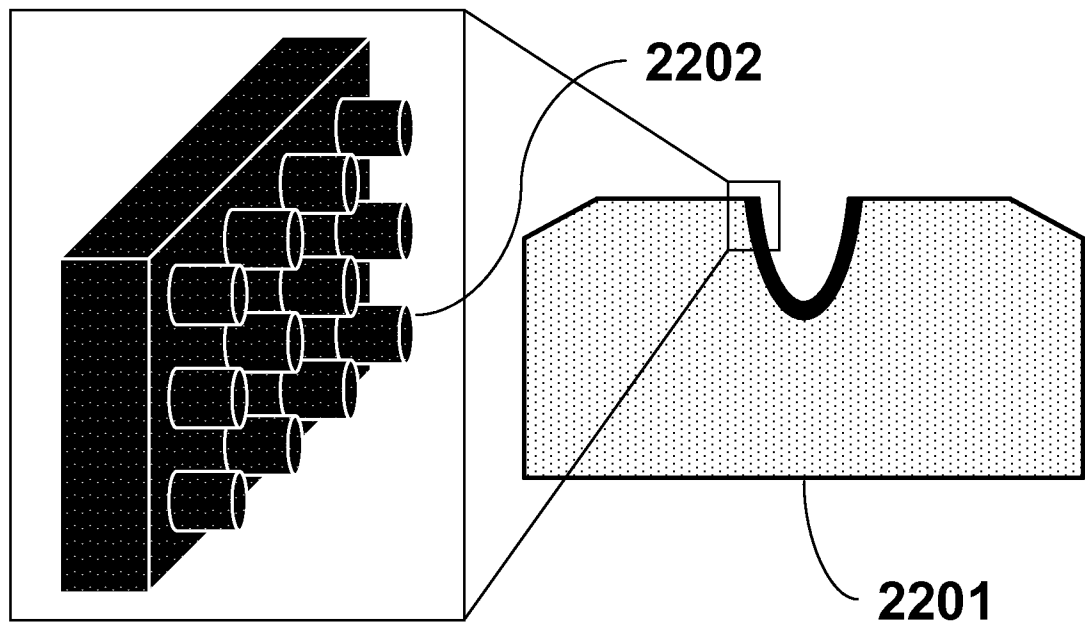
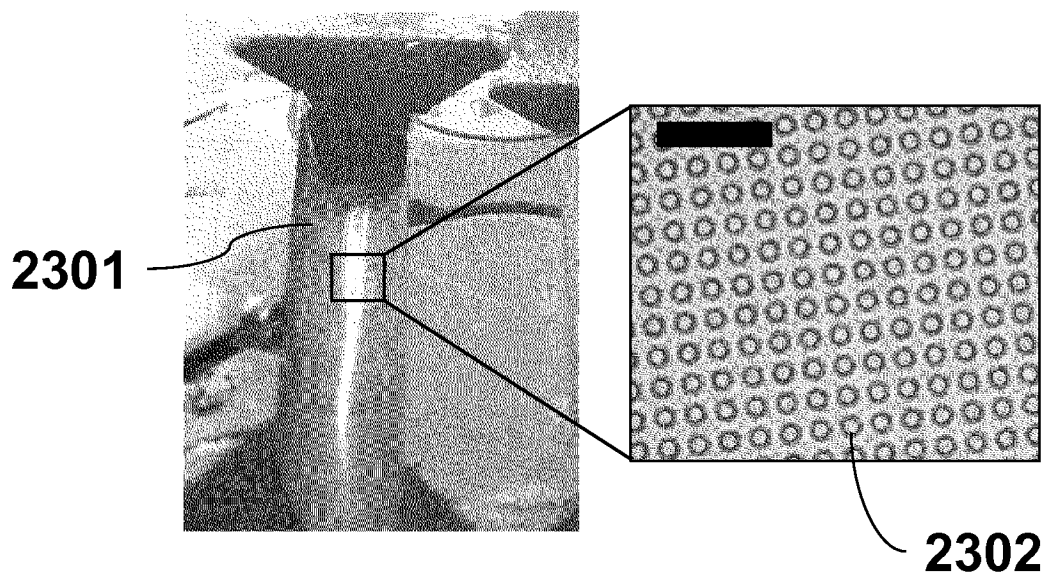


Figure 21

**Figure 22****Figure 23**

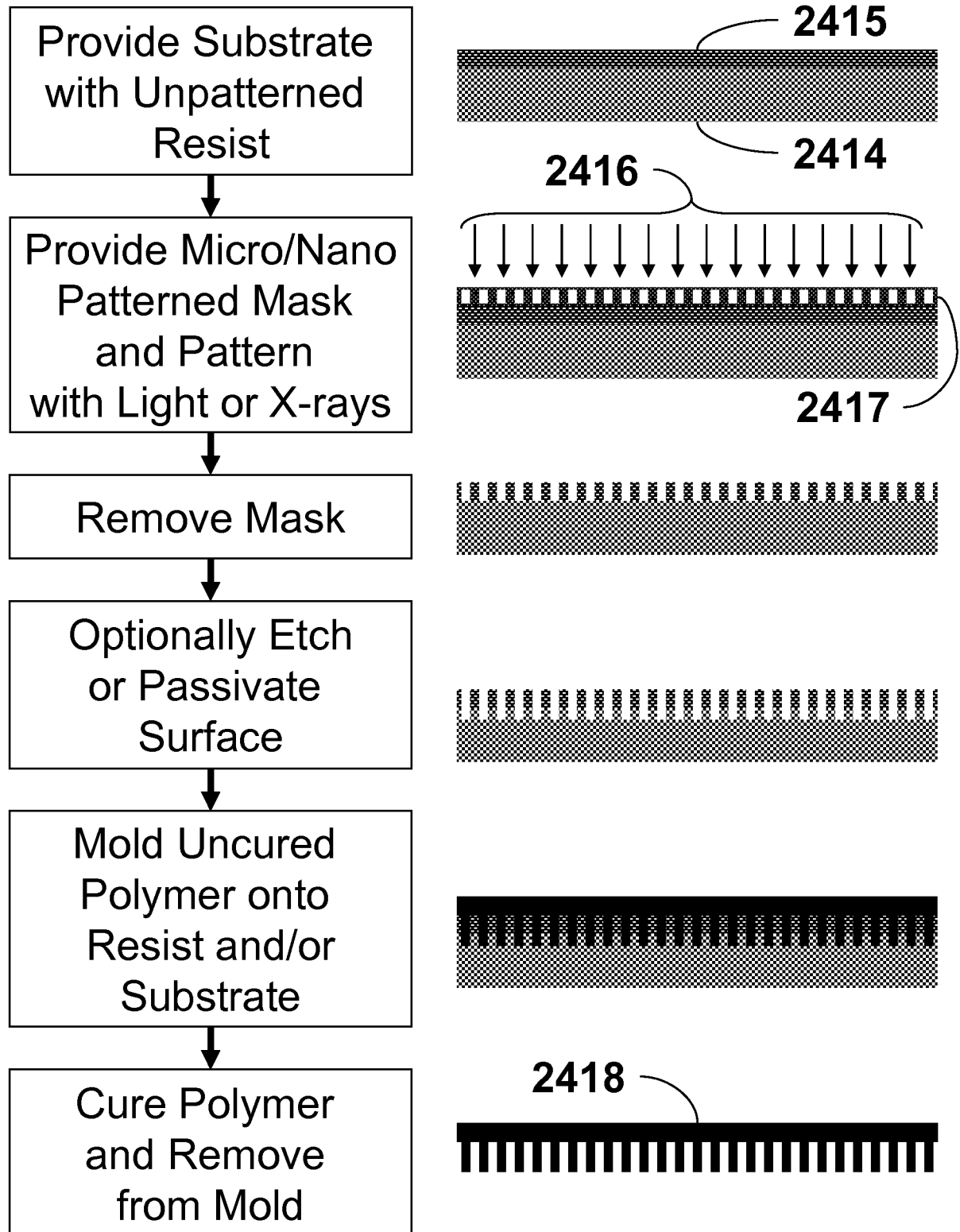
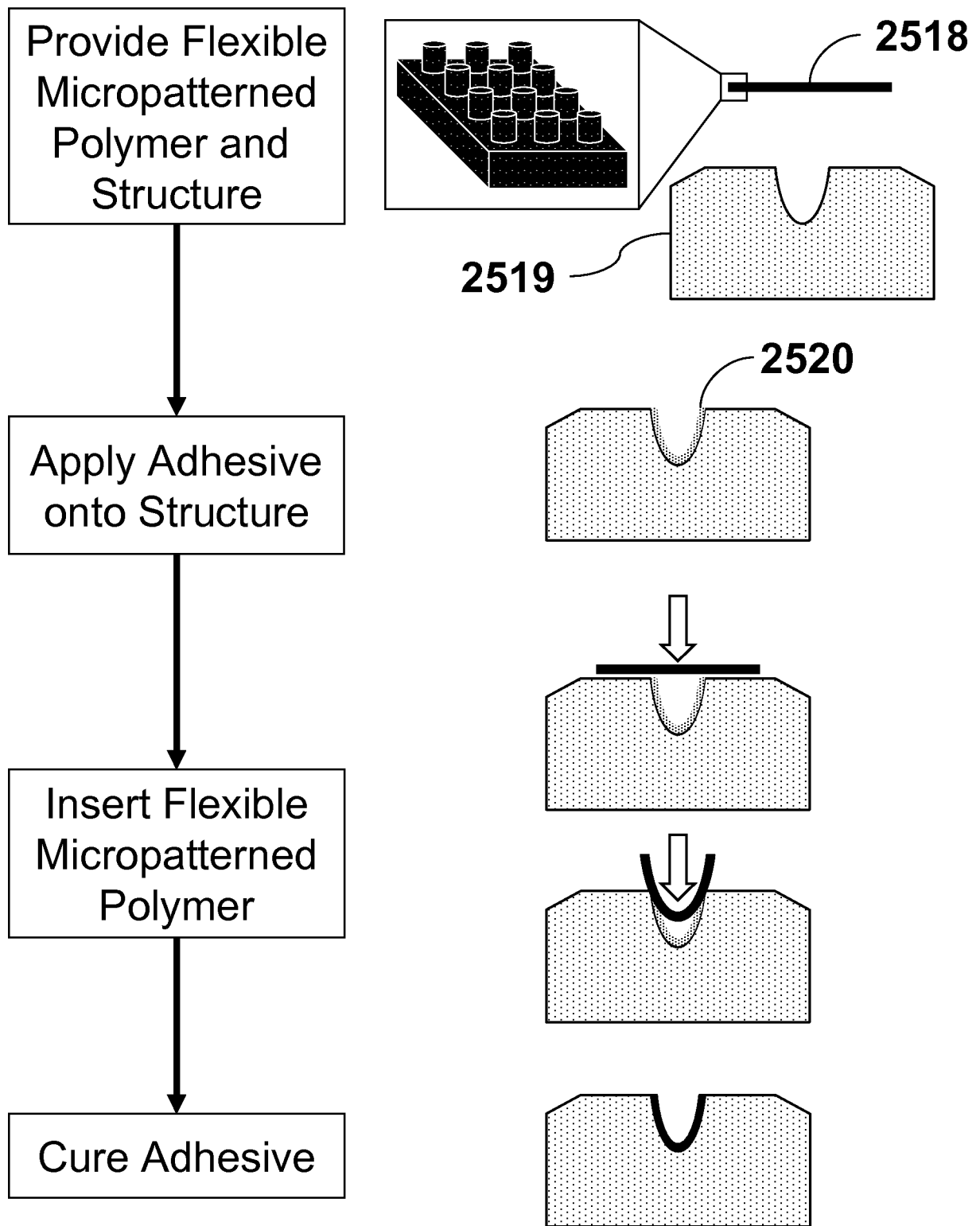


Figure 24

**Figure 25**

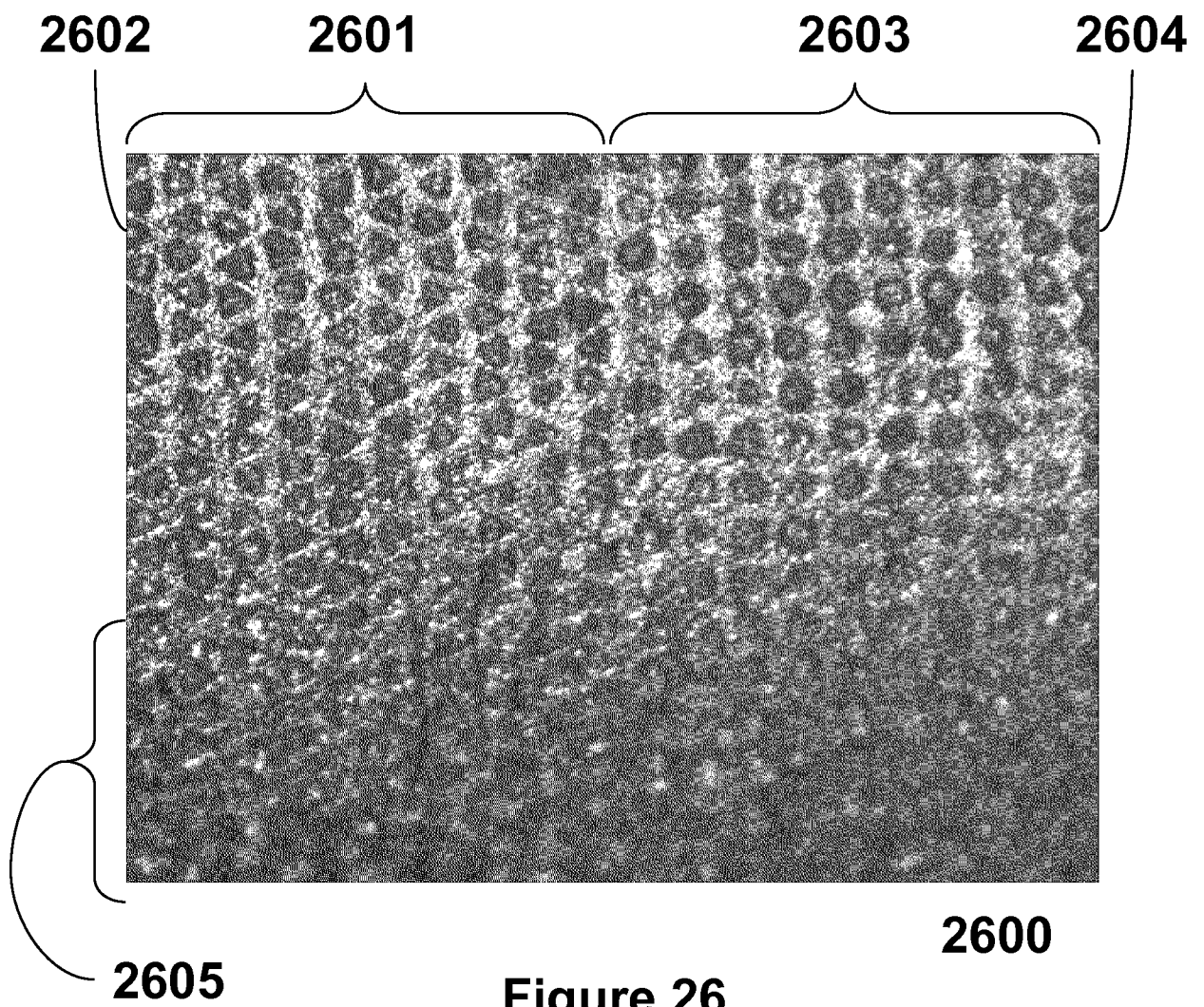


Figure 26

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2009/043306

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B29C 33/40 (2009.01)

USPC - 264/220

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)

IPC(8) - B29C 33/40 (2009.01)

USPC - 264/224, 225, 226, 227

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)

PatBase, Google

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CANNON. Unconventional Microfabrication using polymers. December 2006 (12.2006). [retrieved on 2009-09-03]. Retrieved from internet: <URL: http://etd.gatech.edu/theses/available/etd-08282006-171431/unrestricted/cannon_andrew_h_200612_mast.pdf >. entire document	1-18, 54-75, 76/1, 76/54, 77/76/1, 77/76/54
Y	US 2008/0029239 A1 (MAU) 07 February 2008 (07.02.2008), see entire document	1-18, 54-75, 76/1, 76/54, 77/76/1, 77/76/54
Y	US 6,663,820 B2 (ARIAS et al) 16 December 2003 (16.12.2003), see entire document	15,16/15, 17/15, 18/15, 70, 71/70, 72/70, 73/70, 74/70
Y	US 6,280,090 B1 (STEPHENS et al) 28 August 2001 (28.08.2001), see entire document	9, 66
Y	US 2003/0111150 A1 (ZIMMER et al) 19 January 2003 (19.01.2003), see entire document	67, 68

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"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

03 September 2009

Date of mailing of the international search report

15 SEP 2009

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2009/043306

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-18, 54-75, 76/1, 76/54, 77/76/1, 77/76/54

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2009/043306

Continuation of Box III.

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I – Claims 1-18, 54-75, 76/1, 76/54, 77/76/1, 77/76/54 reciting a method of making a microstructured end product or tire including casting a ceramic from a microstructured rubber, casting a metal from the microstructured ceramic, and casting or molding an end product material or tire rubber from the microstructured metal.

Group II – Claims 19-53, 76/30, 76/33, 76/43, 77/76/30, 77/76/33, 77/76/43 reciting a method for making a microstructured object including fabricating a microstructured prototype comprising one or more microfeatures having dimensions selected over a range of 10nm-100 microns and one or more macroscale features having dimensions selected over a range of 100 microns to 1 m.

Group III – Claims 78-85 reciting a method for making a microstructured object including deforming at least a portion of a microstructured flexible polymer formed using a patterned semiconductor wafer so as to conform to at least a portion of a surface of one or more macro scale features of a large-area prototype.

The inventions listed as Groups I, II and III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature of the Group I invention: casting a ceramic from a microstructured rubber, casting a metal from the microstructured ceramic, and casting or molding an end product material or tire rubber from the microstructured metal as claimed therein is not present in the invention of Groups II and III. The special technical feature of the Group II invention: fabricating a microstructured prototype comprising one or more microfeatures having dimensions selected over a range of 10nm-100microns and one or more macroscale features having dimensions selected over a range of 100 microns to 1 m as claimed therein is not present in the invention of Groups I or III. The special technical feature of the Group III invention: deforming at least a portion of a microstructured flexible polymer formed using a patterned semiconductor wafer so as to conform to at least a portion of a surface of one or more macro scale features of a large-area prototype as claimed therein is not present in the invention of Groups I or II.

Groups I, II and III lack unity of invention because even though the inventions of these groups require the technical feature of casting steps including a rubber microstructured prototype, this technical feature is not a special technical feature as it does not make a contribution over the prior art in view of US 7,141,812 B2 (APPLEBY et al) 28 November 2006, column 20, line 14 – column 21, line 36.

Since none of the special technical features of the Group I, II or III inventions are found in more than one of the inventions, unity of invention is lacking.