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(54) FUNCTIONAL NANOPARTICLES

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(51) **Int. Cl.**

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G03F 7/00	(2006.01)
B82Y 10/00	(2011.01)
B82Y 40/00	(2011.01)
B82Y 30/00	(2011.01)

(52) **U.S. Cl.**

CPC ***G03F 7/0002*** (2013.01); ***B82Y 10/00*** (2013.01); *B82Y 30/00* (2013.01); ***B82Y 40/00*** (2013.01)

USPC **216/40**; 216/36; 216/41; 438/692

(58) **Field of Classification Search**

CPC H01L 21/0272; H01L 21/0274; H01L 21/0331; H05K 3/048; C23F 1/14

USPC 216/13, 24, 26, 41, 106, 8, 36, 40; 438/669, 670, 748, 692

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,696,220	B2	2/2004	Bailey et al.
6,873,087	B1	3/2005	Choi et al.
6,918,946	B2	7/2005	Korgel et al.

(Continued)

FOREIGN PATENT DOCUMENTS

EP	2216680	8/2010
EP	2312393	4/2011

(Continued)

OTHER PUBLICATIONS

Jang et al. Nanoscopic Pd Line Arrays Using Nanocontact Printed Dendrimers, Langmuir 20060328 American Chemical Society vol. 22 No. 7, pp. 3326-3331.

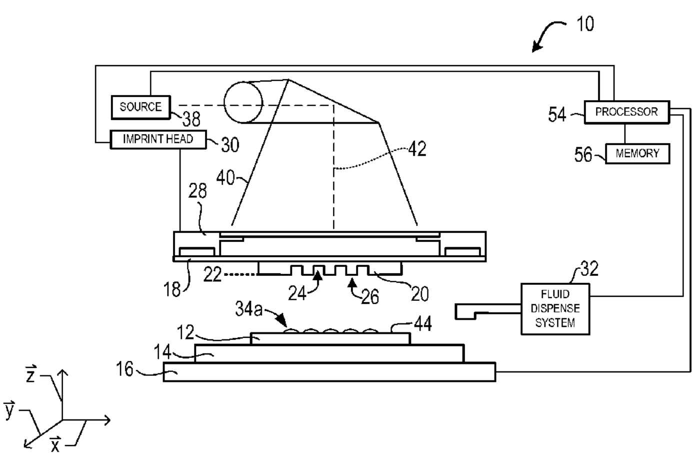
(Continued)

Primary Examiner — Lan Vinh
(74) *Attorney, Agent, or Firm* — Cameron A. King

(57) **ABSTRACT**

Functional nanoparticles may be formed using at least one nano-lithography step. In one embodiment, sacrificial material may be patterned on a multi-layer substrate using an imprint lithography system. The pattern may be further etched into the multi-layer substrate. Functional material may then be deposited on multi-layer substrate and solidified. At least a portion of the functional material may then be removed to provide a crown surface exposing pillars. Pillars may be removed from multi-layer substrate forming functional nanoparticles.

27 Claims, 8 Drawing Sheets



(56) **References Cited**

U.S. PATENT DOCUMENTS

6,936,194	B2	8/2005	Watts	
7,157,036	B2	1/2007	Choi et al.	
7,179,396	B2	2/2007	Sreenivasan	
7,396,475	B2	7/2008	Sreenivasan	
7,635,263	B2	12/2009	Cherala et al.	
7,635,445	B2	12/2009	Choi et al.	
7,636,999	B2	12/2009	Choi et al.	
7,705,237	B2	4/2010	Swanson	
7,759,407	B2	7/2010	Xu	
7,798,801	B2	9/2010	Babbs et al.	
7,811,934	B2 *	10/2010	Jeong et al.	438/669
2004/0065252	A1	4/2004	Sreenivasan et al.	
2004/0065976	A1	4/2004	Sreenivasan et al.	
2004/0178076	A1	9/2004	Stonas et al.	
2004/0211754	A1	10/2004	Sreenivasan	
2004/0241896	A1 *	12/2004	Zhou et al.	438/48
2005/0187339	A1	8/2005	Xu et al.	
2006/0021967	A1	2/2006	Lee	
2006/0063387	A1 *	3/2006	Miller et al.	438/735
2006/0172031	A1	8/2006	Babbs et al.	
2007/0031505	A1	2/2007	Roy et al.	
2008/0122106	A1 *	5/2008	Nitta et al.	257/773
2008/0182070	A1 *	7/2008	Chou et al.	428/138
2009/0061152	A1	3/2009	Desimone et al.	
2009/0196826	A1	8/2009	Gao et al.	
2010/0120251	A1	5/2010	Sreenivasan et al.	
2011/0190463	A1	8/2011	Xu et al.	
2012/0114559	A1	5/2012	Singh et al.	

FOREIGN PATENT DOCUMENTS

GB	2334347	8/1999
WO	WO/02/29136	4/2002
WO	WO/2007/081410 A2	7/2007
WO	WO/2007/094829	8/2007
WO	WO/2008/106503	9/2008
WO	WO/2009/014848	1/2009
WO	WO/2011/025522	3/2011

OTHER PUBLICATIONS

Glangchai et al. Nanoimprint lithography based fabrication of shape-specific, enzymatically-triggered smart nanoparticles. Journal of Controlled Release. 2008. vol. 125 pp. 283-272; Nov. 4, 2007.

Kelly et al. Shape-specific monodisperse nano-molding of protein particles. J. Am. Chem. Soc. 2008, vol. 130, pp. 5437-5439; Apr. 1, 2008.

Canelas et al. Top-down particles fabrication: control of size and shape for diagnostic imaging and drug delivery. WIREs Nanomedicine and Nanobiotechnology, 2009, vol. 1, pp. 391-404; Jul. 1, 2009.

Hu et al., High-Moment Antiferromagnetic Nanoparticles with Tunable Magnetic Properties, Advanced Materials 2008, vol. 20 pp. 1479-1483.

Gratton et al. Nanofabricated particles for engineered drug therapies: a preliminary biodistribution study of PRINT nanoparticles, J Control Release. Aug. 16, 2007; vol. 121 pp. 10-18.

Hamidi et al. Hydrogel nanoparticles in drug delivery, Advanced Drug Delivery Reviews, vol. 60 (2008), pp. 1638-1649, Sep. 20, 2008.

Hans et al. Biodegradable nanoparticles for drug delivery and targeting, Current Opinion in Solid State and Materials Science, 2002. 6(4): p. 319-327, Sep. 4, 2002.

Hughes, Nanostructure-mediated drug delivery, Nanomedicine: nanotechnology, biology, and medicine, 2005. 1(1): p. 22-30; Nov. 30, 2004.

Brigger et al., Nanoparticles in cancer therapy and diagnosis, Advanced Drug Delivery Reviews, 2002. 54(5): p. 631-651; May 10, 2002.

Egitto, Plasma Etching and Modification of Organic Polymers, Pure and Applied Chemistry, 62:9 (1990) 1699-1708.

Kushida et al. Dry-Etching Durability of Copolymers and Polymer Blends of Vinylnaphthalene or α-Methylstyrene with Methyl Methacrylate, Japanese Journal of Applied Physics, 34:1:8A (1995) 4234-4238; May 31, 1995.

Cho et al. Identification of Hydrophilic Group Formation on Polymer Surface during Ar+ Ion Irradiation in O2 Environment; Material Research Society Symposium Proceedings 438 (1997) 517-532.

Koh et al. Surface Modification of Polymer by Ion Assisted Reaction in Reactive Gases Environment; Material Research Society Symposium Proceedings 438 (1997) 505-510.

Hollander et al. On Depth Profiling of Polymers by Argon Ion Sputtering; Plasma Processes and Polymers, 4 (2007) 773-776.

Qui et al. Design and Evaluation of Layered Diffusional Matrices for Zero-Order Sustained-Release; Journal of Controlled Release, vol. 51 (1988), pp. 123-130, May 30, 1997.

Qui et al. Design of a Core-Shelled Polymer Cylinder for Potential Programmable Drug Delivery; International Journal of Pharmaceutics, vol. 219, pp. 151-160, May 5, 2001.

Okuda et al. Time-programmed Dual Release Formulation by Multilayered Drug-loaded Nanofiber Meshes; Journal of Controlled Release, vol. 143, pp. 258-264 (Jan. 13, 2010).

Akita et al. Multilayered Nanoparticles for Penetrating the Endosome and Nuclear Membrane via a Step-wise Membrane Fusion Process; Biomaterials, vol. 30 (2009), pp. 2940-2049, Mar. 4, 2009.

* cited by examiner

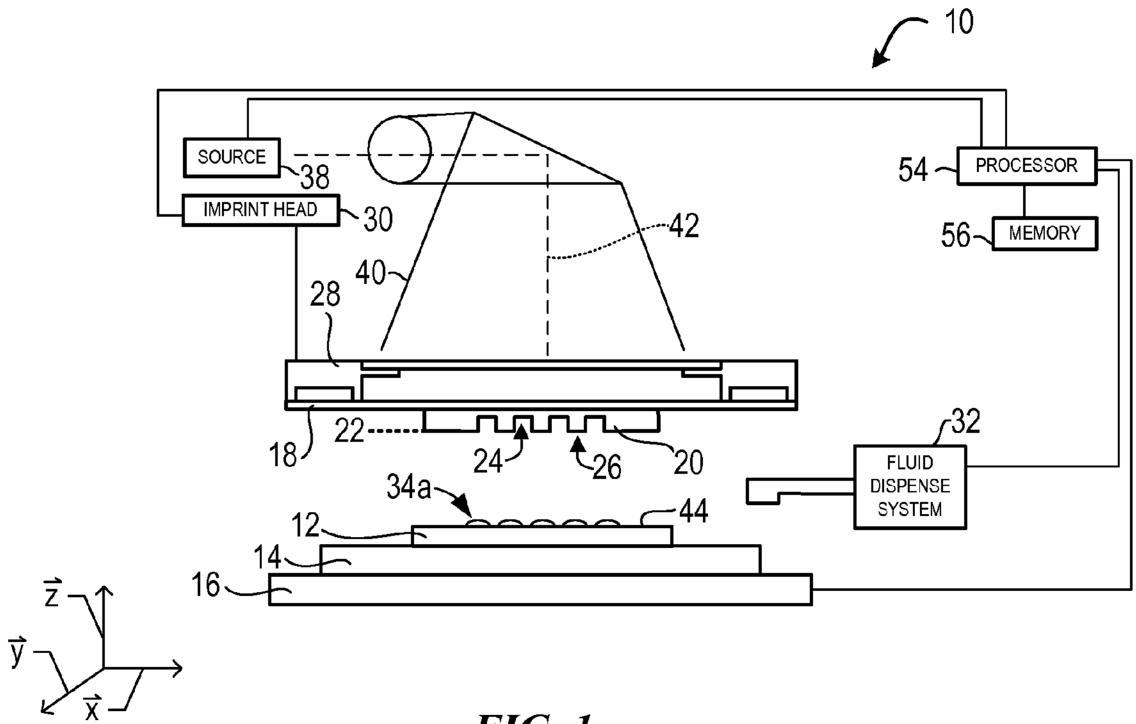

10
SOURCE
38
IMPRINT HEAD
30
PROCESSOR
54
MEMORY
56
42
40
28
22
24
26
20
18
32
FLUID DISPENSE SYSTEM
34a
44
12
14
16
z
y
x

FIG. 1

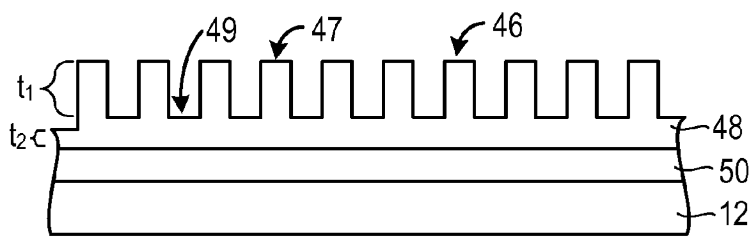

49
47
46
t1
t2
48
50
12

FIG. 2

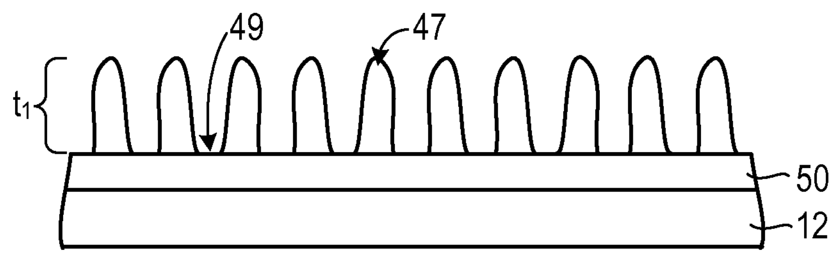


FIG. 3

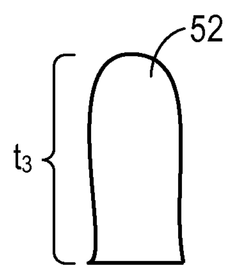


FIG. 4

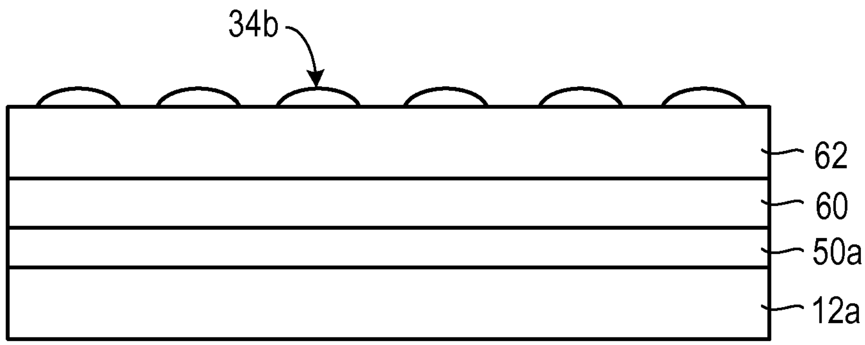


FIG. 5A

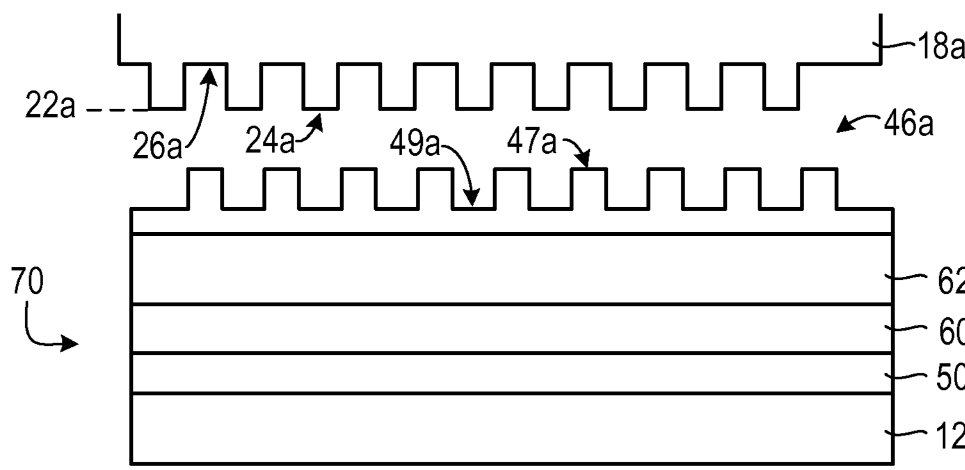


FIG. 5B

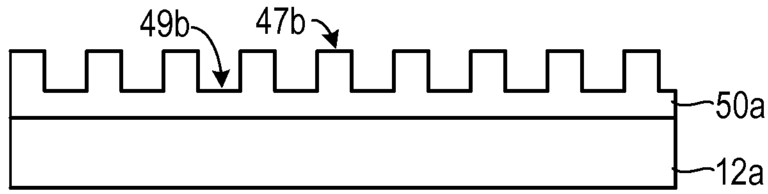


FIG. 5C

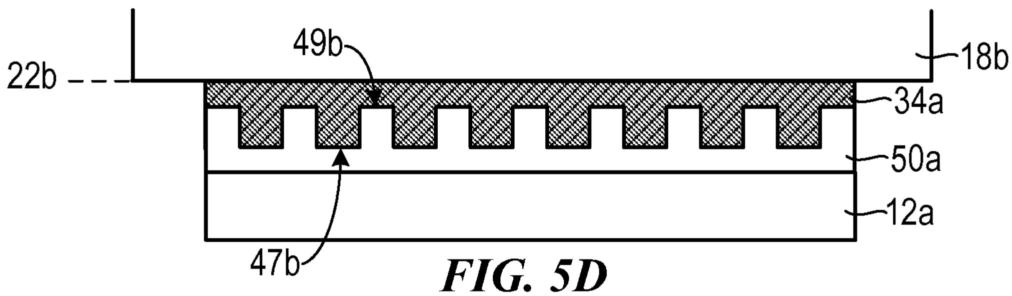


FIG. 5D

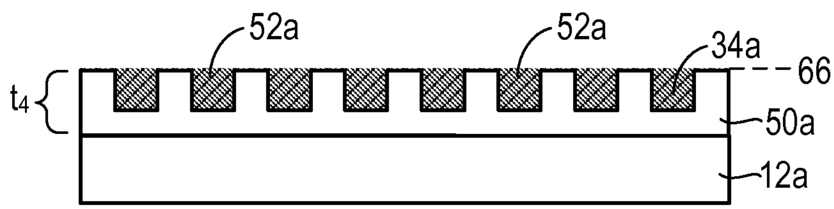


FIG. 5E

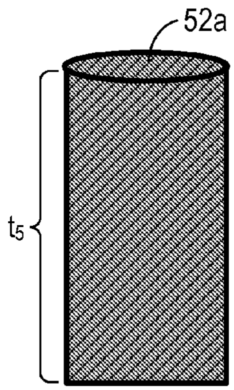


FIG. 5F

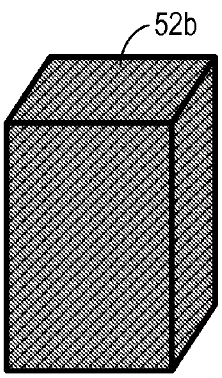


FIG. 6A

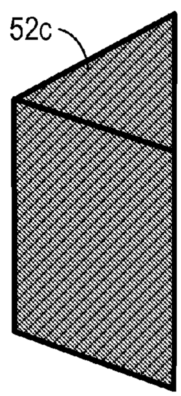


FIG. 6B

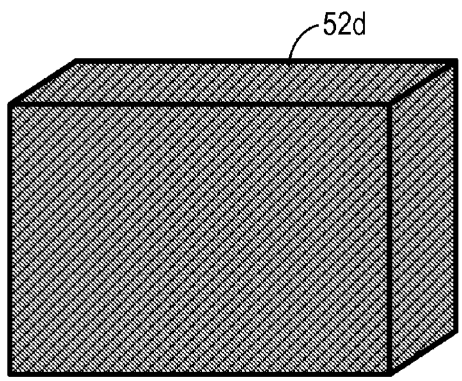


FIG 6C

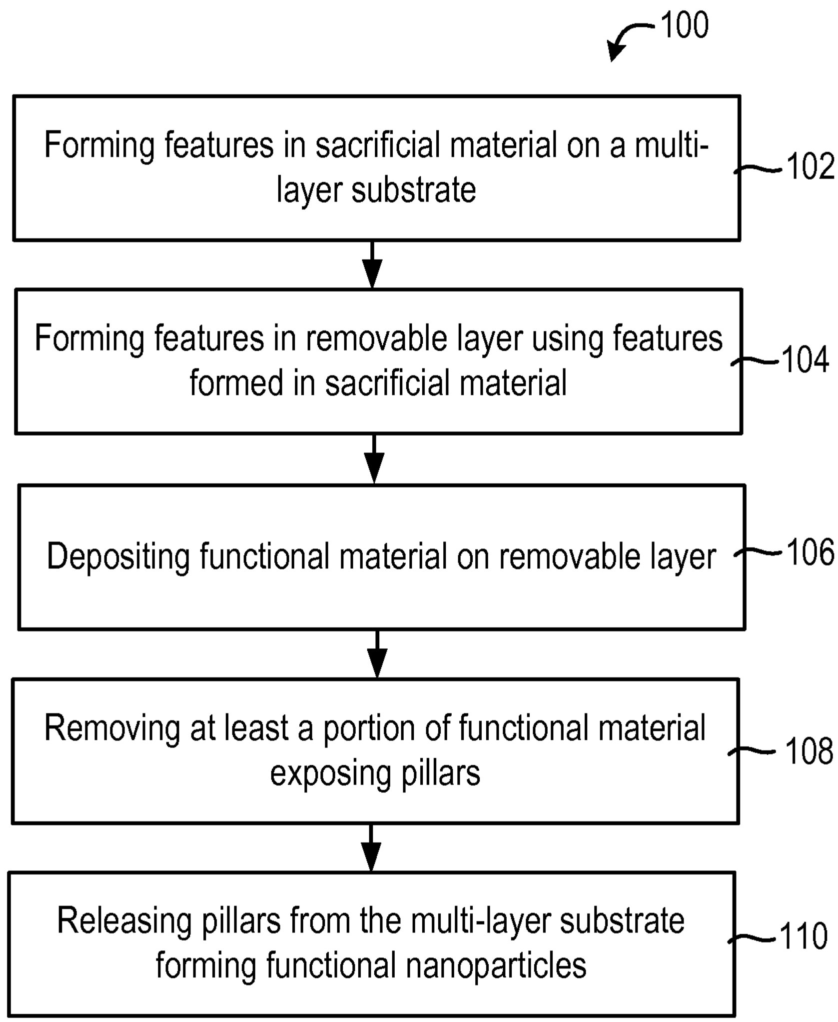

100
Forming features in sacrificial material on a multi-layer substrate
102
Forming features in removable layer using features formed in sacrificial material
104
Depositing functional material on removable layer
106
Removing at least a portion of functional material exposing pillars
108
Releasing pillars from the multi-layer substrate forming functional nanoparticles
110

FIG. 7

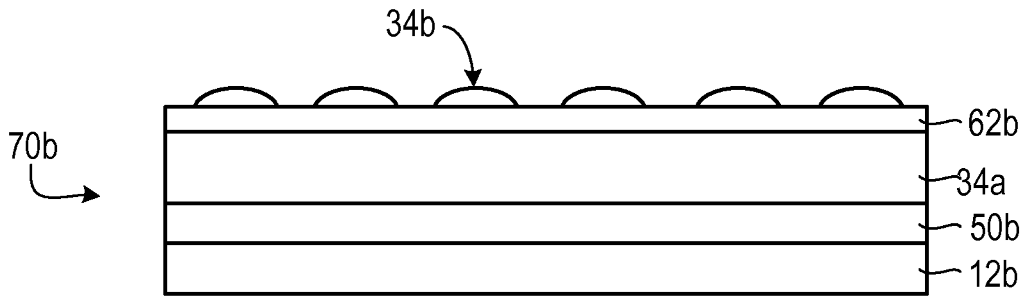


FIG. 8A

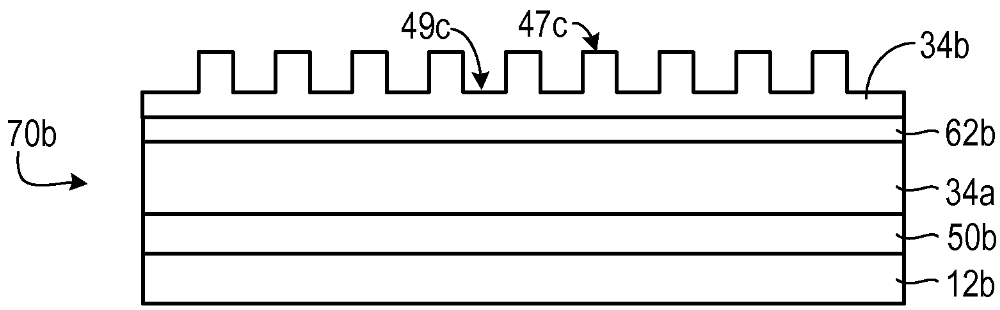


FIG. 8B

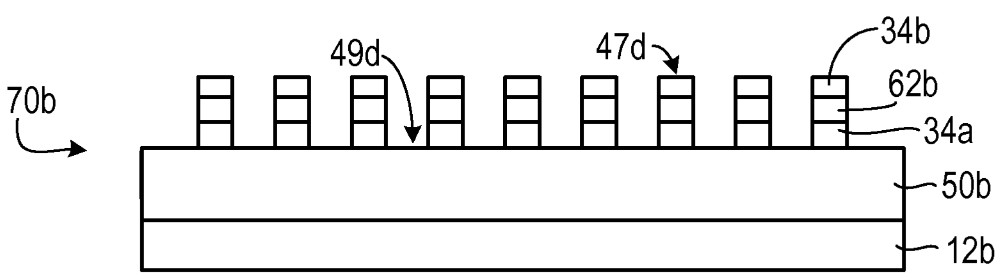


FIG. 8C

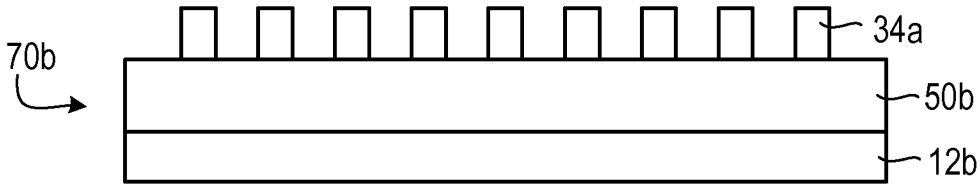


FIG. 8D

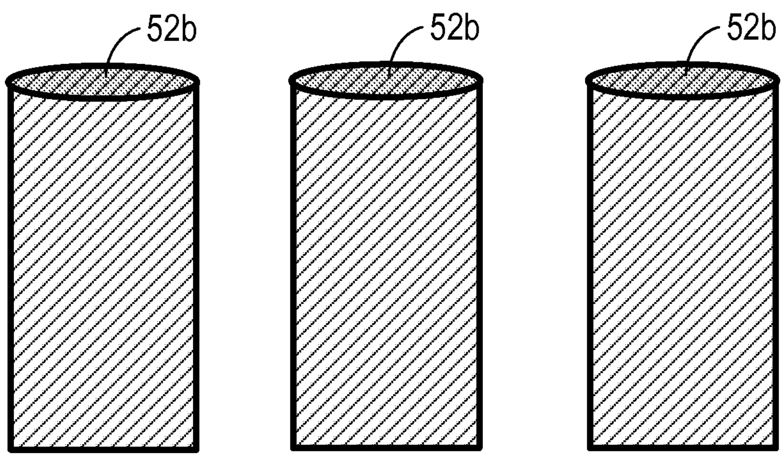


FIG. 8E

FUNCTIONAL NANOPARTICLES

CROSS-REFERENCE TO RELATED APPLICATIONS

The application claims the benefit under 35 U.S.C. §119(e)(1) of U.S. Provisional Application No. 61/236,957, filed on Aug. 26, 2009, which is hereby incorporated by reference in its entirety.

BACKGROUND INFORMATION

Nano-fabrication includes the fabrication of very small structures that have features on the order of 100 nanometers or smaller. Although well known within the integrated circuit industry, nano-fabrication techniques may be applied in the bio-domain, solar cells industry, battery industry and/or other industries. See, for example, U.S. Patent Publication No. 2007/0031505, U.S. Pat. No. 6,918,946, U.S. Patent Publication No. 2008/0121279, Kelly, J. and DeSimone, J., *Shape-specific monodisperse nano-molding of protein particles*, J. Am. Chem. Soc. 2008, vol. 130, pgs. 5437-5439, and Canelas, D., Herlihy, K, and DeSimone, J., *Top-down particles fabrication: control of size and shape for diagnostic imaging and drug delivery*, WIREs Nanomedicine and Nanobiotechnology, 2009, vol. 1, pgs. 391-404.

Imprint lithography techniques include formation of a relief pattern in a formable layer positioned on a substrate. The substrate may be coupled to a motion stage to obtain a desired positioning to facilitate the patterning process. The patterning process may use a template spaced apart from the substrate and the formable liquid applied between the template and the substrate. The formable liquid is solidified to form features on the substrate conforming to the shape of the template that contacts the formable liquid. After solidification, the template is separated from the features and the substrate is subjected to additional processing to form functional nanoparticles (e.g., drug delivery devices, batteries, and the like).

BRIEF DESCRIPTION OF DRAWINGS

So that the present invention may be understood in more detail, a description of embodiments of the invention is provided with reference to the embodiments illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of the invention, and are therefore not to be considered limiting of the scope.

FIG. **1** illustrates a simplified side view of a lithographic system in accordance with embodiments of the present invention.

FIG. **2** illustrates a simplified side view of the substrate shown in FIG. **1** having a patterned layer positioned thereon.

FIG. **3** illustrates a simplified side view of the substrate shown in FIG. **2** having multiple protrusions formed thereon.

FIG. **4** illustrates a simplified side view of a pillar formed by release of the protrusions of FIG. **3**.

FIGS. **5**A-**5**F illustrate simplified side views of formation of pillars in accordance within an embodiment of the present invention.

FIGS. **6**A-**6**C illustrate perspective views of exemplary pillars.

FIG. **7** illustrates a flow chart of an exemplary method **100** of forming pillars **52*a*** using imprint lithography.

FIGS. **8**A-**8**E illustrate simplified side views of formation of pillars in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION

Referring to the figures, and particularly to FIGS. **1** and **2**, illustrated therein is a lithographic system **10** used to form functional nano and/or micro particles on substrate **12**. Substrate **12** may be coupled to substrate chuck **14**. As illustrated, substrate chuck **14** is a vacuum chuck. Substrate chuck **14** however, may be any chuck including, but not limited to, vacuum, pin-type, groove-type, electrostatic, electromagnetic, and/or the like. Exemplary chucks are described in U.S. Pat. No. 6,873,087, U.S. Ser. Nos. 11/108,208, 11/047,428, 11/047,499, and 11/690,480, all of which are hereby incorporated by reference herein in their entirety.

Substrate **12** and substrate chuck **14** may be further supported by stage **16**. Stage **16** may provide rotational and/or translational motion in relation to the x, y and z axes. Stage **16**, substrate **12**, and substrate chuck **14** may also be positioned on a base (not shown).

Spaced-apart from substrate **12** is template **18**. Template **18** may include mesa **20** extending therefrom towards substrate **12**, with mesa **20** having a patterning surface **22** thereon. Further, mesa **20** may be referred to as mold **20**. Alternatively, template **18** may be formed without mesa **20**.

Template **18** and/or mold **20** may be formed from such materials including, but not limited to, fused-silica, quartz, silicon, organic polymers, siloxane polymers, borosilicate glass, fluorocarbon polymers, metal, hardened sapphire, and/or the like. As illustrated, patterning surface **22** comprises features defined by a plurality of spaced-apart recesses **24** and/or protrusions **26**, though embodiments of the present invention are not limited to such a configuration. For example, patterning surface **22** may be substantially flat. Generally, patterning surface **22** may be defined as any original pattern that forms the basis of a pattern to be formed on substrate **12**. Additionally, template **18** may be treated with an anti-adhesion agent (e.g., Relmat, FTOS). Exemplary anti-adhesion agents include, but are not limited to those described in U.S. Ser. No. 09/976,681, which is hereby incorporated by reference in its entirety.

Template **18** may be coupled to chuck **28**. Chuck **28** may be configured as, but not limited to, vacuum, pin-type, groove-type, electrostatic, electromagnetic, and/or other similar chuck types. Exemplary chucks are further described in U.S. Pat. No. 6,873,087, which is hereby incorporated by reference herein in its entirety. Further, chuck **28** may be coupled to imprint head **30** such that chuck **28** and/or imprint head **30** may be configured to facilitate movement of template **18**. Additionally, chuck **28** may be configured to adjust and/or vary the structure of template **18** prior to imprinting, during imprinting, and/or subsequent to imprinting (e.g. during separation).

System **10** may further comprise fluid dispense system **32**. Fluid dispense system **32** may be used to deposit functional material **34*a*** on substrate **12**. Functional material **34*a*** may have use within the bio-domain, solar cell industry, battery industry, and other industries requiring a functional nanoparticle. For example, functional material **34*a*** may include, but is not limited to, biomaterials (e.g., PEG), solar cell material (e.g., N-type material, P-type material), polymerizable materials, and/or the like.

Functional material **34*a*** may be positioned on substrate **12** using techniques such as drop dispense, spin-coating, dip coating, chemical vapor deposition (CVD), physical vapor deposition (PVD), thin film deposition, thick film deposition, and/or the like. It should be noted that the positioning of functional material **34** on substrate **12** may be configured to limit the amount of waste. For example, use of drop dispense in positioning of functional material **34** on substrate **12**, as compared to spin-coating and the like, may limit the amount of non-useable fluid during formation of functional nanoparticles.

Substrate **12** may include the use of a removable layer **50**. Removable layer **50** may facilitate separation of solidified functional material **34***a* from substrate **12** as described herein. Examples of materials for use in removable layer **50** may include, but are not limited to PVA or PMMA.

Referring to FIGS. **1** and **2**, system **10** may further comprise solidification source **38** (e.g., energy source) coupled to direct a medium **40** (e.g., energy) along path **42** to solidify functional material **34***a*. Imprint head **30** and stage **16** may be configured to position template **18** and/or substrate **12** in superposition with path **42**. System **10** may be regulated by processor **54** in communication with stage **16**, imprint head **30**, fluid dispense system **32** and/or source **38**, and may operate on a computer readable program stored in memory **56**.

Either imprint head **30**, stage **16**, or both may vary a distance between mold **20** and substrate **12** to define a desired volume therebetween that is filled by functional material **34***a*. For example, imprint head **30** may apply a force to template **18** such that mold **20** contacts functional material **34***a*. After the desired volume is filled with functional material **34***a*, source **38** may produce medium **40**, e.g. UV radiation, causing functional material **34***a* to solidify and/or cross-link conforming to a shape of surface **44** of substrate **12** and patterning surface **22**, defining patterned layer **46** on substrate **12**. Patterned layer **46** may comprise a residual layer **48** and/or features (e.g., protrusions **47** and recessions **49**). Protrusions **47** may have a thickness t_1 and residual layer **48** may have a thickness t_2.

Referring to FIGS. **2** and **3**, after solidification, patterned layer **46** may be subjected to further processing to clean patterned layer **46** and/or further separate protrusions **47** to form pillars **52**. For example, patterned layer **46** may be subjected to an oxygen plasma etching. Etching may remove at portion of residual layer **48** as illustrated in FIG. **3**.

Referring to FIGS. **3** and **4**, release of protrusions **47** from substrate **12** may form pillars **52**. For example, substrate **12** may be subjected a solution that may include, but is not limited to, water (e.g., de-ionized water), organic solvents (e.g., diluted HF), mild basic components, and/or the like. The solution may release protrusions **47** from substrate **12** to form pillars **52** having a thickness t_3.

Etching of protrusions **47** subsequent to solidification of functional material **34***a* may distort the configuration of protrusion **47** such that thickness t_2 of protrusion **47** is substantially different from thickness t_3 of the resulting pillar **52**. The amount of degradation of shape may limit the accuracy and/or precision of dimensionality when forming pillars **52**. Such distortion may be detrimental depending on the design consideration for the pillar **52**. For example, when pillars **52** are functional nanoparticles used as drug delivery devices, geo-targeting of destinations for pillar **52** within a body (e.g., human, animal, and/or the like) may be misdirected by alterations and/or distortion in shape.

Separation of template **18** from patterned layer **46** may also cause separation defects in pillars **52**. Although release layers (e.g., FOTS, Relmat, and the like) may be provided on substrate **12**, template **18** or both, the surface area of patterned layer **46** coupled to substrate **12** may be less than the surface area of patterned layer **46** coupled to template **18** prior to separation. Materiality of release layers and/or functional material **34** in combination with the dynamics of the surface area may provide separation defects in pillars **52**.

FIGS. **5**A-**5**E illustrate schematic side views of formation of pillars **52***a* minimizing degradation and separation distortion. By minimizing degradation and separation distortion, accuracy and/or precision of pillar formation may be controlled forming functional nanoparticles (i.e., pillars **52***a*).

Pillars **52***a* are formed of functional material **34***a*. Functional material **34***a* includes material used in industries including, but not limited to, the bio-domain, solar cell industry, battery industry, and the like. Functional material **34***a* may have use within the bio-domain, solar cell industry, battery industry, and other industries requiring a functional nano-particle. For example, functional material **34***a* may include, but is not limited to, biomaterials (e.g., PEG), solar cell material (e.g., N-type material, P-type material), polymerizable materials, and/or the like.

FIGS. **5**A-**5**E account for use of (1) properties of functional material **34***a*; and (2) imprint lithography materials (e.g., sacrificial material **34***a*, BT20, release properties of template **18***a* and **18***b*, and/or the like) by using sacrificial material **34***b* and imprint lithography techniques to form recesses recesses **49***a* and **47***a* that may be filled with functional material **34***a*. Without accounting for both properties of functional material **34***a* and properties of imprint lithography materials, degradation and separation distortion increases.

Generally, pillars **52***a* may be formed using one or more imprint lithography processes. For example, sacrificial material **34***a* may form protrusions **47***a* and recessions **49***a* using a first template **18***a* through the processes and systems described in relation to FIGS. **1** and **2**. For example, sacrificial material **34***a* (e.g., monomer mixture) may be solidified on a multi-layer substrate **70** to form patterned layer **46***a* having a first set of protrusions **47***a* and recessions **49***a*. The pattern formed by protrusions **47***a* and recessions **49***a* may be used to form a second set of protrusions **47***b* and recessions **49***b* in removable layer **50***a*. Functional material **34***a* (e.g., biomaterial) may then be deposited in recessions **49***b* in removable layer **50***a* to form pillars **52***a*. Alternatively, functional material **34***a* may be deposited on removable layer **50***a* and patterned by a second template **18***b* using the processes and systems as described in relation to FIGS. **1** and **2** to form pillars **52** in removable layer **50***a*. Pillars **52***a* may then be released from multi-layer substrate **70**.

Referring to FIG. **5**A, sacrificial material **34***b* may be deposited on multi-layer substrate **70**. Sacrificial material **34***b* may be formed of materials including, but not limited to, a polymerizable fluid comprising a monomer mixture as described in U.S. Pat. No. 7,157,036 and U.S. Patent Publication No. 2005/0187339, both of which are hereby incorporated by reference herein in their entirety.

Multi-layer substrate **70** may include a base layer **12***a*, a removable layer **50***a*, a protection layer **60** and an adhesion layer **62**. Base layer **12***a* may be similar to substrate **12** described in relation to FIG. **1**. Base layer **12***a* may be formed of materials including, but not limited to, fused-silica, quartz, silicon, organic polymers, siloxane polymers, borosilicate glass, fluorocarbon polymers, metal, hardened sapphire, and/or the like.

Removable layer **50***a* may be positioned adjacent to base layer **12***a*. Removable layer **50***a* may be similar to removable layer **50** described in relation to FIG. **3**. For example, removable layer **50***a* may release pillars **52***a* when subjected a solution including, but not limited to, water (e.g., de-ionized water), organic solvents (e.g., diluted HF), mild basic components, and/or the like.

Protection layer **60** may be positioned adjacent to removable layer **50***a*. Materiality of protection layer **60** may minimize damage and/or distortion of removable layer **50***a* during imprinting and/or etching. For example, protection layer **60** may be formed of materials such as PECVD silicon oxide and the like.

Adhesion layer **62** (e.g., BT20) may be positioned adjacent to protection layer **60**. During processing of patterned layer **46***a*, adhesion layer **62** may minimize separation distortion by adhering patterned layer **46***a* to multi-layer substrate **70** during separation of template **18** from patterned layer **46***a*.

Referring to FIG. **5**B, features (e.g., **47***a* and **49***a*) of patterned layer **46***a* may be formed on multi-layer substrate **70** using first template **18***a* as described in relation to the system **10** and processes described in FIGS. **1** and **2**. It should be noted that patterned layer **46***a* may be formed by other nanolithography techniques including, but not limited to, optical lithography, x-ray lithography, extreme ultraviolet lithography, scanning probe lithography, atomic force microscopic nanolithography, magneto lithography, and/or the like.

Referring to FIGS. **5**C-**5**D, subsequent to formation of patterned layer **46***a* on multi-layer substrate **70**, features (e.g., **47***a* and **49***a*) may aid in forming features (e.g., **47***b* and **49***b*) in removable layer **50***a*. For example, features (e.g., **47***a* and **49***b*) may be etched in multi-layer substrate **70** forming features (e.g., **47***b* and **49***b*) in removable layer **50***a*. Exemplary techniques include, but are not limited to, techniques described in U.S. Ser. Nos. 10/396,615 and 10/423,642, both of which are hereby incorporated by reference in their entirety.

In an optional step, portions of removable layer **50***a* or entire removable layer **50***a* may be exposed to UV ozone and/or O_2 plasma. Exposure to UV ozone and/or O_2 plasma may alter wetting characteristics of portions of removable layer **50***a* for a given material. Alterations of wetting characteristics may increase depth and/or aspect ratio, and/or reduce filling time and filling defect.

Referring to FIGS. **5**D and **5**E, functional material **34***a* (e.g., biomaterial) may be deposited on patterned removable layer **50***a*. Functional material **34***a* may be deposited using techniques such as drop dispense, spin-coating, dip coating, chemical vapor deposition (CVD), physical vapor deposition (PVD), thin film deposition, thick film deposition, and/or the like depending on design considerations. For example, by depositing functional material **34***a* using drop dispense techniques, the amount of functional material **34***a* deposited on removable layer **50***a* may be conserved.

Functional material **34***a* may fill in recessions **49***b* in removable layer **50***a* forming pillars **52***a*. In one embodiment, portions of functional material **34***a* deposited on removable layer **50***a* may be removed to form pillars **52***a*. Removal of portions of functional material **34***a* provides a crown layer **66** (e.g., substantially planar layer) exposing pillars **52***a*. Portions of functional material **34***a* may be removed using techniques including, but not limited to, blanket etching, CMP polishing, and/or similar methods. For example, if functional material **34***a* is formed of metal, crown layer **66** may be formed by metal etchants including, but not limited to, Cl_2, BCl_3, other Chlorine based etchants, and/or the like. It should be noted that the metal etchants are not limited to chlorine based etchants. For example, some metals, such as Tungsten, may be etched using Fluorine based etchants. Crown layer **66** may be formed by etching using an imprinting resist as a mask or by using a hardmask for pattern transfer. For example, crown layer **66** may be formed by using a hardmask formed of materials including, but not limited to, Cr, Silicon Oxide, Silicon Nitride, and/or the like. Alternatively, if functional material **34***a* is formed of Silicon based material. Crown layer **66** may be formed by etching Silicon using common Silicon etchants including, but not limited to, CF_4, CHF_3, SF_6, Cl_2, HBr, other Fluorine, Chlorine and Bromine based etchants, and/or the like. Additionally, crown layer **66** may be etched using an imprint resist as a mask, a hardmask for pattern transfer, or the like. For example, crown layer **66** may be etched using a hardmask formed of materials including, but not limited to, Cr, Silicon Oxide, Silicon Nitride, and/or the like.

In another embodiment, a second template **18***b* may be used to form pillars **52***a* from functional material **34***a* deposited on removable layer **50***a*. Template **18***b* may be positioned in superimposition with functional material **34***a* on removable layer **50***a*. Template **18***b* may contact functional material **34***a* and functional material **34***a* may be solidified. Template **18***b* may then be separated. It should be noted that template **18***b* may optionally include coatings (e.g., FOTS) that aid in separation of template **18***b* from solidified functional material **34***a* as described herein.

Use of template **18***b* may provide a substantially planar edge in solidified functional material **34***a*. The surface area between solidified functional material **34***a* and template **18***b* may be selected such that it is less than the surface area between solidified functional material **34***a* and removable layer **50***a*. For example, template **18***b* may be substantially planar. By reducing the surface area of solidified functional material **34***a* and template **18***b* as compared to the surface area of solidified functional material **34***a* and removable layer **50***a*, separation defects of solidified functional material **34***a* may be reduced.

Referring to FIG. **5**E, solidified functional material **34***a* and/or removable layer **50***a* may be removed to provide a crown layer **66**. For example, solidified functional material **34***a* and/or removable layer **50***a* may be removed by blanket etching, CMP polishing, and/or similar methods to provide crown layer **66** (e.g., planarized layer). Pillars **52***a* may be positioned in recesses **49***b* of removable layer **50***a*.

Referring to FIGS. **5**E and **5**F, pillars **52***a* may be released from removable layer **50***a*. For example, removable layer **50***a* may be subjected a solution that may include, but is not limited to, water (e.g., de-ionized water), organic solvents, inorganic acids (e.g., diluted HF), mild basic components, and/or the like, causing pillars **52***a* to be released from multi-layer substrate **70**.

Dimensions provided by the crowning of solidified functional material **34***a* and the dimensions provided by removable layer **50***a* may define edges of pillars **52***a*, and as such, the volume of pillars **52***a*. By adjusting these dimensions, pillars **52***a* may be constructed having varying shapes and sizes. For example, as illustrated in FIGS. **6**A-**6**C, pillars **52***a* may be constructed in shapes including, but not limited to, circular, triangular, rectangular, fanciful, and the like. By controlling the dimensions of removable layer **50***a* and planarization of solidified functional material **34***a*, shape, accuracy and precision of formation of pillars **52***a* may also be controlled. Further, pillars **52***a* may be formed using exemplary techniques described in U.S. Ser. No. 12/616,896, which is herein incorporated by references in its entirety.

FIG. **7** illustrates a flow chart of an exemplary method **100** for forming pillars **52***a* using an imprint lithography system. Formation of pillars **52***a* may include one or more lithography steps (e.g., nano-imprint lithography). In a step **102**, sacrificial material **34***b* may be patterned on a multi-layer substrate **70**. For example, sacrificial material **34***b* may be patterned using a first imprint lithography process using first template **18***a* to provide patterned layer **46***a* having features **47***a* and

49*a*. In a step **104**, features **47***a* and **49***a* may be used to form features **47***b* and **49***b* in removable layer **50***a*. For example, features **47***a* and **49***a* may be etched into multi-layer substrate **70** to provide features **47***b* and **49***b* in removable layer **50***a*.

In an optional step, removable layer **50***a* may be exposed to UV ozone and/or O_2 plasma. In a step **106**, functional material **34***a* (e.g., biomaterial) may be deposited on removable layer **50***a* and solidified. In a step **108**, a portion of functional material **34***a* may be patterned and/or removed to provide crown surface **66** exposing pillars **52***a*. In a step **110**, pillars **52***a* may be released from multi-layer substrate **70**.

FIGS. **8**A-**8**E illustrate simplified side views of another embodiment for forming pillars **52***b*. Generally, formation of pillars **52***b* may comprise one or more imprint lithography steps

Referring to FIG. **8**A, sacrificial material **34***b* may be deposited on multi-layer substrate **70***b*. Sacrificial material **34***b* may be formed of materials including, but not limited to, a polymerizable fluid comprising a monomer mixture as described in U.S. Pat. No. 7,157,036 and U.S. Patent Publication No. 2005/0187339, both of which are hereby incorporated by reference herein in their entirety.

Multi-layer substrate **70***b* may include a base layer **12***b* (e.g., Si), a removable layer **50***b* (e.g., SiO_2), and an adhesion layer **62***b* (e.g., BT20). Base layer **12***b* may be similar to substrate **12** described in relation to FIG. **1**. Base layer **12***b* may be formed of materials including, but not limited to, fused-silica, quartz, silicon, organic polymers, siloxane polymers, borosilicate glass, fluorocarbon polymers, metal, hardened sapphire, and/or the like.

Removable layer **50***b* may be positioned adjacent to base layer **12***b*. Removable layer **50***b* may be similar to removable layer **50** described in relation to FIG. **3**. For example, removable layer **50***b* may release pillars **52***a* when subjected a solution including, but not limited to, water (e.g., de-ionized water), organic solvents (e.g., HF), mild basic components, and/or the like.

Functional material **34***a* (e.g., Si) may be positioned adjacent to removable layer **50***b*. Adhesion layer **62***b* (e.g., BT20) may be positioned adjacent to functional material **34***a*. During processing of patterned layer **46***b* (shown in FIG. **8**B), adhesion layer **62***b* may minimize separation distortion by adhering patterned layer **46***b* to multi-layer substrate **70***b* during separation of template **18** from patterned layer **46***b*. In one embodiment, functional material **34***a* may be exposed to UV ozone and/or O_2 plasma. Exposure of functional material **34***a* to UV ozone and/or O_2 plasma may render adhesion layer **62***b* obsolete such that patterned layer **46***b* may be formed directly on functional material **34***a* without use of adhesion layer **62***b*.

Referring to FIG. **8**B, features (e.g., **47***c* and **49***c*) of patterned layer **46***b* may be formed on multi-layer substrate **70***b* using template **18** as described in relation to the system **10** and processes described in FIGS. **1** and **2**. It should be noted that patterned layer **46***b* may be formed by other nano-lithography techniques including, but not limited to, optical lithography, x-ray lithography, extreme ultraviolet lithography, scanning probe lithography, atomic force microscopic nanolithography, magneto lithography, and/or the like.

Referring to FIG. **8**C, features (e.g., **47***c* and **49***c*) may be etched in multi-layer substrate **70***b* forming features (e.g., **47***d* and **49***d*) in functional material **34***a*. Exemplary techniques include, but are not limited to, techniques described in U.S. Ser. Nos. 10/396,615 and 10/423,642, both of which are hereby incorporated by reference in their entirety. For example, portions may be removed using techniques including, but not limited to, blanket etching, CMP polishing, and/or similar methods. For example, metal etchants may be used including, but not limited to, Cl_2, BCl_3, other Chlorine based etchants, and/or the like. It should be noted that the metal etchants are not limited to chlorine based etchants. For example, some metals, such as Tungsten, may be etched using Fluorine based etchants. Additionally, features (e.g., **47***d* and **49***d*) may be formed by etching using an imprinting resist as a mask or by using a hardmask for pattern transfer. For example, features (e.g., **47***d* and **49***d*) may be formed by using a hardmask formed of materials including, but not limited to, Cr, Silicon Oxide, Silicon Nitride, and/or the like. Alternatively, Silicon etchants may be used including, but not limited to, CF_4, CHF_3, SF_6, Cl_2, HBr, other Fluorine, Chlorine and Bromine based etchants, and/or the like. Additionally, features (e.g., **47***d* and **49***d*) may be etched using an imprint resist as a mask, a hardmask for pattern transfer, or the like. For example, features (e.g., **47***d* and **49***d*) may be etched using a hardmask formed of materials including, but not limited to, Cr, Silicon Oxide, Silicon Nitride, and/or the like.

Referring to FIGS. **8**C-**8**E, sacrificial material **34***b* and adhesion layer **62***b* (if needed) may be stripped from functional material **34***a*. Removable layer **50***b* may be subjected to a chemical process (e.g., HF dip) such that functional material **34***a* is removed from multi-layer substrate **70** forming one or more pillars **52***b* (i.e., functional nanoparticles).

What is claimed is:

1. A method of forming functional nanoparticles, comprising:

forming a multi-layer substrate comprising, a removable layer and a sacrificial material layer coupled to the removable layer;

patterning the sacrificial layer using a first imprint lithography template to provide a patterned layer having a residual layer and a pattern of a plurality of protrusions and a plurality of recessions;

transferring the pattern of protrusions and recessions into the removable layer;

depositing functional material within recessions of the removable layer;

patterning the functional material to provide a patterned functional material layer having a plurality of pillars in the removable layer; wherein the patterning of the functional material includes imprinting using a second imprint lithography template and wherein the second imprint lithography template is substantially planar, and,

releasing the pillars from the multi-layer substrate, the released pillars forming functional nanoparticles comprising the functional material.

2. The method of claim **1**, wherein the functional material is a biomaterial.

3. The method of claim **1**, wherein releasing of the pillars includes subjected the removable layer to a solution comprising water, organic solvents, and mild basic components.

4. The method of claim **1**, the sacrificial material layer is formed of a polymerizable fluid comprising a monomer mixture.

5. The method of claim **1**, wherein the multi-layer substrate further comprises a base layer coupled to the removable layer.

6. The method of claim **1**, further comprising exposing at least a portion of the removable layer to UV ozone altering wetting characteristics of the removable layer.

7. The method of claim **1**, wherein functional material of functional material layer is deposited on the patterned layer by drop dispense.

8. The method of claim **1**, wherein surface area between patterned functional material layer and the second template is less than surface area between patterned functional material layer and the removable layer.

9. The method of claim **1**, wherein patterning of the functional material includes forming a crown layer by etching using an imprinting resist as a mask.

10. The method of claim **1**, wherein shape of at least one pillar is selected from the group consisting of circular, triangular, and rectangular.

11. The method of claim **1**, wherein the multi-layer substrate further comprises a protection layer coupled to the removable layer, the protection layer formed of materials minimizing damage and distortion of removable layer during transferring of the pattern of protrusions and recessions into the removable layer.

12. The method of claim **11**, wherein the multi-layer substrate further comprises an adhesion layer coupled to the protection layer, the adhesion layer adhering the patterned layer to the multi-layer substrate during patterning of the functional material using a second imprint lithography template.

13. A method of forming functional nanoparticles, comprising:

forming a plurality of features in a sacrificial material layer of a multi-layer substrate, the multi-layer substrate having a base layer, a removable layer coupled to the base layer, and the sacrificial material layer coupled to the removable layer;

transferring features of the sacrificial material layer into the removable layer forming a plurality of protrusions and a plurality of recessions in the removable layer;

depositing functional material in recessions of the removable layer;

planarizing the functional material by imprinting with a substantially planar imprint lithography template to form a patterned layer of functional material having a plurality of pillars formed in the recessions of the removable layer;

removing functional material positioned outside of recessions of the removable layer such that a crown surface is formed, the crown surface providing an edge of each pillar of functional material formed in the recessions of the removable layer; and,

releasing pillars of functional material from the removable layer, the released pillars forming functional nanoparticles comprising the functional material.

14. The method of claim **13**, further comprising exposing removable layer to UV ozone prior to deposition of functional material.

15. The method of claim **13**, wherein functional material is a biomaterial and sacrificial material layer is formed of polymerizable material comprising a monomer mixture.

16. The method of claim **13**, wherein releasing of the pillars includes subjected the removable layer to a solution comprising water, organic solvents, and mild basic components.

17. The method of claim **13** wherein the multi-layer substrate further comprises a protection layer coupled to the removable layer, the protection layer formed of materials minimizing damage and distortion of removable layer during transferring of the pattern of protrusions and recessions into the removable layer.

18. A method of forming functional nanoparticles, comprising:

forming a plurality of recessions in a removable layer;

depositing functional material in the recessions of the removable layer;

planarizing the functional material to form a patterned layer of functional material having a plurality of pillars formed in the recessions of the removable layer; wherein the planarizing of the functional material includes imprinting using an imprint lithography template that is substantially planar;

removing a portion of the functional material to expose portions of the removable layer between formed pillars of the functional material; and,

releasing pillars of functional material from the removable layer, the released pillars forming functional nanoparticles comprising the functional material.

19. The method of claim **18**, wherein the removable layer is coupled to a base layer.

20. The method of claim **18**, wherein the functional material is deposited in the recessions of the removable layer by drop dispense.

21. The method of claim **18**, wherein the functional material is a biomaterial.

22. The method of claim **18**, wherein releasing the pillars includes subjecting the removable layer to a solution comprising water, organic solvents, and mild basic components.

23. The method of claim **18**, wherein the forming of a plurality of recessions in the removable layer further comprises the steps of:

depositing sacrificial material onto the removable layer;

forming a patterned layer of the sacrificial material, the patterned layer having a plurality of recessions; and

transferring the pattern of the plurality of recessions into the removable layer.

24. The method of claim **23** wherein the forming of a patterned layer further comprises using an imprint lithography template.

25. The method of claim **23** wherein the sacrificial material is deposited on the removable layer by drop dispense.

26. The method of claim **23** wherein the sacrificial material is deposited on the removable layer by spin-on processes.

27. The method of claim **23** wherein forming a patterned layer further comprises UV or thermal curing of the sacrificial layer.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 8,961,800 B2
APPLICATION NO. : 12/854359
DATED : February 24, 2015
INVENTOR(S) : Sidlgata V. Sreenivasan et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

IN THE CLAIMS:

Column 8, line 30, claim 1, after “layer” insert -- coupled --, therefore.

Column 8, line 42, claim 1, delete “layer;” and insert -- layer, --, therefore.

Column 8, line 45, claim 1, delete “planar,” and insert -- planar; --, therefore.

Signed and Sealed this
Twenty-second Day of December, 2015

Michelle K. Lee

Michelle K. Lee
Director of the United States Patent and Trademark Office