



- (51) **International Patent Classification:**
H01L 45/00 (2006.01) *H01L 27/24* (2006.01)
- (21) **International Application Number:**
PCT/US2015/021686
- (22) **International Filing Date:**
20 March 2015 (20.03.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
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- (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, BN, BR, BW, BY, BZ, CA, CH, CL, 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, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, 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, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

- with international search report (Art. 21(3))

(54) **Title:** MEMRISTIVE DEVICE WITH DOPED SOL-GEL SWITCHING LAYER

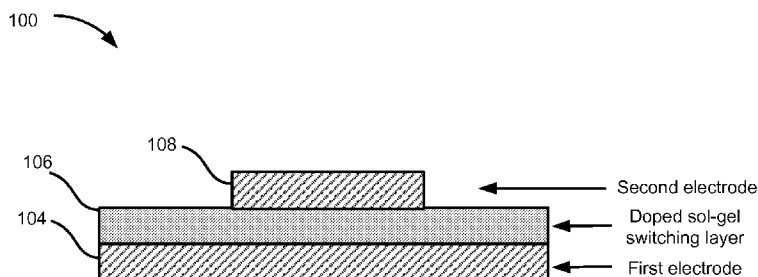


FIG. 1

(57) **Abstract:** In the examples provided herein, a memristive device is disclosed that has a first electrode, a second electrode, and a doped sol-gel switching layer sandwiched between the first electrode and the second electrode. The doped sol-gel switching layer is a sol-gel material doped with nanoparticles or quantum dots of a switching material.



MEMRISTIVE DEVICE WITH DOPED SOL-GEL SWITCHING LAYER

BACKGROUND

[0001] A sol-gel process is a process used for making glass and ceramic materials. A sol is a colloidal suspension of particles in a solution, and a gel is material that has a continuous skeletal structure that is interpenetrated by a liquid. When the liquid evaporates, a strong glass-like material results.

[0002] A spin-on glass material can be used as a thin film dielectric layer between metallization levels in integrated circuit devices. The spin-on glass starts as a liquid solution and is spin-coated onto a silicon wafer to fill submicron gaps in metallic layers and to planarize surfaces. The spin-on glass is then dried and cured to turn the spin-coated liquid film into a thin film material made up of a silicon-oxygen network. The spin-on glass is an application of the sol-gel process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0003] The accompanying drawings illustrate various examples of the principles described below. The examples and drawings are illustrative rather than limiting.

[0004] FIG. 1 depicts a cross-section of an example memristive device with a doped sol-gel switching layer.

[0005] FIGS. 2A-2E depict steps of different manufacturing techniques for manufacturing a memristor structure with a doped sol-gel switching layer.

[0006] FIG. 3 depicts a flow diagram illustrating an example process of manufacturing a doped sol-gel memristive device.

[0007] FIGS. 4A and 4B depict a flow diagram illustrating an example process of manufacturing a doped sol-gel memristive device.

[0008] FIG. 5 depicts a flow diagram illustrating an example process of making a doped sol-gel material and manufacturing a doped sol-gel switching layer of a memristive device.

DETAILED DESCRIPTION

[0009] A sol-gel based process is presented for fabricating a switching layer of a memristive device. A sol-gel material may be doped with nanoparticles and/or quantum dots of a switching material. The resulting doped sol-gel solution is spun on a first electrode and then cured to create the switching layer. Then a second electrode is formed on top of the switching layer to create a metal-insulator-metal sandwich structure of a memristive device.

[0010] Memristive behavior is achieved by the movement of ionic species (e.g. oxygen ions or vacancies) within the switching layer to create localized changes in conductivity via modulation of a conductive filament between the two electrodes, which results in a low resistance “ON” state, a high resistance “OFF” state, or intermediate states. When the memristive device is first fabricated, the entire switching material may be nonconductive. As such, a forming process may be required to form the conductive channel in the switching material between the two electrodes. A known forming process, often called “electroforming”, includes applying a sufficiently high (threshold) voltage across the electrodes for a sufficient length of time to cause a nucleation and formation of a localized conductive channel (or active region) in the switching material. The threshold voltage and the length of time required for the forming process may depend upon the type of material used for the switching material, the first electrode, and the second electrode, and the device geometry.

[0011] FIG. 1 depicts a cross-section of an example memristor structure 100 with a doped sol-gel switching layer 106. The memristor structure 100 may include a first electrode 104, a second electrode 108, and the doped sol-gel switching layer

106 which is sandwiched between the first electrode 104 and the second electrode 108.

[0012] The first electrode 104 and the second electrode 108 may be formed of metal, for example, platinum, tungsten, gold, titanium, silver, ruthenium dioxide, titanium nitride, tungsten nitride, tantalum, and tantalum nitride or other conductive metals or compounds. Alternatively, the first electrode 104 and the second electrode 108 may be formed of a semiconductor, such as doped silicon.

[0013] The doped sol-gel switching layer 106 may be nanoparticles of a switching material or quantum dots mixed in an electrically insulating sol-gel material, where the switching material may be an electrically conducting or semiconducting material. Examples of the insulating sol-gel material may include low dielectric materials, such as hydrogensilsesquioxane (HSQ) and methylsilsesquioxane (MSQ). The nanoparticles or quantum dots mixed into the sol-gel material may include one or a combination of metals, semiconductors, metal suboxides, metal subnitrides, metal-doped oxides, metal-doped nitrides, etc., such as an aluminum-copper alloy (e.g., aluminum copper (AlCu) or aluminum copper silicon (AlCuSi)), silicon, platinum, tantalum, titanium, copper, aluminum, cobalt, nitrogen, niobium, molybdenum, tungsten, hafnium, zirconium, chromium, zinc sulfide, tantalum nitride, titanium nitride, niobium nitride, hafnium nitride, zirconium nitride, ruthenium oxide, iridium oxide, TiO_x , TaO_x , and ZnO_x .

[0014] In some implementations, a surfactant may be added to the sol-gel material to prevent aggregation of nanoparticles or quantum dots of the switching material within the sol-gel solution. Some examples of surfactants that may be used include polyvinylpyrrolidone (PVP), molecules with amine or carboxylic acid terminal groups, cationic surfactants, such as cetyl trimethylammonium bromide (CTAB), and anionic surfactants, such as sodium lauryl sulfate.

[0015] In some implementations, nanoparticles or quantum dots of the switching material may be coated with a surfactant material such as PVP to prevent agglomeration of the nanoparticles and quantum dots in the sol-gel solution.

[0016] The thickness of the doped sol-gel switching layer 106 may be within a range of about 20 nm to about 100 nm. In some implementations, the thickness of the doped sol-gel switching layer 106 may be within a range of about 10 nm to about 90 nm.

[0017] FIGS. 2A-2E depict manufacturing steps for manufacturing a memristive device with a doped sol-gel switching layer. FIG. 2A depicts dopants 210 that are mixed with a sol-gel solution 212 to yield a doped sol-gel solution 214. A single type of dopant or different types of dopants may be mixed with the sol-gel solution 212. Other additives may also be mixed into the sol-gel solution 212, such as a surfactant for stabilization of the solution.

[0018] FIG. 2B depicts a substrate 102 on top of which a first electrode 104 is manufactured. The substrate 102 may be a silicon material or a non-silicon material, such as glass, a printed circuit board (PCB), or other flexible material. The selected substrate material should be able to withstand a curing temperature of the doped sol-gel solution. While the curing temperature for some sol-gel solutions may be as high as 1000°C, for substrate materials like PCB that tolerate a lower range of temperatures, sol-gel solutions may be selected that have a low temperature process, for example, below about 280°C.

[0019] The first electrode 104 may be deposited on the substrate 102, for example, by electroplating, sputtering, evaporation, atomic layer deposition (ALD), co-deposition, chemical vapor deposition, ion beam assisted deposition, and any other film deposition technology. The thickness of the first electrode 104 may be in the range of about 10 nm to a few micrometers.

[0020] FIG. 2C depicts some of the doped sol-gel solution 214 applied to the top of the first electrode 104 deposited on the substrate 102. The doped sol-gel solution 214 may be applied by using a pipette to transport the sol-gel solution 214 to the surface of the first electrode 104, or by dipping the first electrode 104 in the sol-gel solution.

[0021] FIG. 2D depicts the doped sol-gel solution 214 after it has been processed by spinning and subsequently curing the solution 214 to produce a uniform doped sol-gel switching layer 106 on the first electrode 104. The rate of the spinning may be within a range of about 1000 rpm to about 8000 rpm. The speed should be sufficiently fast to allow excess doped sol-gel solution 214 to spin off, leaving a uniform layer 106 on the first electrode 104. In some implementations, a particular thickness of the resulting uniform layer 106 may be achieved by controlling the rate of spinning.

[0022] The curing process may be performed with the application of heat to the uniform layer 106. For example, in some implementations, the temperature to which the doped sol-gel solution 214 may be heated during curing may be within a range of about 100°C to about 450°C, and in some implementations, the curing temperature may be within a range of about 100°C to about 1000°C. The duration for which the solution is heated during curing should be sufficiently long for the doped sol-gel solution to dry. After the doped sol-gel solution has been spun and cured, the switching layer 106 may reach a thickness of approximately 20 nm thickness. If the thickness of the switching layer 106 is significantly less than about 20 nm, additional doped sol-gel solution may be repeatedly applied, spun, and cured to create a thicker doped sol-gel switching layer 106. In some implementations, the desired thickness of the switching layer may be thicker, for example, up to a few microns, depending upon the application. In some implementations, the desired thickness of the switching layer may be thinner. Then the switching layer 106 may be etched to the desired thickness.

[0023] FIG. 2E depicts a second electrode 108 that has been deposited on top of the doped sol-gel switching layer 106. The second electrode 108 may be deposited using one of the deposition technologies described above, and the material of the second electrode 108 may be one of the materials described above for the first electrode 104. The thickness of the second electrode 108 may be similar to the thickness of the first electrode 104.

[0024] FIG. 3 depicts a flow diagram illustrating an example process 300 of manufacturing a doped sol-gel memristive device. The process begins at block 305 where a first electrode may be manufactured on a substrate. The substrate may be a silicon substrate or a non-silicon substrate. As described above, the first electrode may be deposited using a suitable deposition technique and one or more of the materials described above.

[0025] At block 310, a sol-gel solution may be applied on the first electrode. For example, the sol-gel solution may be applied to the first electrode using a pipette. The sol-gel solution may be a suspension of switching nanoparticles or quantum dots in an electrically insulating solution. In some implementations, the sol-gel solution may include a surfactant, or the nanoparticles and the quantum dots may be coated with a material to prevent agglomeration.

[0026] At block 315, the sol-gel solution on the first electrode may be spun. For example, the substrate, first electrode and applied sol-gel solution may be spun on a turntable. In some implementations, a rate of the spinning of the substrate, first electrode, and applied sol-gel solution may be within a range of about 1000 and 8000 revolutions per minute (rpm).

[0027] At block 320, the sol-gel solution may be cured to dry the doped sol-gel solution. In some implementations, a temperature during curing may be within a range of about 100°C and 450°C. Because the sol-gel curing process is a low temperature process, application of the doped sol-gel switching layer may be used for devices that are not able to withstand the higher temperatures of a deposition processing step such as atomic layer deposition and physical vapor deposition. As a result, the physical properties of the substrate remain unaffected after curing of the sol-gel solution during the low temperature sol-gel curing process.

[0028] At block 325, a second electrode may be manufactured on the sol-gel solution after the sol-gel solution has been cured to complete the memristive device.

[0029] FIGS. 4A and 4B depict a flow diagram illustrating an example process 400 of manufacturing a doped sol-gel memristive device. The process begins at block 405, which may be similar to block 305 described with respect to the process 300 of FIG. 3.

[0030] At block 410, the switching nanoparticles and/or quantum dots and the surfactant may be mixed in the electrically insulating solution, or switching nanoparticles and/or quantum dots coated with a surfactant may be mixed in the electrically insulating solution to generate the sol-gel solution. For example, an ultrasound machine may be used to uniformly mix the doped sol-gel solution. Blocks 415, 420, and 425 may also be similar to blocks 310, 315, and 320, respectively, of FIG. 3.

[0031] At decision block 427, it may be determined whether the thickness of the layer of cured sol-gel solution is at a target thickness. If it is determined that the layer thickness is at a target thickness, the process continues to block 435.

[0032] In some implementations, the thickness of the resulting switching layer is below a target thickness, up to several microns thick. At block 430 (layer too thin), additional sol-gel solution may be repeatedly applied, spun and cured on previously spun and cured sol-gel solution until a thickness of the sol-gel solution reaches a target thickness. The process continues to block 435.

[0033] In some implementations, the thickness of the resulting switching layer is above a target thickness. At block 432 (layer too thick), the layer of cured sol-gel solution may be etched down to the target thickness. The process continues to block 435.

[0034] Block 435 may be similar to block 325 described with respect to process 300 of FIG. 3.

[0035] FIG. 5 depicts a flow diagram illustrating an example process 500 of generating a doped sol-gel material and manufacturing a switching layer of a memristive device. The process begins at block 505, where switching nanoparticles

or quantum dots and a surfactant may be mixed in a spin-on glass material, such as a sol-gel solution; or switching nanoparticles or quantum dots coated with a surfactant may be mixed in a spin-on glass material.

[0036] At block 510, an electrode of a memristive device may be coated with the spin-on glass material mixed with the switching nanoparticles or quantum dots and the surfactant, or the spin-on glass material mixed with the switching nanoparticles or quantum dots coated with the surfactant. For example, the spin-on glass material may be pipetted onto the electrode and spun to create a uniform layer of the spin-on glass material with the switching nanoparticles or quantum dots and the surfactant on the electrode. The rate of spinning may be within a range of about 1000 rpm to about 8000 rpm.

[0037] At block 515, the spin-on glass material may be cured to dry the spin-on glass material. The temperature during curing of the spin-on glass material may be within a range of about 100°C to about 450°C.

[0038] In some implementations, coating the electrode of the memristive device may include pipetting the spin-on glass material with the switching nanoparticles or quantum dots and the surfactant, or pipetting the spin-on glass material with the switching nanoparticles or quantum dots coated with the surfactant onto the electrode and spinning the spin-on glass material on the electrode.

[0039] Not all of the steps, or features presented above are used in each implementation of the presented techniques.

[0040] As used in the specification and claims herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise.

CLAIMS

What is claimed is:

1. A memristive device comprising:
a first electrode;
a second electrode; and
a doped sol-gel switching layer sandwiched between the first electrode
and the second electrode,
wherein the doped sol-gel switching layer comprises a sol-gel material
doped with nanoparticles or quantum dots of a switching material.
2. The memristive device of claim 1, wherein a thickness of the sol-gel
switching layer is within a range of about 20 nm and 100 nm.
3. The memristive device of claim 2, further comprising:
a substrate, wherein the first electrode is manufactured on the substrate,
and further wherein the substrate is selected from a group
comprising: a silicon wafer, glass, a printed circuit board
substrate, and a flexible material substrate.
4. The memristive device of claim 1, wherein the sol-gel material is
selected from the following: hydrogensilsesquioxane (HSQ) and
methylsilsesquioxane (MSQ).
5. The memristive device of claim 1, wherein the sol-gel material includes a
surfactant.

6. The memristive device of claim 5, wherein the surfactant is selected from a group comprising: polyvinylpyrrolidone (PVP), molecules with amine or carboxylic acid terminal groups, cationic surfactants, and anionic surfactants.
7. A method for manufacturing a memristive device, the method comprising:
 - forming a first electrode on a substrate;
 - applying a sol-gel solution on the first electrode, wherein the sol-gel solution comprises a suspension of switching nanoparticles or quantum dots in an electrically insulating solution;
 - spinning the sol-gel solution;
 - curing the sol-gel solution; and
 - forming a second electrode on the sol-gel solution after the sol-gel solution has been cured.
8. The method of claim 7, wherein the sol-gel solution further comprises a surfactant.
9. The method of claim 8, further comprising mixing the switching nanoparticles or quantum dots and the surfactant in the electrically insulating solution to generate the sol-gel solution.
10. The method of claim 7, wherein a rate of the spinning is within a range of about 1000 rpm and 8000 rpm.
11. The method of claim 7, wherein a temperature during curing is within a range of about 100°C and 450°C.
12. The method of claim 7, wherein physical properties of the substrate remain unaffected after curing the sol-gel solution.

13. The method of claim 7, further comprising: when a thickness of the cured sol-gel solution is below target thickness, repeatedly applying, spinning and curing additional sol-gel solution on previously spun and cured sol-gel solution until a thickness of the sol-gel solution reaches a target thickness; or when the thickness of the cured sol-gel solution is above target thickness, etching the cured sol-gel solution to the target thickness.

14 A method for creating a switching layer for a memristive device, the method comprising:

- mixing switching nanoparticles or quantum dots and a surfactant in a sol-gel material, or mixing switching nanoparticles or quantum dots coated with a surfactant in a sol-gel material;
- coating an electrode of a memristive device with the mixed sol-gel material; and
- curing the mixed sol-gel material.

15. The method of claim 14, wherein coating comprises spinning the mixed sol-gel material on the electrode.

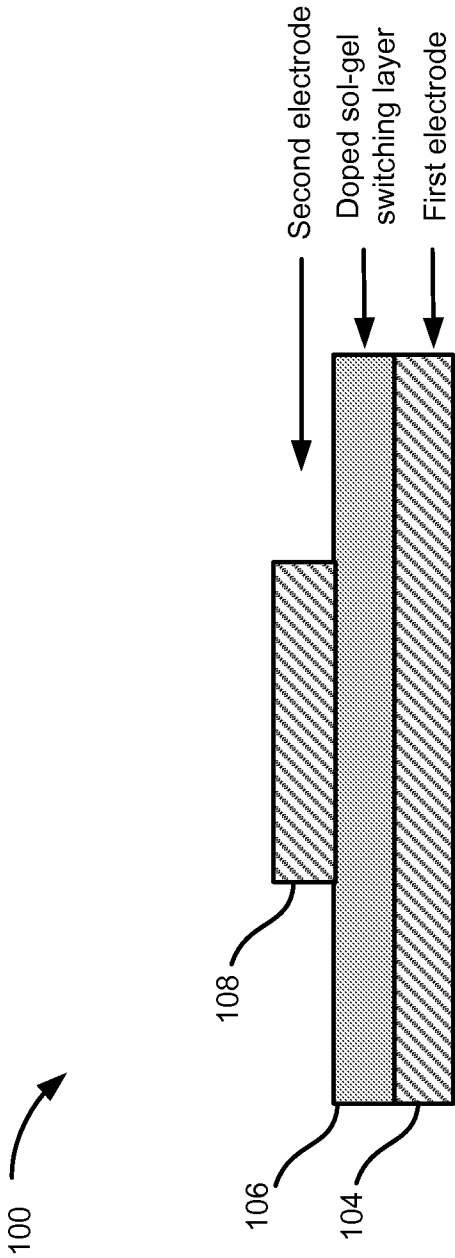


FIG. 1

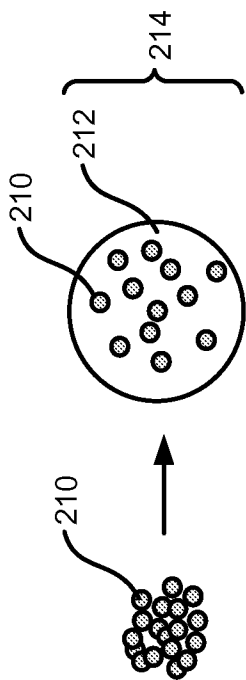


FIG. 2A

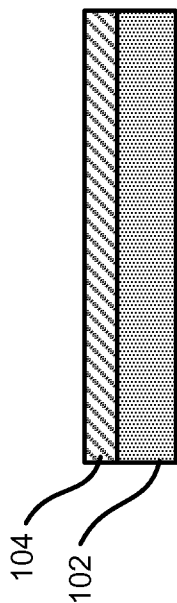


FIG. 2B

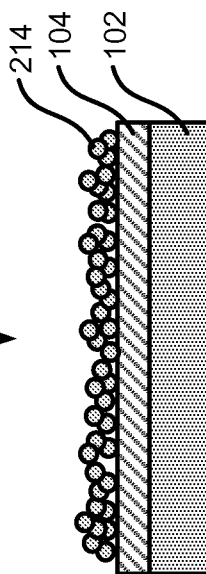
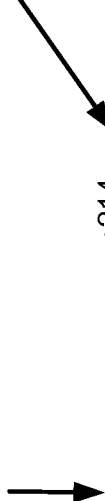


FIG. 2C

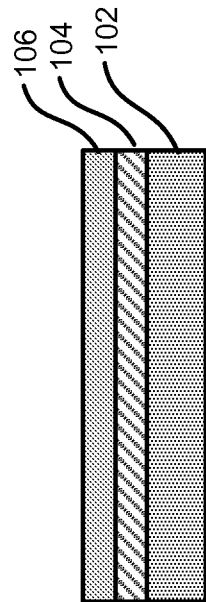


FIG. 2D

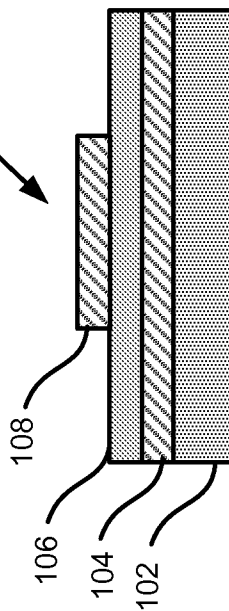
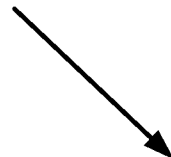
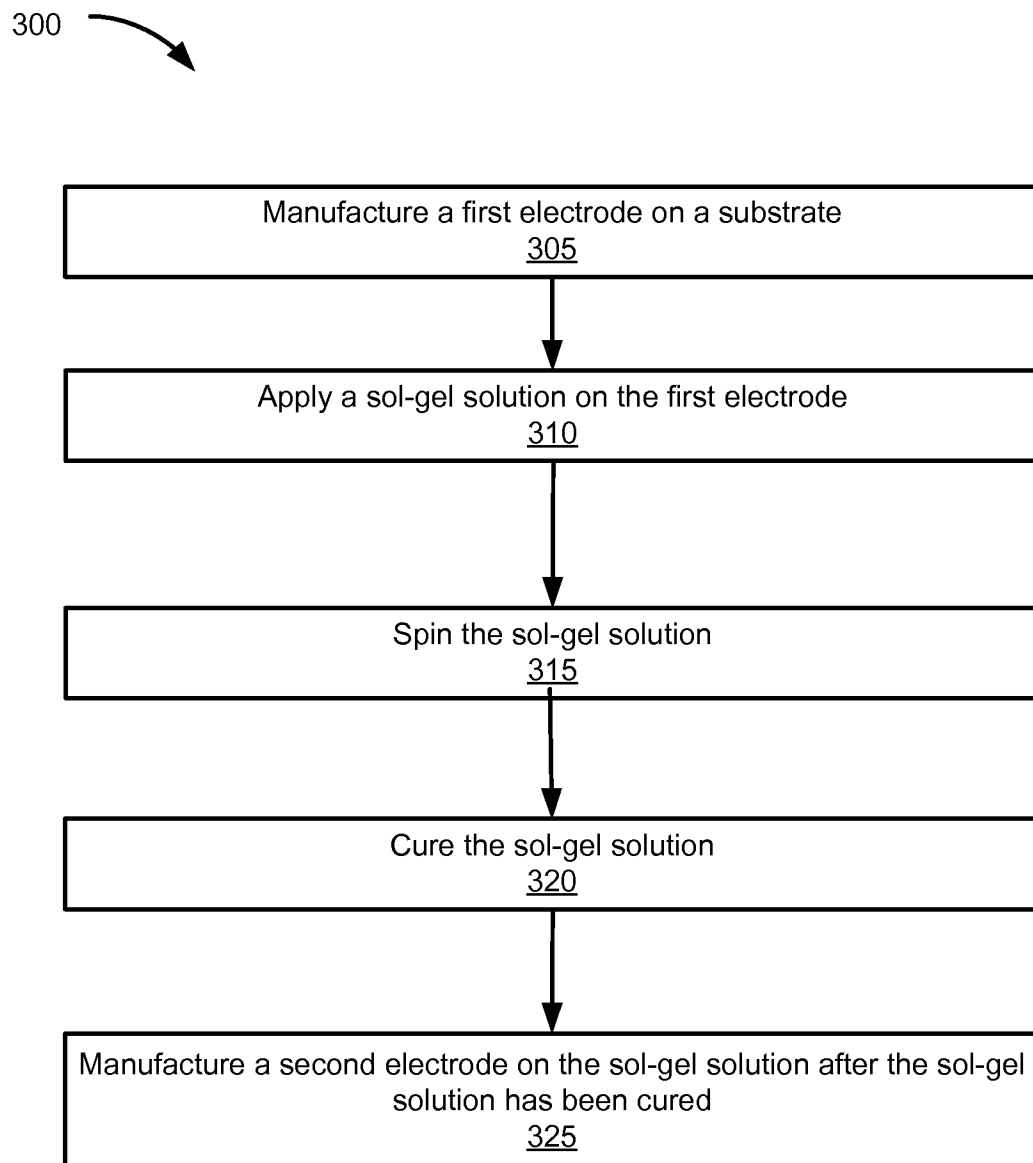
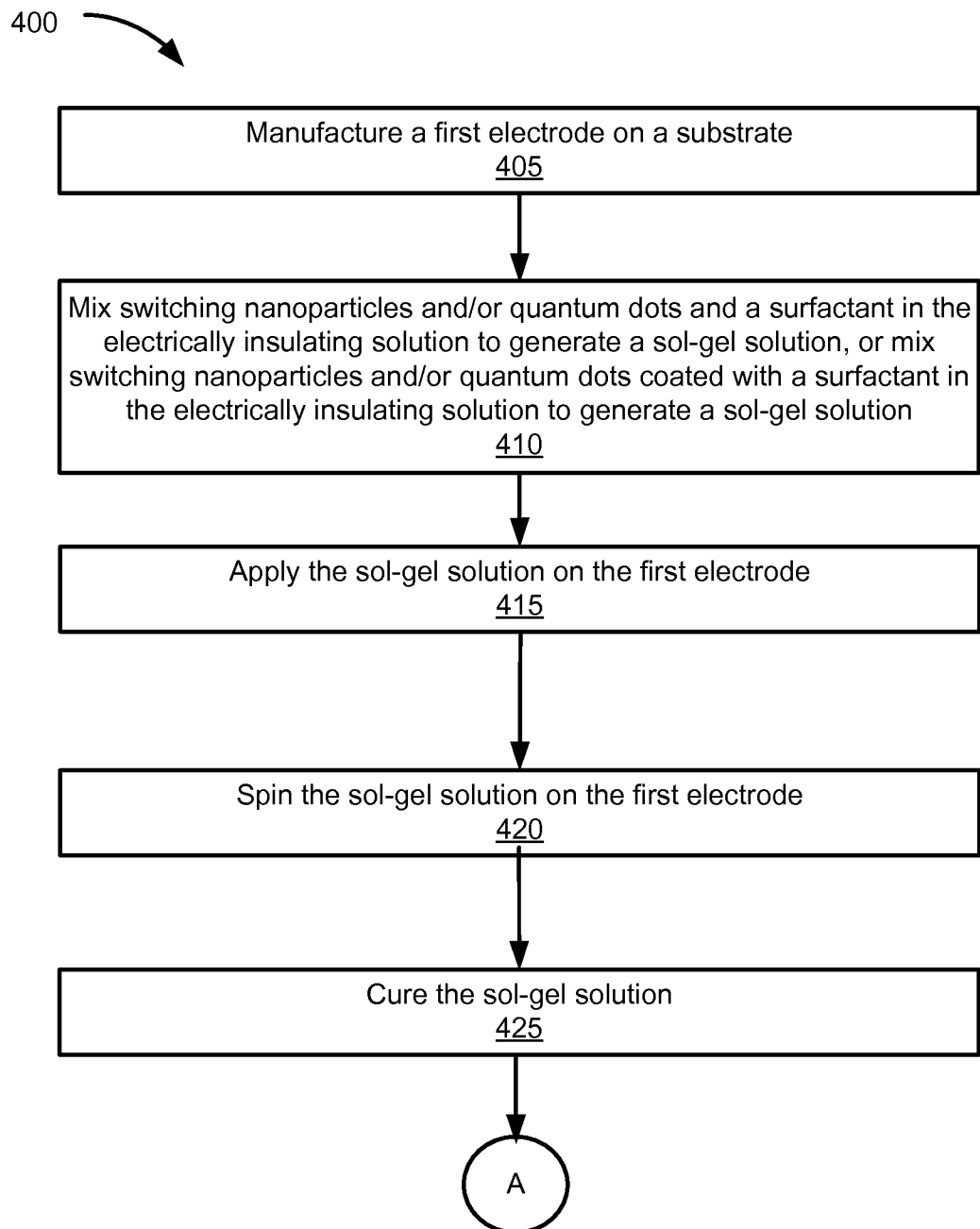


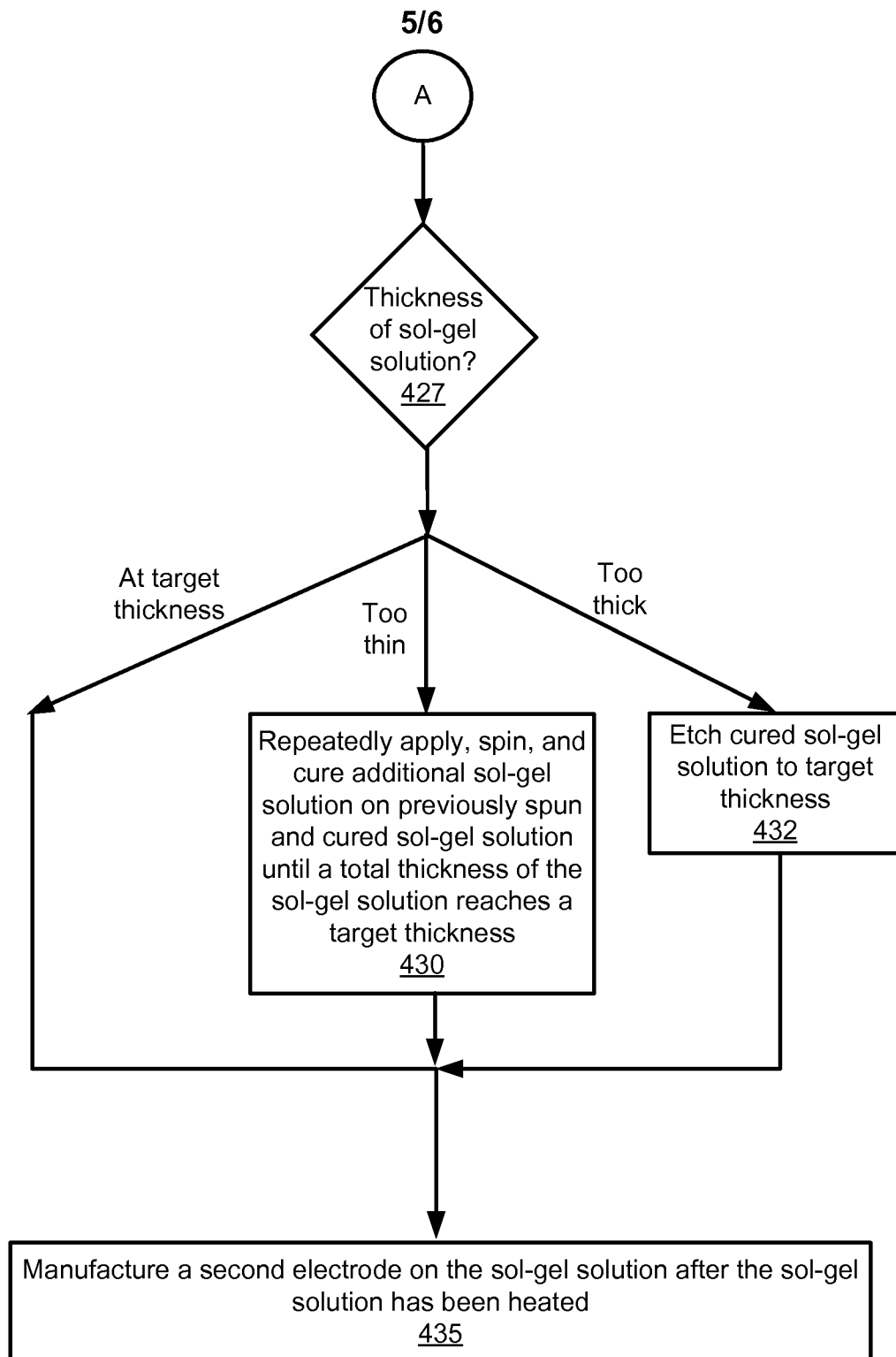
FIG. 2E

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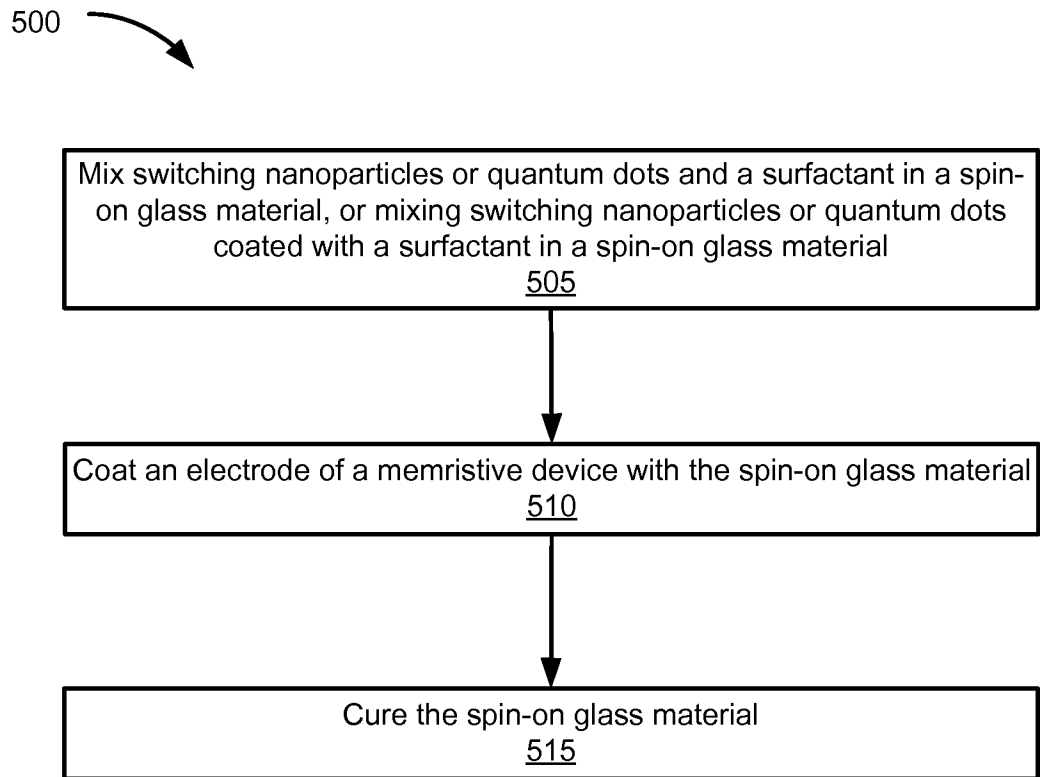
**FIG. 3**

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**FIG. 4A**

**FIG. 4B**

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**FIG. 5**

A. CLASSIFICATION OF SUBJECT MATTER**H01L 45/00(2006.01)i, H01L 27/24(2006.01)i**

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)

H01L 45/00; H01L 21/46; G11C 11/56; C01G 25/00; H01L 21/316; H01B 19/04; H01B 3/44; H01L 27/24

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: memristor, sol-gel, nanoparticle, surfactant, spin

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014-0138601 A1 (VANDERBILT UNIVERSITY) 22 May 2014 See paragraphs [0038]-[0062], claim 16 and figure 4.	1,7
Y		2-6,8-15
Y	US 2011-0176353 A1 (ZHIYONG LI et al.) 21 July 2011 See paragraphs [0018]-[0032], claim 1 and figure 5.	2,3
Y	WO 2013-168159 A1 (RAMOT AT TEL-AVIV UNIVERSITY LTD. et al.) 14 November 2013 See page 7, lines 26-28 and page 20, lines 28-29, claim 11 and figure 1.	4,11,12
Y	US 2014-0295197 A1 (MITSUBISHI MATERIALS CORPORATION) 02 October 2014 See paragraphs [0042]-[0066], claim 1 and figure 4.	5,6,8-10,13-15
A	JP 2014-222685 A (MITSUBISHI MATERIALS CORP.) 27 November 2014 See paragraphs [0015]-[0041], claim 1 and figure 1.	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

14 December 2015 (14.12.2015)

Date of mailing of the international search report

15 December 2015 (15.12.2015)

Name and mailing address of the ISA/KR

International Application Division

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/021686

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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