

(51) International Patent Classification:
H01L 21/02 (2006.01)(21) International Application Number:
PCT/MY2019/050132(22) International Filing Date:
26 December 2019 (26.12.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PI 2018002936 26 December 2018 (26.12.2018) MY(71) Applicant: **MIMOS BERHAD** [MY/MY]; Technology
Park Malaysia, Kuala Lumpur 57000 (MY).(72) Inventors: **LEE, Hing Wah**; c/o Mimos Berhad, Tech-
nology Park Malaysia, Kuala Lumpur 57000 (MY).
LEE, Mai Woon; c/o Mimos Berhad, Technology Park
Malaysia, Kuala Lumpur 57000 (MY). **BIN MOHAM-
MAD HANIFF, Muhammad Aniq Shazni**; c/o Mimos
Berhad, Technology Park Malaysia, Kuala Lumpur 57000
(MY). **BINTI SORIADI, Nurhidaya**; c/o Mimos Berhad,
Technology Park Malaysia, Kuala Lumpur 57000 (MY).
BIN ADOM, Abdul Halim; c/o Mimos Berhad, Technol-
ogy Park Malaysia, Kuala Lumpur 57000 (MY).(74) Agent: **H A RASHID, Ahmad Fadzlee**; Ipvolusi Sdn Bhd,
A-3-3A, Centrio Pantai Hillpark, No. 1, Jalan Pantai Murni,
Kuala Lumpur 59200 (MY).(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, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, 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).

(54) Title: METHOD OF FORMING GRAPHENE BUMP STRUCTURE

200

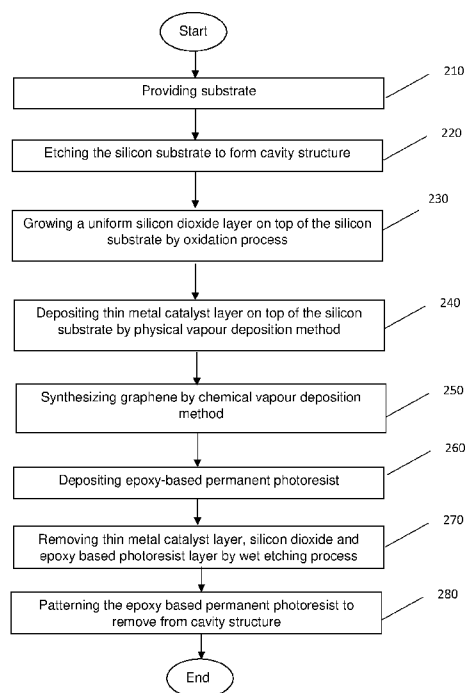


Figure 2

(57) Abstract: The present invention relates to a method (200) of forming graphene bump structure (100) comprising the steps of providing (210) a substrate (10); etching (220) the substrate (10) to form a cavity structure (20); growing (230) a silicon dioxide layer (30) on top of the substrate (10); depositing (240) a thin metal catalyst layer (40) on top of the substrate (30); synthesizing (250) graphene layer (50) on top of the metal catalyst layer (40); depositing (260) an epoxy-based photoresist (60); removing (270) the thin metal catalyst layer (40), the silicon dioxide layer (30) and the epoxy-based photoresist (60) from the substrate (10); and patterning (280) the epoxy-based photoresist (60) to remove from the cavity structure (20) to form the graphene bump structure (100).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

METHOD OF FORMING GRAPHENE BUMP STRUCTURE

FIELD OF THE INVENTION

5

This invention relates to graphene nanostructures. In particular relates to a method of forming graphene bump structure in three dimensional format.

BACKGROUND OF THE INVENTION

10

Graphene is a carbon based material consisting of a single layer of carbon atom arranged in a hexagonal lattice. Graphene draws as an important attention nowadays as a next-generation material for electronic devices due to its high mobility at a room temperature. The graphene also exists as a continuous sheet in nature for applications in electronics, sensor and electronic packaging.

Graphene in three dimensional (3D) structure growing rapidly in electronic industries as it can offer high electrical conductivity and improved structural stability. The three dimensional (3D) graphene-based structures such as 3D graphene-based hydrogels, aerogels, foams, and sponges have attracted huge attention owing to the combination of the structural interconnectivities and the outstanding properties of graphene which offer these interesting structures with low density, high porosity, large surface area, stable mechanical properties, fast mass and electron transport. However, there are several challenges in forming the 3D graphene structure for applications in the electronics parts.

One of the challenge is the graphene itself is unable to be grown directly on patterned polymer substrate due to high temperature growth process. Different structures/ pattern of the graphene also cannot be transferred at exact and precise location on the polymer substrate. Other than that, the current method of forming the graphene electrode on flexible substrate includes printing and roll to roll technology which is not capable to form 3D monolayer graphene structures.

US patent application no. 2012/0248401 A1 relates to a three dimensional graphene structure and method of manufacturing and transferring the same. The method includes forming at least one layer of graphene having a periodically repeated in three-dimensional shape. The three-dimensional graphene structure is formed by forming a pattern having a three dimensional shape on a surface of a substrate. A graphene is grown on the substrate on which the pattern is formed. The 3D structure is then transferred by injecting a gas between the three-dimensional graphene structure and the substrate. The step further separating the three-dimensional graphene structure from the substrate by bonding the three-dimensional graphene structure to an adhesive support, combining the three-dimensional graphene structure with an insulating substrate, and removing the adhesive support.

Another US patent no. 8,66,593 B2 disclose a method for fabricating a three dimensional graphene structure using a catalyst template, in which the three dimensional graphene structure in various forms can be obtained through a simple process by using a metal catalyst in various forms as a template and growing graphene thereon. There also provided a method for controlling length of the three dimensional graphene structure from a few nanometers to a few millimeters by controlling length of the metal catalyst template.

Accordingly, it can be seen in the prior arts that there exists a need to provide a method of forming the graphene bump structure in 3D format for applications in electronics, sensors and electronic packaging.

SUMMARY OF INVENTION

The following presents a simplified summary of the invention in order to provide a basic understanding of some aspects of the invention. This summary is not an extensive overview of the invention. Its sole purpose is to present some concepts of the invention in a simplified form as a prelude to the more detailed description that is presented later.

It is an objective of the present invention to provide a method of forming graphene bump structure in three dimensional monolayer structure.

5 It is also an objective of the present invention to provide a method of forming the graphene bump structure without a need for graphene or metal etching patterning process for applications in electronics preferably for sensors and electronic packaging.

10 Accordingly, the present invention provides a method of forming graphene bump structure is characterized by the steps of providing a substrate; etching the substrate to form a cavity structure; growing a silicon dioxide layer on top of the substrate; depositing a thin metal catalyst layer on top of the silicon substrate; synthesizing graphene layer on top of the metal catalyst layer; depositing an epoxy-based photoresist; and removing the thin metal catalyst layer, the silicon
15 dioxide layer and the epoxy-based photoresist layer from the substrate.

In another aspect of the present invention, the method further comprising a step of patterning the epoxy-based photoresist to remove from the cavity structure.

20 Preferably, the substrate is selected from a group of silicon dioxide.

In another aspect of the present invention, the substrate is etched with a combination of sulphur hexafluoride (SF₆) and octafluorocyclobutane (C₄F₈) plasma.
25

Preferably, the depth of the cavity structure is between 500nm – 1500nm.

In another aspect of the present invention, the silicon dioxide layer is grown by wet or dry oxidation process.
30

In another aspect of the present invention, the thin metal catalyst layer is deposited by physical vapour deposition method.

Preferably, thickness of the metal catalyst layer is not more than half of the depth of the cavity structure.

5 In another aspect of the present invention, the graphene layer is synthesized by chemical vapour deposition method.

In another aspect of the present invention, the thin metal catalyst layer and the silicon dioxide layer are removed from the substrate by wet etching process.

10 The present invention consists of features and a combination of parts hereinafter fully described and illustrated in the accompanying drawings, and it is being understood that various changes in the details may be made without departing from the scope of the invention or scarifying any of the advantages of the present invention.

15

BRIEF DESCRIPTION OF THE DRAWINGS

The features of the invention will be more readily understood and appreciated from the following detailed description when read in conjunction with the accompanying
20 drawings of the preferred embodiment of the present invention, in which:

Figure 1 (a-g) is a cross-sectional view illustrating a method of forming graphene bump structure according to one embodiment of the present invention.

25 Figure 2 is a flow chart showing a method of forming graphene bump structure according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

30 As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore,

specific structural and functional details disclosed herein are not to be interpreted as limiting but merely as a basis for claims.

As used throughout this application, the word "may" is used in a permissive sense (i.e., meaning having the potential to), rather than the mandatory sense (i.e., meaning must). Similarly, the words "include," "including," and "includes" mean including, but not limited to. Further, the words "a" or "an" mean "at least one" and the word "plurality" means one or more, unless otherwise mentioned. Where the abbreviations of technical terms are used, these indicate the commonly accepted meanings as known in the technical field. For ease of reference, common reference numerals will be used throughout the figures when referring to the same or similar features common to the figures.

The present invention relates to a method (200) of forming graphene bump structure (100) in accordance to an embodiment of the present invention. The method of forming the graphene bump structure (100) of the present invention may exempts a need for the graphene or metal etching process through self-assembled of the graphene bump, introducing permanent epoxy based photoresist as a flexible substrate and removing a metal catalyst and dioxide layer.

20

In an embodiment of the present invention, the method (200) of forming the graphene bump structure will now be described with reference to Figure 1 and 2. Referring to Figure 1(a-g), the figures show a cross sectional view of the method (200) of forming the graphene bump structure step by step respectively. Further description on the process of forming the graphene bump structure process will be described further in Figure 2.

25

In Figure 2, the method of forming the graphene bump structure comprising a step of providing (210) a substrate (10) layer. The substrate layer preferably selected from a group of silicon dioxide. The substrate is then etched (220) to form a cavity structure (20) on the substrate (10), whereby the etched is performed by combining the substrate with sulphur hexafluoride (SF₆) and

30

octafluorocyclobutane (C₄F₈) plasma. The depth of the cavity structure (20) is between 500nm – 1500nm as illustrated as in figure 1a.

5 A silicon dioxide layer (30) as illustrated in figure 1b is grown (230) on top of the substrate (10), whereby the silicon dioxide layer is thermally grown by wet or dry oxidation process. The thickness of the dioxide layer is preferably less than 100nm to form a uniform thickness. The process then further continue by depositing (240) a thin metal catalyst layer (40) on top of the silicon dioxide substrate (30) as illustrated as in figure 1c, whereby the metal catalyst layer is
10 deposited onto the substrate by physical vapour deposition method such as radio frequency, RF sputtering method. Material of the metal catalyst layer is preferably but not limited to copper, nickel, platinum, ruthenium and iridium. The thickness of metal catalyst layer is preferably within range of 200nm to 1000nm. The oxidation layer formed earlier in step (240) acts as an isolation layer between the metal
15 catalyst layer and the substrate.

Further to above steps, the substrate then undergoes a chemical vapour deposition process, whereby a graphene (50) is synthesized (250) on top of the metal catalyst layer (40). Illustration of this step shown as in figure 1d. As the metal
20 catalyst layer (40) as somehow been patterned through the silicon structure (30) formation, the synthesized of the graphene (50) will self-assemble to the metal catalyst layer (40), hence forming a graphene bump structure extending outwards of the substrate (10) or inwards to the substrate (10).

25 In order to form a three dimensional (3D) graphene bump structure on a flexible substrate, a thick layer of epoxy-based photoresist (60) will then be deposited (260) onto the graphene layer (50), whereby the epoxy-based photoresist is preferably SU-8 material with thickness range is between 50µm to 100µm. An illustration of this step is shown as in figure 1e.

30

Remaining layer of the thin metal catalyst (40), silicon dioxide (30) and epoxy-based photoresist (60) are then be removed (270) from the substrate by wet etching process. In a further embodiment of the present invention, the method

of forming the graphene bump structure comprises the steps of patterning (280) the epoxy-based photoresist (60) in the cavity structure in order to remove a remaining photoresist from the cavity (20) structure. The aforementioned step illustrated as in figure 1f and 1g.

5

Although the present invention has been described with reference to specific embodiments, also shown in the appended figures, it will be apparent for those skilled in the art that many variations and modifications can be done within the scope of the invention as described in the specification and defined in the following claims.

10

15

20

25

30

CLAIMS

- 1) A method (200) of forming graphene bump structure (100) is characterized by the steps of:
 - 5 providing (210) a substrate (10);
 - etching (220) the substrate (10) to form a cavity structure (20);
 - growing (230) a silicon dioxide layer (30) on top of the substrate (10);
 - depositing (240) a thin metal catalyst layer (40) on top of the silicon substrate (30);
 - 10 synthesizing (250) graphene layer (50) on top of the metal catalyst layer (40);
 - depositing (260) an epoxy-based photoresist (60); and
 - removing (270) the thin metal catalyst layer (40), the silicon dioxide layer (30) and photoresist layer from the substrate (10).
- 15 2) The method according to Claim 1, wherein the method further comprising a step of patterning (280) the epoxy-based photoresist (60) to remove from the cavity (20) structure.
- 20 3) The method according to Claim 1, wherein the substrate is etched with a combination of sulphur hexafluoride, SF₆ and octafluorocyclobutane, C₄F₈ plasma.
- 4) The method according to Claim 1, wherein depth of the cavity structure is
25 between 500nm – 1500nm.
- 5) The method according to Claim 1, wherein the silicon dioxide layer is grown by wet or dry oxidation process.
- 30 6) The method according to Claim 1, wherein the thin metal catalyst layer is deposited by physical vapour deposition method.

- 7) The method according to Claim 1, wherein thickness of the metal catalyst layer is not more than half of the depth of the cavity structure.
- 8) The method according to Claim 1, wherein the graphene layer is synthesized by chemical vapour deposition method.
- 9) The method according to Claim 1, the thin metal catalyst layer (40), the silicon dioxide layer (30) and photoresist layer are removed from the substrate by wet etching process.

10

15

1/4

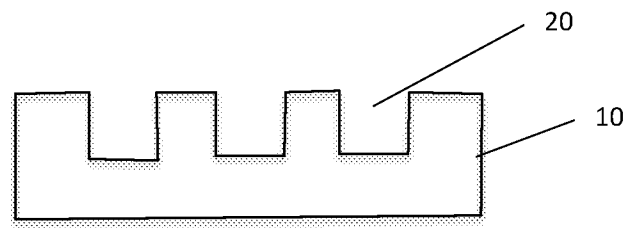


Figure 1a

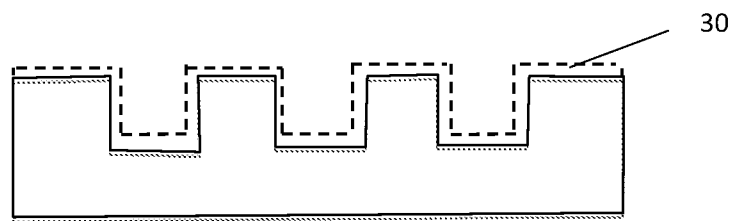


Figure 1b

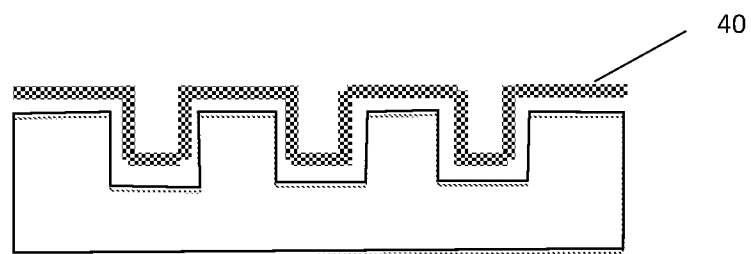


Figure 1c

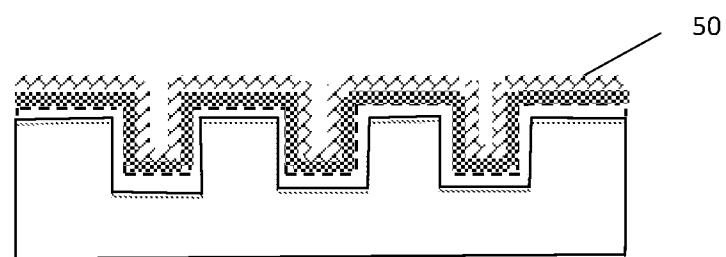


Figure 1d

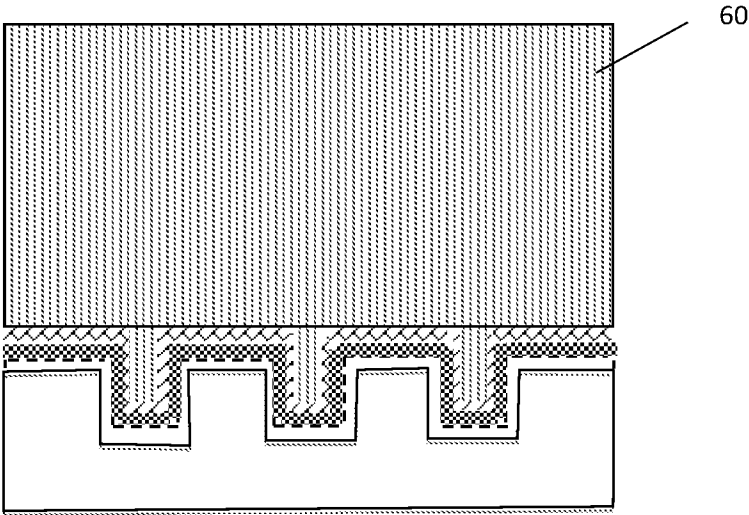


Figure 1e

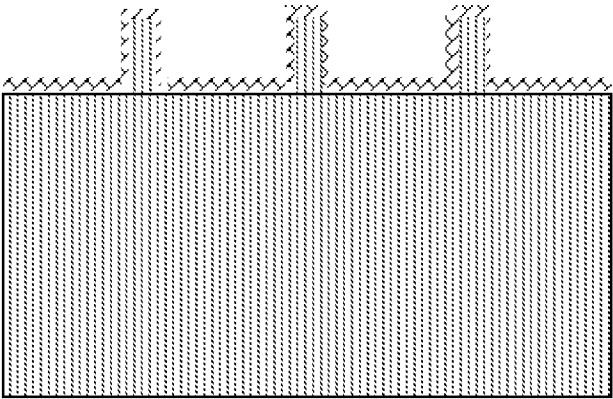


Figure 1f

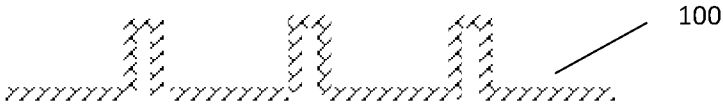


Figure 1g

4/4

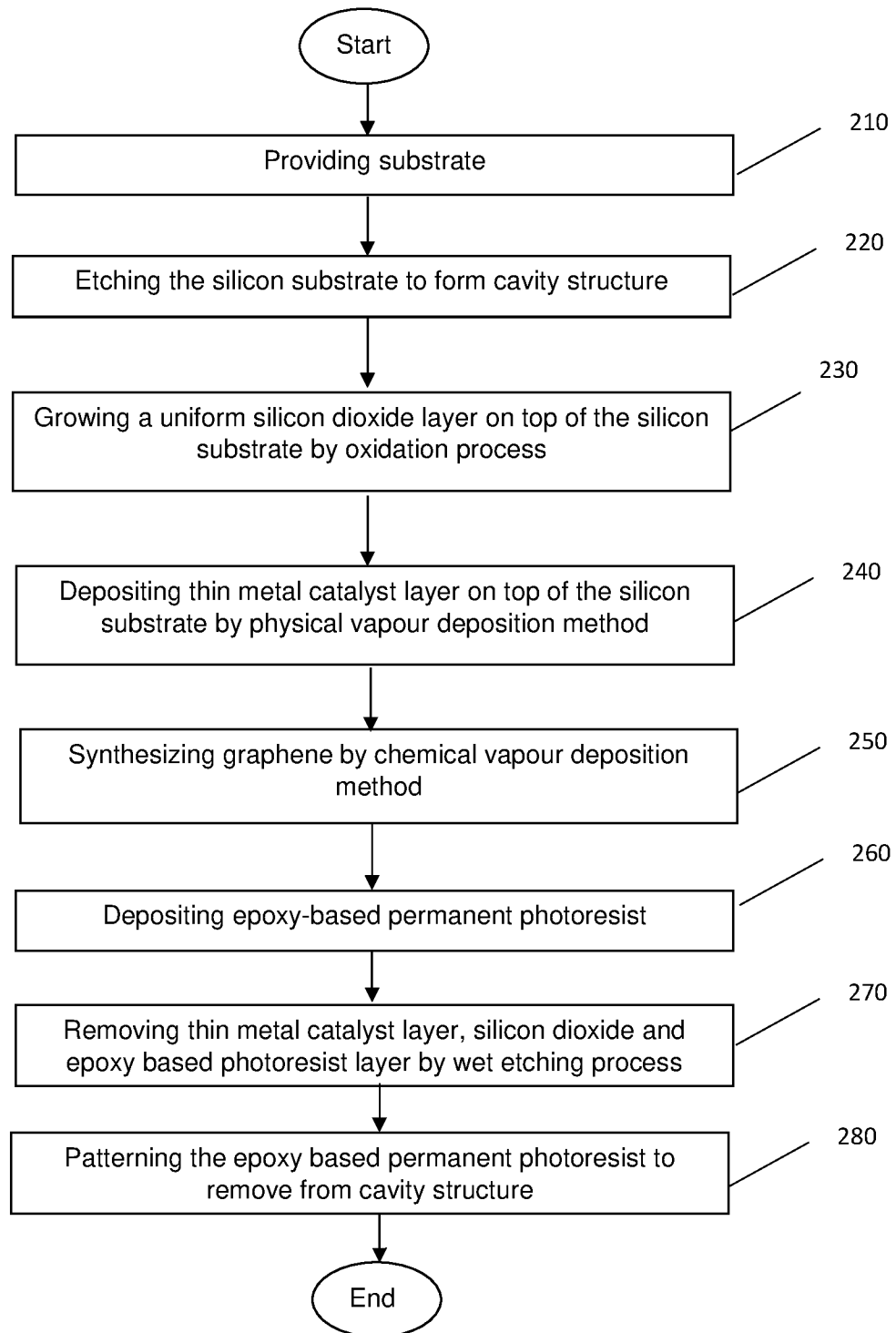
200

Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2019/050132**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/02(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 21/02; B81C 1/00; B82B 3/00; C01B 31/04; C23C 16/02; C23C 16/26; C23C 16/44; C30B 1/02; H01L 29/786; H01L 33/08; H01L 33/18

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: graphene, bump, silicon dioxide, metal catalyst

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2015-0094284 A (KWANGJU INST SCI & TECH) 19 August 2015 claims 1-7 and figure 2	1-9
A	KR 10-2015-0132816 A (KOREA ADVANCED INST SCI & TECH) 26 November 2015 claim 1 and figure 3	1-9
A	KR 10-2011-0018851 A (INDUSTRY-ACADEMIA COOPERATION GROUP OF SEJONG UNIVERSITY) 24 February 2011 claims 1-6 and figures 3, 5	1-9
A	US 2016-0230304 A1 (GRIFFITH UNIVERSITY) 11 August 2016 claims 1-3 and figures 2-3	1-9
A	US 2018-0204976 A1 (CRAYONANO AS et al.) 19 July 2018 claims 1-4 and figures 1a-1b	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

"D" document cited by the applicant in the international application

"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

07 May 2020 (07.05.2020)

Date of mailing of the international search report

07 May 2020 (07.05.2020)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



Facsimile No. +82-42-481-8578

Authorized officer

PARK, Hye Lyun

Telephone No. +82-42-481-3463



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/MY2019/050132

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 10-2015-0094284 A	19/08/2015	KR 10-1564038 B1	29/10/2015
KR 10-2015-0132816 A	26/11/2015	KR 10-1687313 B1	16/12/2016
		KR 10-2014-0121137 A	15/10/2014
		US 2014-0299975 A1	09/10/2014
		US 9129811 B2	08/09/2015
KR 10-2011-0018851 A	24/02/2011	KR 10-1219769 B1	18/01/2013
US 2016-0230304 A1	11/08/2016	CN 105745173 A	06/07/2016
		CN 105745173 B	18/01/2019
		EP 3046872 A1	27/07/2016
		JP 2016-537292 A	01/12/2016
		JP 6680678 B2	15/04/2020
		KR 10-2016-0070073 A	17/06/2016
		US 9771665 B2	26/09/2017
		WO 2015-035465 A1	19/03/2015
US 2018-0204976 A1	19/07/2018	AU 2016-292850 B2	16/05/2019
		BR 112018000612 A2	18/09/2018
		CA 2992156 A1	16/01/2017
		CN 108352424 A	31/07/2018
		EA 201890168 A1	31/08/2018
		EP 3323153 A1	23/05/2018
		JP 2018-523631 A	23/08/2018
		KR 10-2018-0053640 A	23/05/2018
		TW 201717425 A	16/05/2017
		US 10347791 B2	09/07/2019
		WO 2017-009395 A1	19/01/2017