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(54) Title: METHOD FOR FORMING BERNAL-STACKING GRAPHENE LAYERS

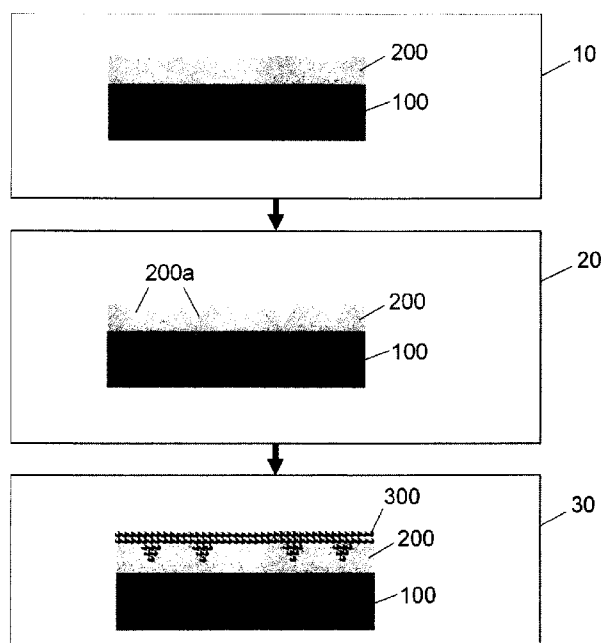


Figure 1

(57) Abstract: A method for forming Bernal-stacked graphene layers (300) through catalytic surface reactions at a low temperature regime is presented. The method comprises the steps of: depositing a metal layer (200) on a substrate (100) (10); direct-annealing the metal layer (200) to form a groove-like structure (200a) (20); characterised by the steps of: forming the graphene layers (300) in Bernal-stacking on the metal layer (200) (30) with gas and benzene precursors at a low temperature regime; and direct-annealing the metal layer (200) (20) at a low temperature regime in an inert or reducing atmosphere.

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))*
- *of inventorship (Rule 4.17(iv))*

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- *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))*

METHOD FOR FORMING BERNAL-STACKING GRAPHENE LAYERS

FIELD OF THE INVENTION

- 5 This invention relates to a method for forming graphene, and more particularly, to a method for forming Bernal-stacking graphene layers through catalytic surface reactions at a low temperature regime.

10 BACKGROUND OF THE INVENTION

- Graphene is made up of clusters of carbon atoms forming crystal lattices that are a single-atom in thickness. Due to its high-speed mobility, graphene is a highly sought-after material used for semiconductor devices. In general, graphene is produced using a metal film catalyst as a base film. Since the
- 15 surface state of the metal film affects the quality of graphene, the metal film is normally heated to remove impurities. In some inventions, the formed graphene film comprises a plurality of layers, such as a bi-layer.

- Controlling the stacking order of few-layer graphene is one way to control its
- 20 properties. Among few-layer graphenes, bi-layer and tri-layer graphene are the most extensively studied materials due to the potential of their tuneable band gap under an applied perpendicular electric field. Generally, graphene layers can be stacked in various ways in a sequence of AA, AA', AB, ABA, ABC, or twist configuration to form bi-layer, tri-layer or multi-layer graphene. Stacking
- 25 of each individual graphene layer modifies the electronic structure and leads to the formation of a material with unique properties.

- Most applications of graphene require a macroscale-sized graphene layer, with one or a few layers of carbon atoms which is then transferred onto a substrate.
- 30 One solution to form such a macroscale-sized graphene layer is to use chemical vapor deposition (CVD). To date, controlled stacking of graphene layers by CVD remains challenging as evidenced by the difficulty in obtaining bi-layer or tri-layer graphene due to the utilization of high pressure and temperature in its growth

processes. In the existing methods, graphene is typically formed under a temperature range of 800 - 1100°C. For certain substrates with low melting points, the existing methods are impractical and could limit the graphene growth process. In view of the above, there is a need for a controllable method to obtain
5 few-layer graphene in a desired stacking order through a low temperature regime.

United States patent application no. US 2013/0001515 A1 relates to a method for forming graphene layers that uses benzene as a carbon precursor and
10 anneals a metal film and a substrate at a temperature as high as 1100°C. Due to the reaction conditions, carbon atoms diffuse through the metal film and an additional step is required to remove the metal film after graphene is formed.

United States patent application no. US 2014/0178688 A1 discloses a controlled
15 method of forming Bernal-stacked graphene layers by cleaning a surface of a catalyst, annealing the surface of the catalyst at a temperature of at least 1000°C, applying a carbon source, and growing the Bernal-stacked graphene layers on the catalyst. At the end, the Bernal-stacked graphene layers are transferred from the surface of the catalyst to a substrate.

20

Accordingly, it can be seen in the prior arts that there exists a need to provide a method for forming graphene layers directly on the catalytic metal film through a reaction condition using low temperature.

25

SUMMARY OF INVENTION

It is an objective of the present invention to provide a method for forming graphene layers directly on a catalytic metal film.

30 It is also an objective of the present invention to provide a method for forming Bernal-stacked graphene by catalytic surface reactions at a low temperature regime.

It is another embodiment of the present invention to provide a method for forming Bernal-stacked graphene by utilising a polycrystalline nickel film and a benzene precursor in optimum reaction conditions.

- 5 It is yet another embodiment of the present invention to provide a Bernal-stacked bi-layer or tri-layer graphene in AB or ABA configuration in a controlled manner.

Accordingly, these objectives may be achieved by the following embodiments of a method for controlling the formation of Bernal-stacked graphene layers by catalytic surface reactions at a low-temperature regime. The method comprises the steps of: depositing a metal layer comprising a polycrystalline nickel film with grain boundary on a substrate; direct-annealing the metal layer at a low temperature of 200 - 700°C in an inert or reducing atmosphere to remove impurities of oxygen and carbon atoms and partly recrystallise metal atoms of the metal layer in the form of groove-like structures; and applying gas and benzene at a ratio of 250 sccm to 3 sccm, at a low temperature of 200 - 700°C, to the metal layer to form the Bernal-stacked graphene layers.

20 **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 drawings of the preferred embodiment of the present invention, in which:

25

Figure 1 is a flowchart with schematic drawings illustrating a method for forming the Bernal-stacking of graphene layers;

Figure 2(a) is an image of transmission emission microscopy (TEM) of a bi-layer graphene suspended on a lacey carbon-coated copper (Cu) grid;

Figure 2(b) is an image of TEM of a tri-layer graphene suspended on a lacey carbon-coated Cu grid;

Figure 3(a) is a high-resolution TEM image of the bi-layer graphene, with an inset of the corresponding Fast Fourier transform (FFT) pattern;

- 5 Figure 3(b) is a high-resolution TEM image of the tri-layer graphene, with an inset of the corresponding FFT pattern;

Figure 3(c) is a selective area electron diffraction (SAED) pattern of the bi-layer graphene;

10

Figure 3(d) is a SAED pattern of the tri-layer graphene;

Figure 3(e) is shows a profile plot of diffraction spot intensities based on the SAED pattern of bi-layer graphene;

15

Figure 3(f) is shows a profile plot of diffraction spot intensities based on the SAED pattern of tri-layer graphene;

Figure 4(a) shows Raman spectra of the bi-layer graphene;

20

Figure 4(b) shows optical transmittance spectra of the bi-layer graphene in visible range;

Figure 4(c) shows Raman spectra of the tri-layer graphene; and

25

Figure 4(d) shows optical transmittance spectra of the tri-layer graphene in visible range.

30 DETAILED DESCRIPTION OF THE INVENTION

The above mentioned and other features and objects of this invention will become more apparent and better understood by reference to the following detailed description. It should be understood that the detailed description made

known below is not intended to be exhaustive or limit the invention to the precise disclosed form as the invention may assume various alternative forms. On the contrary, the detailed description covers all the relevant modifications and alterations made to the present invention, unless the claims expressly state otherwise.

The present invention relates to a method for forming graphene layers (300) in Bernal-stacked form on a catalytic metal layer (200) by applying a carbon precursor at low temperature regime to initiate graphene layer (300) formation.

10

As illustrated in Figure 1, the method comprises the steps of: depositing a metal layer (200) with grain boundary on a surface of a substrate (100) (10); direct-annealing the metal layer (200) to remove impurities of oxygen and carbon atoms and partly recrystallising metal atoms of the metal layer (200) in the form of groove-like structure (200a) (20); characterised by the steps of: forming the graphene layers (300) on the metal layer (200) (30) by catalytic surface reactions with gas and benzene precursors in the ratio of 250 to 3 in standard cubic centimetres per minute (sccm) at a temperature of 200 - 700°C; and direct-annealing the metal layer (200) (20) at a temperature of 200 - 700°C in an inert or reducing atmosphere.

20

Sccm is a flow measurement term that refers to $\text{cm}^3 \text{ min}^{-1}$ in standard conditions for temperature and pressure.

Due to the reaction conditions in the method of the present invention, the graphene layers (300) are directly formed on the metal layer (200) without having to remove the metal layer (200) or transfer the graphene layers (300).

25

In an embodiment of the present invention, the substrate (100) comprises insulating substrate, semiconducting substrate, and conducting substrate.

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In an embodiment of the present invention, the metal layer (200) is deposited on the surface of the substrate (100) (10) via ionised physical vapor deposition at

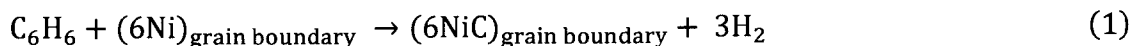
room temperature. The metal layer (200) does not evaporate and is stable for subsequent processes at low temperature.

In another embodiment of the present invention, the metal layer (200) comprises nickel (Ni) film and has a thickness of 50 – 70nm, preferably 60nm. The Ni film is typically in a polycrystalline form with large grain boundaries that works well in low-temperatures for subsequent processes.

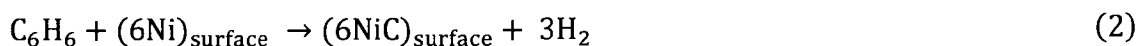
In a further embodiment of the present invention, the reducing atmosphere in the direct-annealing step (20) is made of hydrogen (H₂) or ammonia (NH₃) gas. In an embodiment of the present invention, the direct-annealing step (20) is conducted for one hour. The groove-like structures (200a) of the metal layer (200) traps heat locally to catalyse the adsorption of the carbon atoms and initiates the growth of graphene seeds. The groove-like structures (200a) of the metal layer (200) also suppresses excessive catalytic surface reactions to control the lateral growth of the Bernal-stacked graphene layers (300).

When benzene is applied to the metal layer (200), carbon adatoms from the benzene attaches to the surface of the metal layer (200), enabling the graphene (300) formation to slowly grow into a Bernal-stacked form, depending on the kinetic energy applied during graphene growth. To control the order of graphene (300) stacking at low-temperature, the decomposition of benzene is expected to occur on the surface only without any significant precipitation or diffusion of the carbon adatoms into the metal layer (200). The reaction mechanism for the formation of Bernal-stacked graphene (300) on the metal layer (200) at low temperature via chemical vapor deposition is assumed to be as follows:

Adsorption on grain boundary:



Adsorption on surface:



Surface reaction



In an embodiment of the present invention, the graphene layers (300) are formed
5 at a low pressure of above 66.7 Pa (0.5 Torr) but less than 133.3 Pa (1.0 Torr)
for one hour. The Bernal-stacked graphene layers (300) of the present invention
is in bi-layer of AB-stacked as shown in Figure 2 or tri-layer of ABA-stacked
configuration. The bi-layer or tri-layer graphene (300) in the present invention
provides a tuneable energy band gap which can be used to construct field effect
10 transistors or tunnelling field effect transistors.

In another embodiment of the present invention, argon gas is used in
combination with the benzene precursor to form the graphene layers (300) on
the metal layer (200) (30).

15

To visualise the formation of graphene layers (300) according to the
embodiments of the present invention, the structural analysis of Bernal-stacked
graphene layers (300) grown in low-temperature was performed by transmission
electron microscopy (TEM) as shown in Figure 2(a)-(b) and Figure 3(a)-(b), and
20 selective area electron diffraction (SAED) as shown in Figure 3(c)-(d).

Referring to low-magnification TEM images in Figures 2(a)-(b), there is a large
area of graphene sheets almost equivalent to a few hundred square nanometres
observed on top of the lacey carbon-coated copper (Cu) grid. This area is almost
25 electron transparent and stable under the electron beam at low magnification.
The most transparent regions in Figure 2(a) are likely representing the bi-layer
graphene (300), wherein the visibility of colour contrast of the graphene sheets
indicates the nature of stacking or folding structures with each other. On the
other hand, the darker regions in Figure 2(b) are mostly representing tri-layer
30 graphene (300) with less wrinkles or ripples structures.

The high-resolution TEM image of bi-layer and tri-layer graphene (300) is as
shown in Figures 3(a) and (b) respectively. In these figures, the single-crystalline

nature of the graphitic domains arranged in hexagonal lattices is clearly visible with carbon-carbon lengths estimated at 1.42 Å and lattice-spacings estimated at 2.45 Å. Inset of Figure 3(a) and (b) is the fast Fourier transform (FFT) pattern of the corresponding high-resolution TEM image. Both FFT patterns show one set
5 of six-fold spots corresponding to [001] zone axis, suggesting no possible rational stacking faults in graphene layers (300).

Selective area electron diffraction (SAED) was also performed to confirm the stacking configuration of the bi-layer and tri-layer graphene (300). Both
10 corresponding SAED patterns shown in Figures 3(c) and (d) exhibit a hexagonal pattern. The profile plot of diffraction spot intensities along {1-210} to {-2110} in Figures 3(c)-(d) is as shown in Figures 3(e)-(f). The first-order intensity of {0-110} is likely much weaker than the second-order intensity of {1-210}, reflecting the features of bi-layer or tri-layer graphene (300). Based on the SAED analysis
15 labelled by Bravais-Miller indices, the intensity ratios of I_{0-100}/I_{1-210} and I_{-1010}/I_{-2110} are estimated to be 0.30 for the bi-layer and 0.37 for the tri-layer graphene. This observation suggests that the graphene (300) structure is consistent with a Bernal-stacking order.

20 Raman spectroscopy analysis was also performed to further evaluate the structural properties of the graphene nanosheets. The Raman spectra of the as-grown bi-layer and tri-layer graphene (300) at 400 and 700 °C is shown in Figures 4(a) and (c). For ease of referencing hereon, 'I' refers to intensity while '2D', 'G', and 'D' refer to the peaks in Figures 4(a) and (c). The I_{2D}/I_G peak
25 ratio correlates quantitatively to the number of layers, while the I_D/I_G peak intensity ratio demonstrates the disorder quantification. Here, the formation of graphene layers (300) is confirmed from the calculated I_{2D}/I_G peak ratio, for example, a bi-layer if $1 < I_{2D}/I_G < 2$; a tri-layer or more layers if $I_{2D}/I_G < 1$. For the as-grown bi-layer and tri-layer graphene, the I_{2D}/I_G peak ratio is 1.28 and
30 0.84, respectively. Further, the bi-layer and tri-layer graphene (300) also exhibit lower intensity of D band compared to that of G band, indicating a low degree of defects. The I_D/I_G peak ratio for the bi-layer is about 0.47 while for the tri-layer graphene is about 0.34. The intensity of the D band does not

change much in the spectra for both bi-layer and tri-layer graphene (300). The appearance of D band is possibly due to grain-boundaries or edge defects during the graphene growth process.

- 5 Further evidence of bi-layer and tri-layer graphene (300) can be found from the analysis of optical transmittance spectra as shown in Figures 4(b) and (d). At a wavelength of 550 nm, it was observed that the bi-layer and tri-layer graphene (300) were almost transparent with a light transmittance of about 95.4 % and about 92.8 % respectively.

CLAIMS

- 1) A method for forming Bernal-stacked graphene layers (300) comprising the steps of:
- 5
- a) depositing a metal layer (200) with grain boundary on a substrate (100) (10);
- b) direct-annealing the metal layer (200) to remove impurities and recrystallise the metal layer (200) in the form of groove-like structure (200a) (20);
- 10
- characterised by the steps of:
- c) forming the graphene layers (300) in Bernal-stacking on the metal layer (200) (30) by catalytic surface reactions with gas and benzene precursors in the ratio of 250 to 3 cm³ min⁻¹ at a temperature of 200 - 700°C; and
- 15
- d) direct-annealing the metal layer (200) (20) at a temperature of 200 - 700°C in an inert or reducing atmosphere.
- 20
- 2) The method according to Claim 1, wherein the substrate (100) comprises insulating substrate, semiconducting substrate, and conducting substrate.
- 3) The method according to Claim 1, wherein the metal layer (200) comprises polycrystalline nickel (Ni) film.
- 25
- 4) The method according to Claim 1, wherein the metal layer (200) is deposited on the substrate (100) via ionised physical vapor deposition.
- 5) The method according to Claim 1, wherein the reducing atmosphere is made up of hydrogen (H₂) or ammonia (NH₃) gas.
- 30

- 6) The method according to Claim 1, wherein argon gas is used in combination with the benzene precursor to form the graphene layers (300) on the metal layer (200).
- 5 7) The method according to Claim 1, wherein the graphene layers (300) are formed at a pressure of 66.7 – 133.3 Pa.
- 8) The method according to Claim 1, wherein the Bernal-stacked graphene layers (300) are in a bi-layer or tri-layer of AB or ABA configuration.

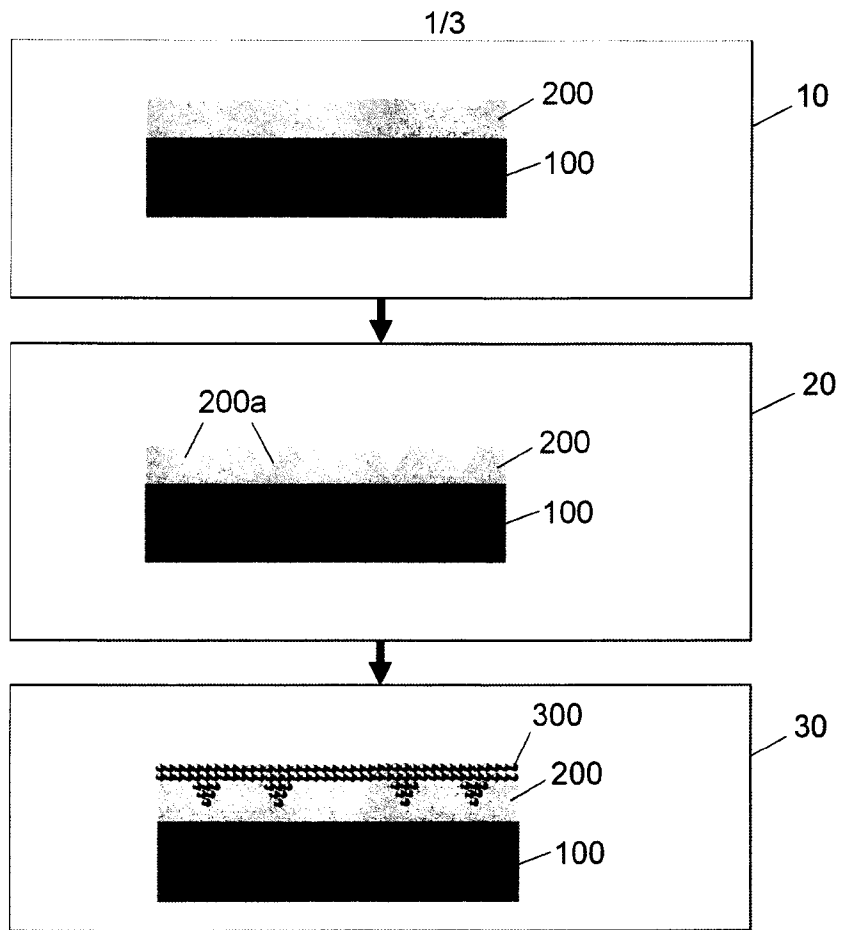


Figure 1

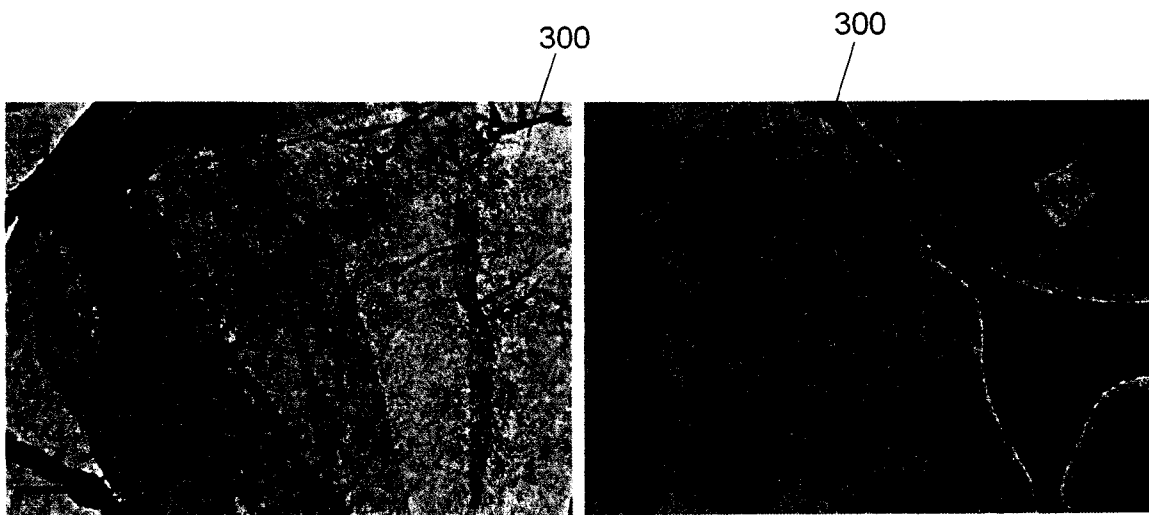


Figure 2(a)

Figure 2(b)

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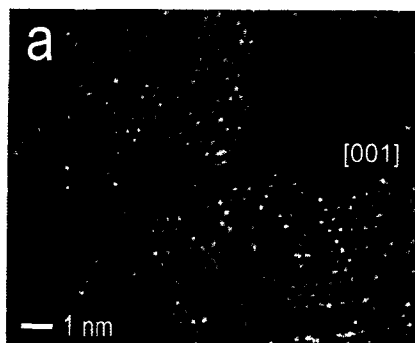


Figure 3(a)

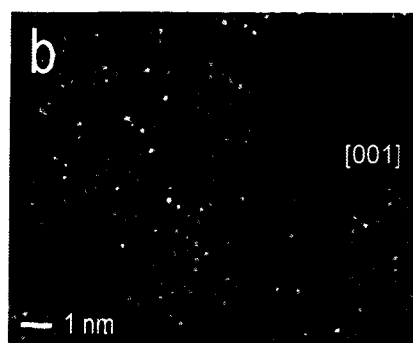


Figure 3(b)

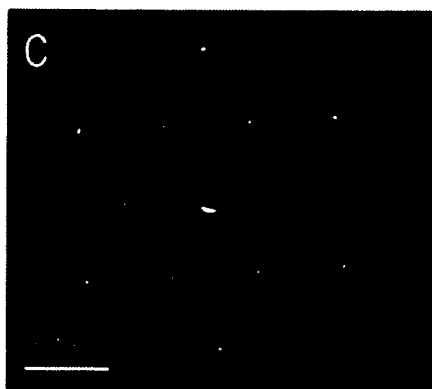


Figure 3(c)



Figure 3(d)

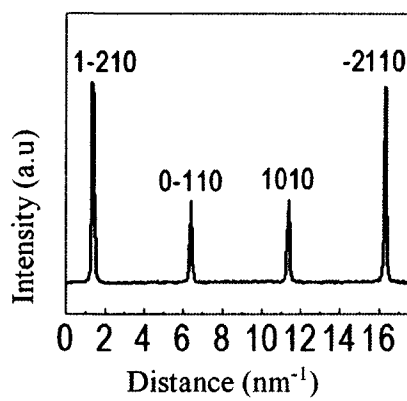


Figure 3(e)

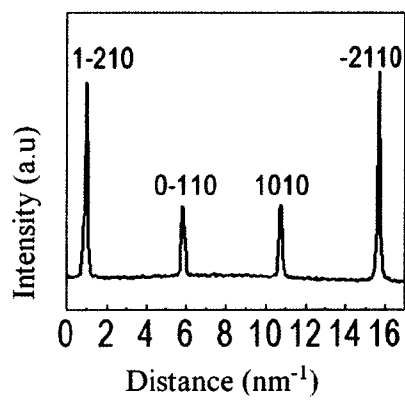


Figure 3(f)

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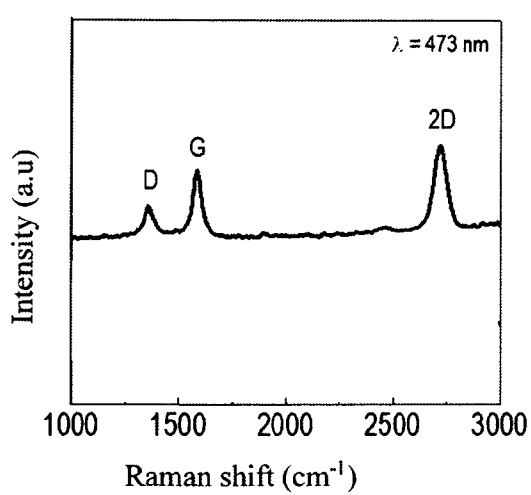


Figure 4(a)

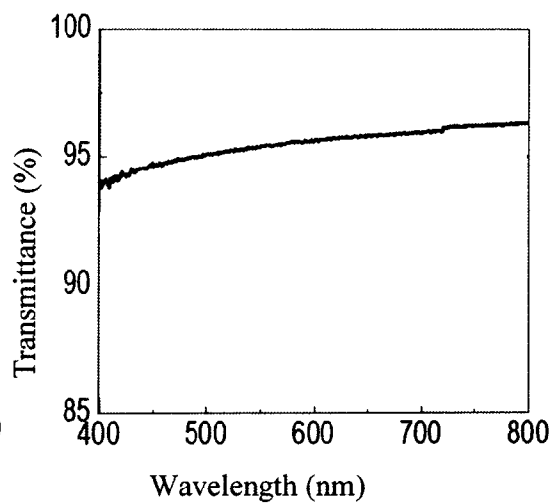


Figure 4(b)

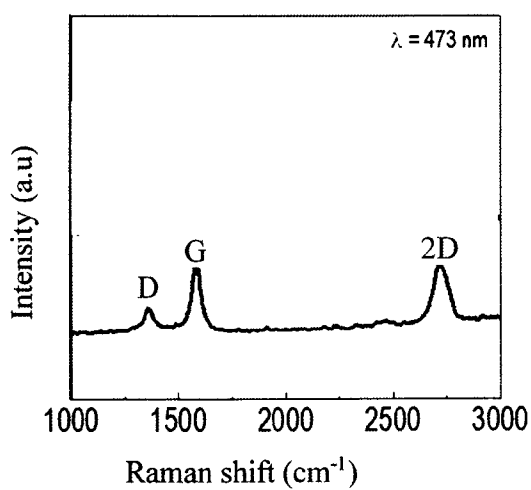


Figure 4(c)

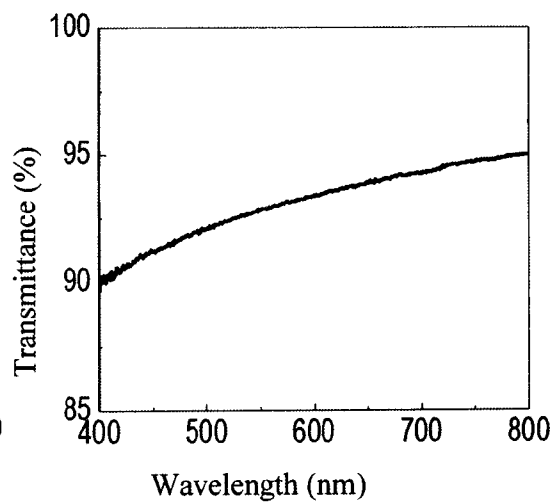


Figure 4(d)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2019/000044**A. CLASSIFICATION OF SUBJECT MATTER****C01B 32/186(2017.01)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)

C01B 32/186; B32B 9/00; B44C 1/22; C01B 31/02; C01B 31/04; C23C 16/18; C23C 16/26; C23C 16/44; H01B 1/04; H01L 29/775

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, grain boundary, metal layer, annealing, low temperature, benzene, bi-layer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2016-0018257 A (UNIST ULSAN NAT. INST. SCIENCE & TECHNOLOGY) 17 February 2016 claims 8, 16; paragraphs [0073], [0081], [0082], [0110], [0129]	1-8
Y	US 2013-0001515 A1 (LI, L.-J. et al.) 03 January 2013 claims 1, 5, 9, 22; paragraphs [0040], [0052]	1-8
A	US 2010-0021708 A1 (KONG, J. et al.) 28 January 2010 the whole document	1-8
A	WO 2011-111932 A2 (UNIST ACADEMY-INDUSTRY RESEARCH CORPORATION) 15 September 2011 the whole document	1-8
A	US 9702039 B2 (TOKYO ELECTRON LIMITED) 11 July 2017 the whole document	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of mailing of the international search report

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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



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/MY2019/000044

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