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(54) Title: METHOD FOR OBTAINING STABLE N-TYPE DOPED GRAPHENE

(57) Abstract: The invention concerns a method for producing N-type doped graphene, comprising the provision of an initial graphene layer which can be a CVD-graphene grown on a Cu foil, the annealing in a forming gas at a temperature between 300°C to 400°C for a time period between 2h to 4h of a graphene-based material issued from the initial graphene layer, and the N-doping of the annealed graphene-based material for obtaining the N-type doped graphene. The invention also concerns the N-type doped graphene obtained by the above method, that is a N-type doped graphene characterized by a Raman spectrum having a 2D peak at a wavelength between 2665 to 2675 cm⁻¹ and a G peak at a wavelength between 1565 to 1575 cm⁻¹. Thanks to the annealing, the N-doping is particularly efficient and stable.



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Method for obtaining stable N-type doped graphene

FIELD OF THE INVENTION

5 The invention deals with a method for obtaining N-type doped graphene, preferably N-type doped CVD-graphene, which can be used, for example, in the manufacturing of graphene-based cathodes.

 It is recalled that graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice, in which one atom forms each
10 vertex. The attractive properties of graphene, such as near-zero band-gap, high electrical conductivity, high mobility, flexibility, and high transparency have stimulated a lot of research interest. A transparent electrode is one of the promising applications for graphene.

 It is also recalled that doping a semi-conductor consists in modifying
15 the equilibrium between electrons and holes in the semi-conductor either by implementing electron acceptor impurities (P-type doping) which creates states near the valence band and increase the rate of holes in the semi-conductor, or by implementing electron donor impurities (N-type doping) which creates states near the conduction band and increase the rate of electrons in the semi-
20 conductor.

 In all the description, the expression "N-type graphene" is equivalent to "N-type doped graphene" or "N-doped graphene".

BACKGROUND OF THE INVENTION

 So far, a stable and efficient P-type graphene has been efficiently
25 achieved. In contrast, the task of achieving a stable and efficient N-type graphene is difficult to accomplish. To achieve N-type graphene, doping processes such as immersing graphene samples in ammonia, introducing nitrogen sources through a chemical vapor deposition and coating layers on graphene were applied, where electron donation to graphene by dopant materials during these processes
30 results in N-doping in the graphene.

 However, Raman results showed there was very small shifts (offsets in terms of wavelength) of the G and 2D peak in the spectrum of graphene

samples after doping. Additionally, the intensity of the D peak in the Raman spectrum of doped graphene increased, which indicates too a defect in the graphene lattice. Besides, the stability of manufactured devices made of doped graphene was no more than a few days when exposed to air.

5 N-doping by deposition of terbium atoms by electron-beam evaporation in ultrahigh vacuum was also proposed. But, here again, defects in the doped graphene layer were noted. Besides, the obtained N-doped graphene appeared to be unstable in time as the Tb layer oxidizes even in ultrahigh vacuum. An annealing at 800°C or more after deposition of the Tb atoms on the
10 graphene layer is then needed to expect that the Tb atoms are intercalated below the graphene layer and thus protected against oxidation.

Consequently, a need exists to provide a straightforward method for producing N-type graphene resulting in a stable and efficient material.

SUMMARY OF THE INVENTION

15 In that context, the invention proposes a method for producing N-type graphene, comprising the following stages:

- provision of a graphene to be doped from an initial graphene layer,
- N-doping the graphene to be doped for obtaining the N-type graphene.

20 This method is characterized in that

- the provision of the graphene to be doped includes an annealing step, where a graphene-based material issued from the initial graphene layer is annealed, whereby the graphene to be doped is an annealed graphene-based material,
- in the annealing step, the graphene based material is annealed in a forming gas
25 at a temperature between 300°C to 400°C for a time period between 2h to 4 h.

In other words, the invention proposes a method for producing N-type graphene comprising the following steps: provision of a graphene-based material, annealing of the graphene-based material at 300-400°C during 2-4h, and N-doping of the annealed graphene-based material.

30 According to a possible feature of the invention, the initial graphene layer and the graphene-based material are monolayer graphenes.

Advantageously, the provision of the graphene to be doped in the method according to the invention includes a transferring step prior to the annealing step, where the initial graphene layer or a pretreated graphene layer derived from the initial graphene layer is transferred onto a SiO₂/Si substrate to form the graphene-based material which is next submitted to the annealing step; so the graphene-based material (to be annealed then doped) is a graphene wafer.

In a preferred embodiment of the invention, in the annealing step, the graphene-based material is annealed in a forming gas for 3 hours at 350°C.

According to a possible feature of the invention, the forming gas includes Ar (Argon) and H₂ (dihydrogen) in a rate Ar:H₂ between 85:15 to 95:05, preferably 90:10.

In a preferred embodiment of the invention, the N-doping step involves ammonia adsorption. In this case, the annealing appears to be particularly advantageous because it greatly enhances the ammonia adsorption in the graphene layer.

According to a possible feature of the invention, in the N-doping step, the annealed graphene-based material (that is the graphene to be doped) is immersed in an ammonium hydroxide solution which includes NH₃ molecules. The ammonium hydroxide solution advantageously includes an ACS NH₃-based reagent in a rate between 20% to 40%, preferably 28-30%. It is recalled that an ACS reagent is a reagent which meets the grade (that is to say the limits of purity) for inorganic chemicals as established by the American Chemical Society. In a preferred embodiment, the immersion of the annealed graphene-based material lasts for a time period of more than 4 hours; preferably the time period of immersion is 5h.

According to a possible feature of the invention, after the N-doping step, the N-type graphene is dried with nitrogen.

According to a possible feature of the invention, the initial graphene layer is combined with a polymethyl methacrylate (PMMA) dissolved in chlorobenzene with a concentration between 10 to 50mg/mL to form the pretreated graphene layer (which is so a PMMA/graphene layer).

It might be noted that it is known to carry out an annealing at about 160°C for about 5 min before transferring a PMMA/graphene onto a silicon substrate in order to relax the PMMA film. This has nothing to do with the annealing step according to the invention which is carried out after the
5 transferring of the graphene or PMMA/graphene onto a silicon substrate and whose main effect is to enhance the adsorption of ammonia in the subsequent N-doping step.

The initial graphene layer can be a CVD-graphene monolayer grown on a Cu (copper) foil. Other sources or processes for providing graphene
10 monolayers can be used such as a graphene ink, reduced Graphene Oxide, etc. But the Chemical Vapor Deposition process is preferred because it easily leads to a single layer moreover having a higher quality.

The invention extends to the N-type graphene obtained by a method according to the invention.

15 The inventors have demonstrated that such an N-type graphene can be characterized by its Raman spectrum, which has a 2D peak at a wavelength between 2665 to 2675 cm^{-1} , that is a lower wavelength than the known N-type graphenes and lower than N-doped graphenes which are not previously annealed, and a G peak at a wavelength between 1565 to 1575 cm^{-1} (again such
20 a wavelength value for the G peak is lower than the known N-type graphenes and lower than a non-annealed N-type graphene).

The invention also concerns an electrode characterized in that it comprises an N-type graphene according to the invention.

Such an electrode is advantageously used in various applications of
25 solar cells, OLED (Organic Light Emitting Diodes), lithium batteries and transistors.

BRIEF DESCRIPTION OF THE DRAWINGS

Additional features and advantages of the present invention are described in, and will be apparent from, the description of the presently preferred
30 embodiments which are set out below with reference to the drawings in which:

Fig. 1 shows the Raman shift spectra of an annealed graphene wafer before and after doping for 5h.

Fig. 2 and Fig. 3 show the Raman shift spectra of various N-type doped graphene, two of which being N-type graphene according to the invention.

Fig. 4 shows the Raman shift spectra of an N-type graphene according to the invention before and after storage for ten weeks.

5 Fig. 5 shows current-voltage (I_D - V_G) transfer curves of gFETs (Field Effect Transistors) formed with various graphene, one of which being an N-type graphene according to the invention.

Fig. 6 shows current-voltage (I_D - V_G) transfer curves of a gFETs formed with an N-type graphene according to the invention before and after storage for
10 ten weeks.

DETAILED DESCRIPTION OF THE INVENTION

For comparison purposes, four N-type graphene samples are prepared.

The first sample is an N-type graphene according to the invention. It is
15 produced by:

A/ providing a monolayer CVD-graphene grown on a Cu foil, here after referred to as a graphene/Cu layer,

B/ combining the graphene/Cu layer with a PMMA dissolved in chlorobenzene with a concentration of 46 mg/mL,

20 C/ wet-transferring the PMMA/graphene/Cu layer onto a SiO_2/Si substrate using a conventional wet-transfer process, whereby obtaining a graphene wafer,

D/ annealing the graphene wafer at a 350°C for 3h, in a forming gas composed of Argon and Dihydrogen in a rate Ar: H_2 of 90:10, whereby obtaining
25 an annealed graphene wafer,

E/ N-doping the annealed graphene wafer by immersion for 5h in an ammonium hydroxide solution that includes at least one ACS NH_3 -based reagent in a rate of 28-30%, whereby obtaining a N-type graphene according to the invention.

30 This sample #1 is here after referred to as an N-doped annealed graphene wafer.

The second N-type graphene sample is also a N-type graphene according to the invention produced by directly annealing the graphene/Cu, and next by N-doping the annealed graphene/Cu layer using the same step E described above. In other words, the above-described steps B and C are omitted.

5 This sample #2 is here after referred to as an N-doped annealed graphene/Cu.

The third and fourth N-type graphene samples are not N-type graphene according to the invention. Nevertheless, they are N-doped using the same step E/ above-described.

10 Sample #3 is an N-doped graphene wafer (or N-doped transferred but non annealed graphene) obtained by N-doping the graphene wafer obtained at the end of step C/; in other words, the transferring step (step C/) is carried out but the annealing step (step D/) is omitted.

15 Sample #4 is a N-doped graphene/Cu obtained by directly N-doping graphene/Cu layer; in other words, the above-described steps B, C and D are omitted.

These samples are summed up in the following table:

		transferring	annealing	N-doping
1	N-doped annealed graphene wafer	X	X	X
2	N-doped annealed graphene/Cu		X	X
3	N-doped graphene wafer	X		X
4	N-doped graphene/Cu			X

20 Figure 1 represents the Raman Spectrum of the sample #1 after doping (N-doped annealed graphene wafer, bottom curve in dotted line) and the Raman Spectrum of this sample before doping (annealed graphene wafer, top curve in continuous line). Thus, Figure 1 shows the effect of the doping on the Raman Spectra. The effect of the doping is a significant shift of the 2D peak that is to say an offset of the 2D peak toward a lower wavelength. It is known that this
25 shift confirms the doping.

Figure 2 represents the Raman spectrum of an N-doped annealed graphene/Cu (sample #2, top curve in dotted line) and the Raman spectrum of

the N-doped graphene/Cu (sample #3, bottom curve in continuous line) thereby showing the effect of the annealing alone (without previous transferring) on the Raman spectrum. The effect of the annealing is a further shift (offset toward a lower wavelength) of the 2D peak that shows that the doping is rendered efficient and even enhanced by the annealing.

Figure 3 represents the Raman spectra of the following samples: an N-doped graphene/Cu (sample #4, bottom curve in dashed line), an N-doped graphene wafer (sample #3, medium curve in continuous line) and a N-doped annealed graphene wafer (sample #1, top curve in dotted line). The Raman spectrum of the N-doped annealed graphene/Cu (sample #2) is not reported on figure 3 but can be observed on figure 2.

The following wavelength values for the G peak and the 2D peak are obtained:

Samples		G peak (cm^{-1})	2D peak (cm^{-1})
1	N-doped annealed graphene wafer	1571	2669
2	N-type annealed graphene/Cu	1575	2671
3	N-doped graphene wafer	1585	2683
4	N doped graphene/Cu	1583	2685

For sake of analysis, sample #4 can be considered as the reference sample since the graphene layer is neither transferred nor annealed.

It can be noticed that when the transferring step is carried out but not the annealing one (sample #4 compared with sample #3), a very slight shift (offset toward a lower wavelength) in the 2D peaks occurs, this shift being too slight to be significant. Besides, the G peak is very slightly offset toward a higher wavelength. Again, this offset is too slight to be significant and moreover it is not desirable because it shows that the N-doping in graphene is too weak.

When the annealing step is carried out, in combination with the transferring step (sample #1) or without previously transferring the graphene/Cu onto a SiO_2/Si substrate (sample #2), a significant shift (offset toward a lower wavelength) occurs in the 2D peak. This shift confirms the N-doping in the graphene. Besides, the G peak of the two annealed samples according to the

invention (samples #1 and #2) is unchanged or even decreased (that is to say offset toward a lower wavelength) compared with the non-annealed samples (#3 and #4). This also confirms the essential role played by the annealing in the improvement of the adsorption of NH₃ on graphene. The decrease in the G peak is slightly more significant for sample #1 than for sample #2, that is to say when the transferring is carried out in addition to the annealing.

The electronic band structures of the tested samples are also reported on figure 3, showing that the conduction band of the N-doped annealed graphene wafer (sample #1) is more fulfilled than the ones of the N-doped (non-annealed) graphene wafer (sample #3) and of the N-doped (non-annealed) graphene/Cu (sample #4), which are similar. This is another way to illustrate that the doping with the method according to the invention is more efficient.

Another important advantage of the method according to the invention is that the obtained N-type graphene is unexpectedly stable, as evidenced by Figure 4. Figure 4 represents the Raman spectrum of the N-doped annealed graphene wafer (sample #1) before storage (in continuous line) and after storage for ten weeks (in dotted line), thereby showing the stability of the N-type graphene according to the invention. It can be observed that the two curves are almost superimposed on the entire spectrum of wavelengths. In particular, the two peaks (G and 2D) occur at the same wavelengths before and after storage and there is no significant loss of intensity on the entire wavelengths range. Similar curves are obtained with the N-doped annealed graphene/Cu (sample #2), illustrating no significant differences before and after storage for ten weeks that confirm the amazing stability of the product.

Fig. 5 shows current-voltage (I_D - V_G) transfer curves of gFETs (Field Effect Transistors), as follows: the curve in continuous line corresponds to a gFET made with a non-doped annealed graphene, namely the annealed graphene wafer obtained at the end of step D/ above described; the curve in dashed line corresponds to a gFET made with a non-annealed and non-doped graphene, namely the graphene wafer obtained at the end of step C/ above described; the curve in dash-dotted line corresponds to a gFET made with a N-doped (non-annealed) graphene wafer (that is to say sample #3); the curve in dotted line

corresponds to a gFET made with a N-doped annealed graphene wafer (sample #1). Measurements of gFETs are achieved at room temperature and $V_D = 10\text{mV}$. It can be observed that, in response to a positive voltage applied at its gate, only the gFET made with the N-doped annealed graphene wafer according to the invention can deliver a useful current that moreover increases with the applied gate voltage. Besides, there is more shift in a Dirac point towards zero voltage for annealed graphene samples than that for transferred graphene samples without annealing. This additional proves that the annealing process before immersing samples in ammonia solution is the key to achieve the efficient N-doping process.

Besides, Figure 6 also illustrates the stability of gFETs made with a N-doped annealed graphene, in that case a N-doped annealed graphene wafer according to sample #1. There is a small shift in Dirac point after storage, which is due to the air. But the two ($I_D - V_G$) curves before storage (in continuous line) and after storage for ten weeks (in dotted line) do not diverge, showing that the electric specifications and ability of the gFET have not deteriorated. Similar curves are obtained with a gFET made with an N-doped annealed graphene /Cu according to sample #2.

The invention extends to all the alternative embodiments that are covered by the appended claims. For example, the step/B above described can be omitted, whereby the graphene-based material to be annealed then to be doped is a graphene wafer obtain by transferring a CVD-graphene/Cu layer onto a SiO_2/Si substrate without the use of PMMA. Likewise, the transferring itself is optional and can then be omitted. As another example, the initial graphene layer is not limited to a layer obtained by chemical vapor deposition.

CLAIMS

1. Method for producing N-type graphene comprising the following stages:

- 5 - provision of a graphene to be doped from an initial graphene layer,
 - N-doping the graphene to be doped for obtaining the N-type graphene,

characterized in that:

- the provision of the graphene to be doped includes an annealing step where a
10 graphene-based material issued from the initial graphene layer is annealed,
whereby the graphene to be doped is an annealed graphene-based material,
- in the annealing step, the graphene-based material is annealed in a forming gas
at a temperature between 300°C to 400°C for a time period between 2h to 4 h.

2. Method according to claim 1, wherein the provision of the
15 graphene to be doped further includes a transferring step prior to the annealing
step, where the initial graphene layer or a pretreated graphene layer derived from
the initial graphene layer is transferred onto a SiO₂/Si substrate to form the
graphene-based material which is next submitted to the annealing step.

3. Method according to claim 1 or 2, wherein the forming gas
20 includes Ar (Argon) and H₂ (dihydrogen) in a rate Ar/H₂ comprised between 85:15
to 95:05.

4. Method according to any one of claims 1 to 3, wherein in the
N-doping step, the annealed graphene-based material is immersed in an
ammonium hydroxide solution which includes NH₃ molecules.

5. Method according to claim 4, wherein the ammonium hydroxide
25 solution includes an ACS NH₃-based reagent in a rate between 20% to 40%.

6. Method according to any one of claims 3 to 5, characterized in
that the immersion of the annealed graphene-based material lasts for a period of
more than 4 hours.

7. Method according to any one of the claims 1 to 6, wherein the
30 N-type graphene obtained at the end of the N-doping step is next dried with
nitrogen.

8. Method according to any one of claims 1 to 7, wherein the initial graphene layer is pretreated by combining the initial graphene layer with a polymethyl methacrylate (PMMA) dissolved in chlorobenzene with a concentration between 10 to 50mg/mL.

5 9. Method according to any one of claim 1 to 8, wherein the initial graphene layer is a CVD-graphene monolayer grown on a Cu foil.

10 10. N-type graphene characterized by a Raman spectrum having a 2D peak at a wavelength between 2665 to 2675 cm^{-1} and a G peak at a wavelength between 1565 to 1575 cm^{-1} .

10 11. Electrode characterized in that it comprises an N-type graphene produced by a method according to any one of claims 1 to 9 or an N-type graphene according to claim 10.

15 12. Organic Light Emitting diodes (OLED) characterized in that it comprises an N-type graphene produced by a method according to one of claims 1 to 9 or an N-type graphene according to claim 10.

15 13. Lithium battery characterized in that it comprises a N-type graphene produced by a method according to one of claims 1 to 9 or an N-type graphene according to claim 10.

20 14. Transistor characterized in that it comprises an N-type graphene produced by a method according to one of claims 1 to 9 or an N-type graphene according to claim 10.

25 15. Solar cell characterized in that it comprises a N-type graphene produced by a method according to one of claims 1 to 9 or an N-type graphene according to claim 10.

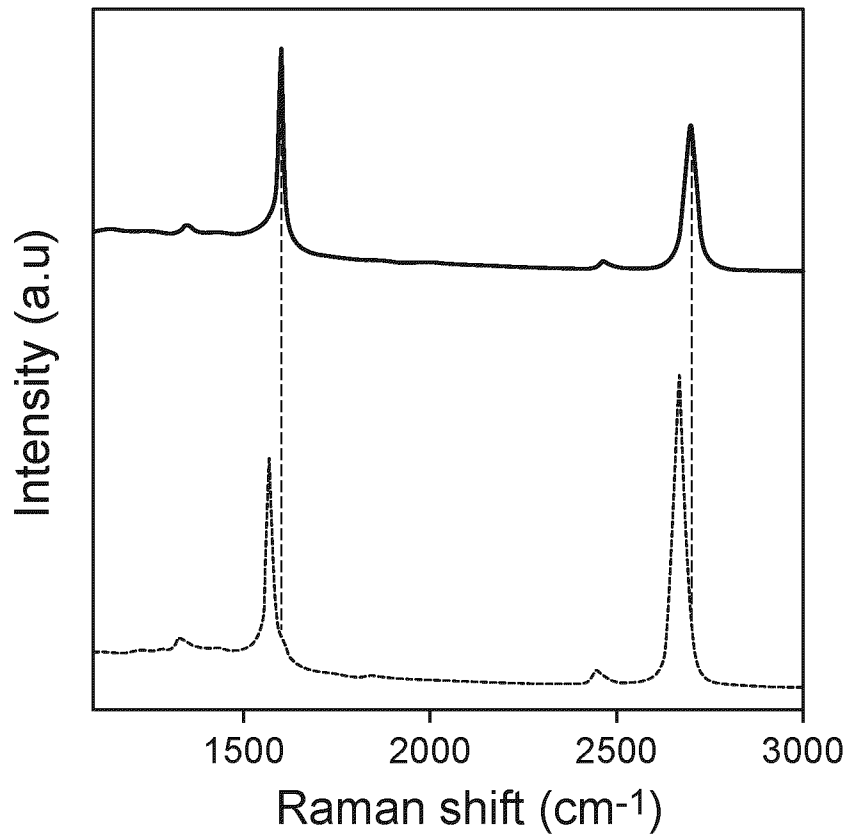


Fig.1

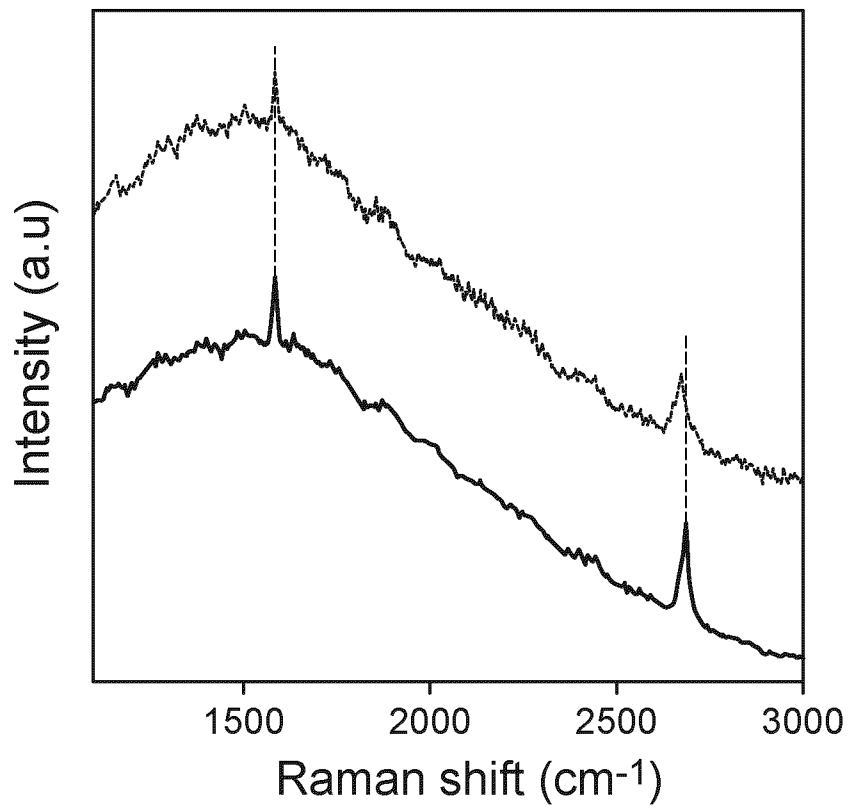


Fig.2

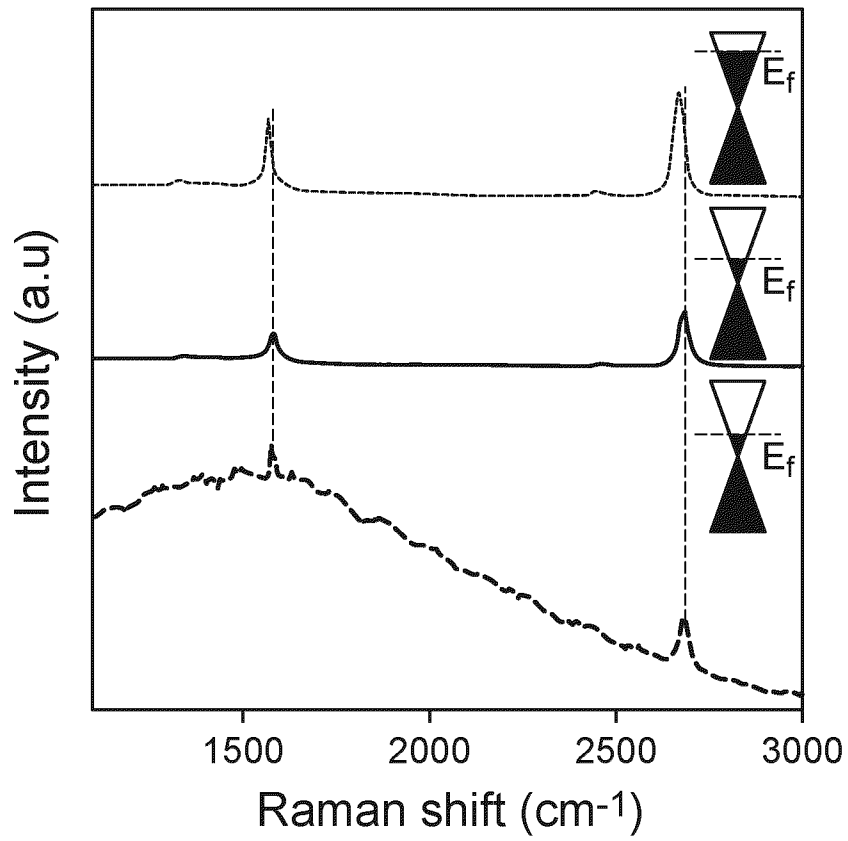


Fig.3

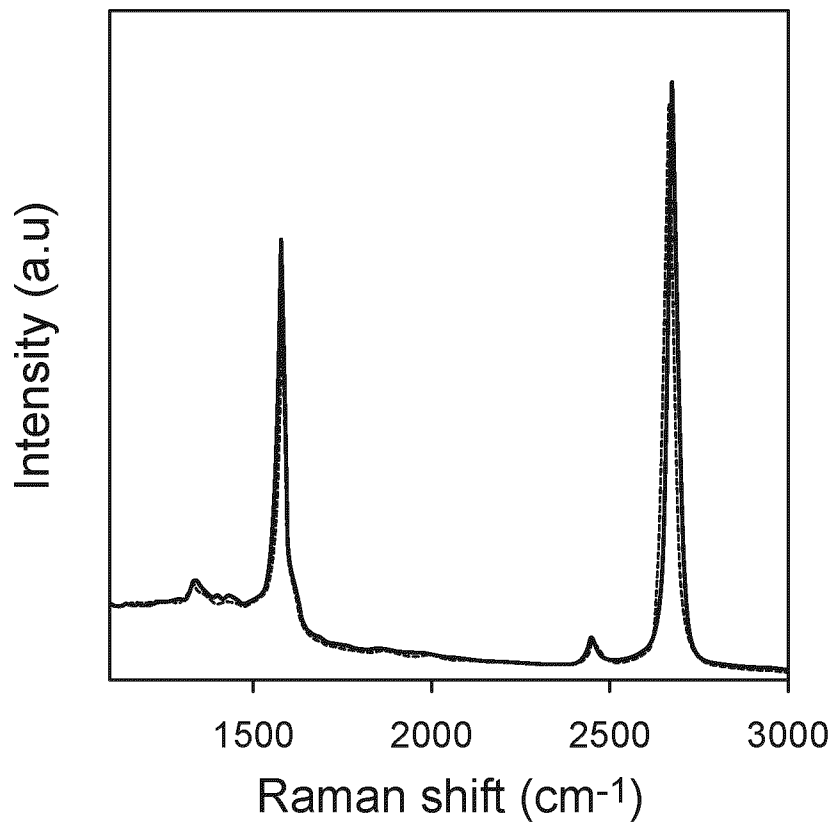


Fig.4

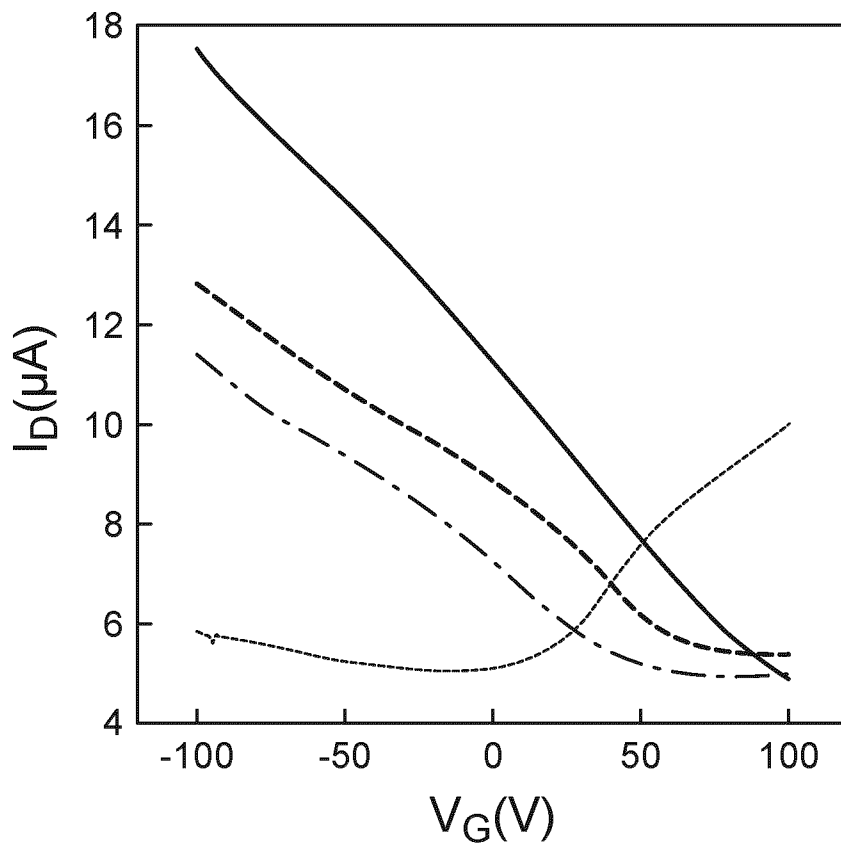


Fig.5

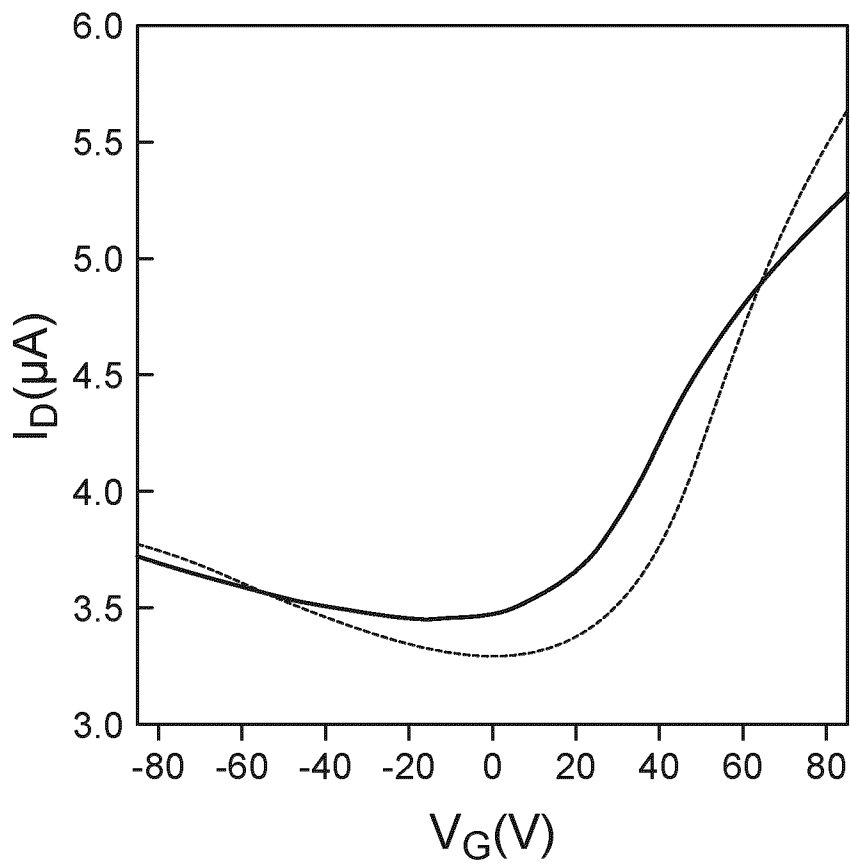


Fig.6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/068655

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B32/186 C01B32/194
ADD.
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
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 102 953 118 A (UNIV BEIJING) 6 March 2013 (2013-03-06) abstract example 1	1-15
A	L. DAUKIYA ET AL: "-doped graphene generated through intercalated terbium atoms", PHYSICAL REVIEW B, vol. 97, no. 3, 1 January 2018 (2018-01-01), XP055659186, ISSN: 2469-9950, DOI: 10.1103/PhysRevB.97.035309 abstract paragraph [Experimental methods]	1-15
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 18 September 2020	Date of mailing of the international search report 03/11/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Mertins, Frédéric

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/068655

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	L. S. PANCHAKARLA ET AL: "Synthesis, Structure, and Properties of Boron- and Nitrogen-Doped Graphene", ADVANCED MATERIALS, 14 August 2009 (2009-08-14), pages NA-NA, XP055139397, ISSN: 0935-9648, DOI: 10.1002/adma.200901285 abstract figure 5; table 1	10-15
A	----- CLAUDIA BAUTISTA-FLORES ET AL: "Doping Graphene by Chemical Treatments Using Acid and Basic Substances", JOURNAL OF MATERIALS SCIENCE AND CHEMICAL ENGINEERING, vol. 03, no. 10, 1 January 2015 (2015-01-01), pages 17-21, XP055659188, ISSN: 2327-6045, DOI: 10.4236/msce.2015.310003 abstract paragraph [experimental details]	1-15
A	----- SHEN Y L ET AL: "The annealing effect of chemical vapor deposited graphene", 2013 IEEE 10TH INTERNATIONAL CONFERENCE ON ASIC, IEEE, 28 October 2013 (2013-10-28), pages 1-4, XP032594161, ISSN: 2162-7541, DOI: 10.1109/ASICON.2013.6812069 ISBN: 978-1-4673-6415-7 [retrieved on 2014-05-07] the whole document	1-15
A	----- S. D. COSTA ET AL: "Monitoring the doping of graphene on SiO ₂ /Si substrates during the thermal annealing process", RSC ADVANCES, vol. 6, no. 76, 1 January 2016 (2016-01-01), pages 72859-72864, XP055659190, DOI: 10.1039/C6RA10764H the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/068655

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 102953118	A	NONE	