



(51) International Patent Classification:

B31B 1/60 (2006.01)

B32B 37/00 (2006.01)

(21) International Application Number:

PCT/US2012/071377

(22) International Filing Date:

21 December 2012 (21.12.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/579,347 22 December 2011 (22.12.2011)

US

(71) Applicant: THE TRUSTEES OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK [US/US];

116 Street And Broadway, New York, NY 10027 (US).

(72) Inventors: KYMISSIS, Ioannis; 526 West 113th Street,

Apt. 43, New York, NY 10025 (US). COX, Marshall; 119 Montague Street, Apt. 3, Brooklyn, NY 11201 (US).

(74) Agents: RAGUSA, Paul A. et al; Baker Botts LLP, 30

Rockefeller Plaza, New York, NY 10112-4498 (US).

(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, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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, 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, ML, MR, NE, SN, TD, TG).

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))

(54) Title: ASSISTED TRANSFER OF GRAPHENE

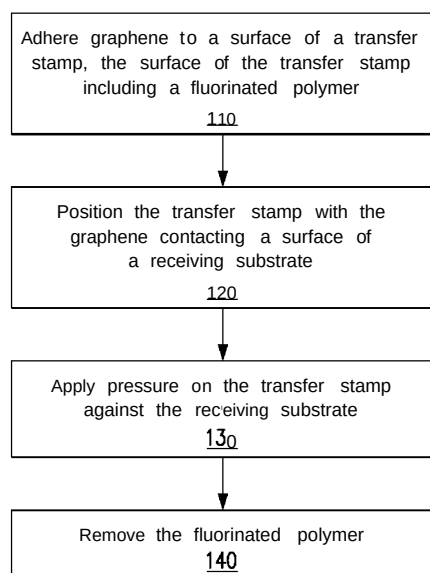


FIG. 1

(57) Abstract: The disclosed subject matter provide techniques for transferring graphene onto a receiving substrate such as organic semiconductor thin-film. Graphene can be adhered to a surface of a transfer stamp which includes a fluorinated polymer. The transfer stamp can be positioned with the graphene contacting a surface of a receiving substrate, and pressure can be applied on the transfer stamp. The fluorinated polymer can then be removed, leaving the graphene attached to the surface of the receiving substrate.

ASSISTED TRANSFER OF GRAPHENE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Patent Application Serial No. 61/579,347, filed on December 22, 2011, which is incorporated by
5 reference herein in its entirety.

BACKGROUND

An allotrope of carbon in atomically thin planar form, graphene is emerging as a nanomaterial due to its unique combination of physical and electrical properties. Graphene can be incorporated in organic semiconductor devices, e.g., as a
10 transparent electrode for organic optoelectronics devices, and as a component into various electronic devices. In these device applications, there can be requirements that graphene be transferred onto device substrates.

In certain organic electronics devices, the material that graphene is transferred onto can be sensitive to impurities. For example, in transferring graphene as
15 a recombination layer in an organic tandem solar cell, it can be desirable that the semiconducting layers are not exposed to any materials that can contaminate and/or degrade the performance of the semiconducting layers. Furthermore, the transfer processes can also require the use of solvents or heat, which can damage the semiconducting properties of small molecule or polymer semiconducting materials in
20 the organic electronics devices.

As such, there is a need for techniques for transferring graphene to substrates, in particular, organic substrates, that do not adversely affect the properties of the substrates.

SUMMARY

25 The disclosed subject matter provides techniques for transfer of graphene onto a receiving substrate. Graphene can be adhered to a surface of a transfer stamp which includes a fluorinated polymer. The transfer stamp can be positioned with the graphene contacting a surface of a receiving substrate, and pressure can be applied on the transfer stamp. The fluorinated polymer can then be
30 removed, leaving the graphene attached to the surface of the receiving substrate.

In some embodiments of the disclosed techniques, the transfer stamp can be removed from the receiving substrate, thus leaving the graphene attached to the surface of the receiving substrate with the fluorinated polymer adhering to the graphene. Thereafter, the fluorinated polymer can be removed. In other
5 embodiments, removing the fluorinated polymer can be performed without first removing the transfer stamp.

In some embodiments, the fluorinated polymer is soluble in a fluoruous solvent, such as segregated hydrofluoroether. In certain embodiments, removing the fluorinated polymer can include using a fluoruous solvent, such as a segregated
10 hydrofluoroether, or using supercritical CO₂.

In some embodiments, the receiving substrate can include an inorganic material. In other embodiments, the receiving substrate can include a non-fluorinated organic material, such as an organic material used in organic electronics or semiconductor devices.

15

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flowchart for an example method for graphene transfer according to some embodiments of the disclosed subject matter.

Figures 2a-2c are schematic diagrams for an example graphene transfer
20 procedure according certain embodiments of the disclosed subject matter.

Figures 3a and 3b are Raman spectra of graphene on different substrates according to an example embodiment of the disclosed subject matter.

Figures 4a and 4b are SEM images of graphene transferred onto an example organic thin-film (in 4a) and onto silicon (in 4b), respectively, according
25 certain embodiments of the disclosed subject matter.xx

Figure 5a is a plot of I-V curves of a control OLED versus an OLED including a graphene cathode transferred according to the disclosed subject matter; Figure 5b depicts a photo of an OLED having a graphene cathode transferred according to the disclosed subject matter.

30

DETAILED DESCRIPTION

The disclosed subject matter relates to systems and methods for transfer of graphene onto a receiving substrate such as a semiconductor thin film. Graphene transferred according to the disclosed subject matter can be used as a component in organic electronics devices, such as a transparent electrode for Organic Light Emitting Diodes (OLEDs).

Referring to Figure 1, an exemplary procedure for transferring grapheme is disclosed. Graphene can be adhered to a surface of a transfer stamp which includes a fluorinated polymer (at 110). The transfer stamp with the adhered graphene can be positioned on a receiving substrate such that the graphene is in contact with a surface of the receiving substrate (at 120). Pressure can be applied on the transfer stamp against the receiving substrate (at 130), thus pushing the graphene against the surface of the receiving substrate. The fluorinated polymer can be removed (at 140), e.g., by using a suitable solvent, leaving the graphene attached on the surface of the receiving substrate. This procedure is further described below in conjunction with Figures 2a-2c.

As used herein, graphene can include single-layer graphene and graphene sheet that include multiple layers, e.g., 2-10 layers. The physical characteristics and quality of graphene (such as the number of layers, defects, impurities, grain boundaries, domain structure) can depend on the conditions and parameters for manufacturing processes of the graphene, e.g., chemical vapor deposition, exfoliation, epitaxial growth, etc. Large areas (e.g., about 100 microns on edge or larger) of graphene can be produced, for example, by chemical vapor deposition on metal substrates, such as copper backing.

Figure 2a illustrates an example procedure to prepare a transfer stamp. The transfer stamp (240 in Figures 2a-2c) can have a planar surface for contacting graphene during the transfer process. The transfer stamp can include a base (210 in Figure 2a) made of various materials, such as plastic, metal, inorganic materials, etc. in certain embodiments, the transfer stamp can include a base made from a soft material, such as a pliant polymer, e.g., silicones including polydimethylsiloxane (PDMS). The transfer stamp can include a passivation layer on the base, such as a Parylene C layer, serving as a chemically inert moisture and dielectric barrier (220 in Figure 2a shows a base coated with a passivation layer).

The transfer stamp can be sized suitably for handling by hand tools (such as tweezers), robotic hand, or other automated tools. The contact surface of the transfer stamp can be made to be of similar size or larger size than the graphene to be transferred. As an example, the stamp can have a contact surface of about 1 mm x 1 mm. For
5 transferring an array or matrix of graphene samples onto a receiving substrate with an array or matrix of receiving areas, a plurality of transfer stamps (e.g., one for each graphene sample) can be attached to a holding device or tool, or one transfer stamp can include an array or matrix of protrusions of areas each used for transferring an individual graphene sample.

10 As noted above, the surface of the transfer stamp for contacting graphene can include a fluorinated polymer (230 in Figures 2a-2c). The fluorinated polymer can be present as a coating or layer, e.g., by spin-coating, and can serve as a "sacrificial" layer in the transfer process (which will be later removed). Thus, the transfer process disclosed herein can also be referred to as "assisted transfer" or "Fl-assisted transfer." Fluorinated
15 polymers (also referred to as Fl resist herein, although it does not need to be a photoresist) can include polymers or copolymers that have appropriate molecular structure and fluorine content that render them soluble in supercritical CO₂ or the various fluoruous solvents described below. For example, fluorinated polymer can include resorcinarene, a copolymer of perfluorodecyl methacrylate and 2-nitrobenzyl methacrylate, derivatives
20 thereof or other polymer photoresist or molecular glass photoresists having sufficient fluorine content. Other fluorinated polymers include those disclosed in U.S. Patent Application Publication No. 2011/0159252, which is incorporated herein by reference in its entirety.

For adhering graphene onto the fluorinated polymer layer of the transfer
25 stamp, the graphene can be first cut (e.g., by laser, plasma, Ni nanoparticle, etc.) into pieces with desired dimensions, for example, according to the electronics devices applications where the graphene is to be incorporated. If the graphene has been obtained from a CVD process, a metallic backing material used in the CVD process, e.g., copper foil, can be still attached to the graphene. In such a case, adherence of the graphene with
30 copper foil to the transfer stamp can be accomplished by placing the transfer stamp with the fluorinated polymer layer facing up, placing the graphene in contact with the fluorinated polymer layer of the transfer stamp, and pressing a second object, such as a glass-backed PDMS stamp, against the graphene and the transfer stamp. In this

manner, the graphene together with the copper foil (250 in Figure 2b) can be transferred onto the fluorinated polymer layer of the transfer stamp 240. The copper foil can then be removed by an etchant, e.g., ammonium persulfate, which results in the bare graphene (270) being left attached to the transfer stamp 240 (shown in Figure 2b). Other metallic backing material for the graphene can be similarly removed by suitable etchants.

As shown in Figure 2c, the transfer stamp with adhered graphene (metallic backing, if any, has been removed) can then be brought into contact with a surface of a receiving substrate (280), with the graphene (270) to contact the surface of the substrate (280). Pressure can be applied for a duration of time, e.g., a few seconds or a few minutes, on the transfer stamp to press the graphene onto the substrate surface. The amount of pressure and the time during which the pressure is applied can be selected based on factors such as ambient temperature and the adhesion of the graphene to the fluorinated polymer relative to its adhesion to the surface of the receiving surface.

Graphene can be transferred according to the above-outlined procedure to various substrates, including inorganic substrates, such as silicon, silica, metal, or substrates made of organic materials. The surfaces of organic substrates can be low-energy, fragile, and chemically vulnerable surfaces. In some embodiments, the surfaces of the organic substrates comprise materials that are not fluorinated polymers discussed above, and thus are not soluble in the fluorinated solvents or supercritical CO₂ described below. Example organic substrates can include small organic molecules as well as polymers commonly used in organic electronics or semiconductor devices, such as hole transport layer materials, hole injection layer materials, electron or hole transport layer materials, electron injection layer materials, phosphorescent host materials, fluorescent host materials, organic photovoltaic materials, organic thin film transistor materials, liquid crystal display materials, conducting polymers (such as PEDOT, polypyrrole, polyaniline), insulator polymers (such as PMMA, polycarbonate, PVA, etc.), etc. In some embodiments, the substrate can include organic electronics components of an OLED. Thus, the graphene laminated on the surface of the substrate can constitute a component of the device, e.g., a transparent cathode.

In some embodiments as shown in Figure 2c, when the transfer stamp is removed, the fluorinated polymer 230 can peel off from the stamp and stay adhered to the graphene 270, which is attached to the substrate surface (shown as configuration 290 in

Figure 2c). This can be attributed to the greater adhesion between the graphene with the surface of the receiving substrate than that between the fluorinated polymer coating with the underlying material of the stamp (e.g., Parylene C layer on the transfer stamp as shown). The fluorinated polymer layer transferred along with the graphene can then be removed using a suitable solvent, such as supercritical CO₂ or various fluoruous solvents as further discussed below. Alternatively, the solvent can be applied while the transfer stamp is still positioned on the substrate. This can also strip away the fluorinated polymer, and thereafter, the stamp can be removed, leaving the graphene attached to the substrate surface.

The solvent for removing the fluorinated polymer from the graphene can be a fluoruous solvent (or mixtures of various fluoruous solvents) that can dissolve the fluorinated polymer but does not dissolve or chemically react with the surface of the substrate. Example fluoruous solvents include perfluorinated or highly fluorinated liquids, which are immiscible with organic solvents and water. One class of such fluoruous solvents can be segregated hydrofluoroethers (HFEs), such as methyl nonafluorobutyl ether, methyl nonafluoroisobutyl ether, isomeric mixtures of methyl nonafluorobutyl ether and methyl nonafluoroisobutyl ether, ethyl nonafluorobutyl ether, ethyl nonafluoroisobutyl ether, isomeric mixtures of ethyl nonafluorobutyl ether and ethyl nonafluoroisobutyl ether, 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6-dodecafluoro-2-trifluoromethyl-hexane, 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane, 1,1,1,2,3,3-hexafluoro-4-(1,1,2,3,3,3-hexafluoropropoxy)-pentane, and combinations thereof. In some embodiments, the HFE can be generally described using the formula R_h-O-R_f , wherein R_h is a straight-chained or branched alkyl group, and R_f is a perfluorinated straight-chained or branched alkyl group. Other fluoruous solvents include chlorofluorocarbons (CFCs): $C_xCl_yF_z$, hydrochlorofluorocarbons (HCFCs): $C_xCl_yF_zH_w$, hydrofluorocarbons (HFCs): $C_xF_yH_z$, perfluorocarbons (FCs): C_xF_y , perfluoro ethers: $C_xF_yOC_zF_w$, perfluoroamines: $(C_xF_y)_3N$, trifluoromethyl (CF_3)-substituted aromatic solvents: $(CF_3)_xPh$ [benzotrifluoride, bis(trifluoromethyl)benzene]. The fluoruous solvents can further include the fluoruous or fluorinated solvents disclosed in U.S. Patent Application Publication No. 2011/0159252, noted above.

The following Example is provided to more fully illustrate the principles of the disclosed subject matter, but is not to be construed as limiting the scope thereof.

EXAMPLE

This example describes the use of a fluorinated (Fl) polymer or resist material for the transfer of graphene onto organic thin films using an exemplary method of the disclosed subject matter.

As a target small-molecule organic substrate, 2,2',2''-(1,3,5-benzinetriyl)-tris(4-phenyl-1-H-benzimidazole (TPBi, LumTec) films were evaporated on indium Tin Oxide (ITO)-coated glass (LumTec) at 1 Angstrom per second to a thickness of 40 nm via an Angstrom Engineering thermal evaporator mated to an MBraun glovebox.

To evaluate the electrical quality of the graphene transferred using the method described, organic LED (OLED) devices were evaporated on pre-patterned ITO substrates (LumTec) for graphene cathode lamination. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, HC Stark) was spin-coated on cleaned substrates at 3000 rpm at 1000 rpm/s and baked at 120°C for 1 hour. Following the PEDOT deposition the substrates were taken into the nitrogen environment of the glovebox. 40 nm of N,N'-Bis(3-methylphenyl)-N,N'-diphenyl-9,9-spirobifluorene 2,7-diamine (El 05, LumTec) was evaporated, followed by the evaporation of 40 nm of Tris(8-hydroxyquinolato)aluminum (AlQ₃, LumTec). A 60 nm Aluminum cathode was evaporated on control devices (devices that do not include transferred graphene). All OLED devices were kept in nitrogen for the duration of the experiment.

A transfer stamp was prepared as follows. PDMS was cured in a petri dish at 80°C for 1 hour. Small stamps of PDMS base were cut from this mold, and coated with 0.4g (approximately 400 nm) of Parylene-C via a Specialty Coating Systems Labcoater. These PDMS-Parylene stamps were then spin-coated with a fluorinated polymer (manufactured by Orthogonal, Inc.) at 3000 rpm and 1000 rpm/s acceleration.

Small sections of graphene/copper was cut from large-area films of graphene grown using a CVD process (including copper foil backing), and placed, graphene-side down, on the transfer stamp. Copper was then etched in ammonium persulfate (Transene APS- 100 copper etchant) until no copper was evident (periodic removal of bubbles via deionized water as necessary). After the application of

Parylene and for the remainder of the test, flexing the stamp was avoided to avoid graphene/copper delamination. To adhere the graphene/copper foil to the stamps without significant flexion, the transfer stamp was placed on a non-adhesive side of scotch tape (3M), while uniform pressure was applied to the top of the
5 graphene/copper foil by a glass-backed PDMS stamp with an additional scotch tape layer. The non-adhesive side of scotch tape did not adhere to PDMS.

For transferring graphene onto organic thin films, the transfer stamp was placed, graphene-side down, onto the organic thin films in the desired location. Pressure was applied with a thumb for 5 seconds. The stamp was then removed from
10 the substrate. The graphene was left on the substrate, along with a thin film of the fluorinated resist. This resist was removed by two subsequent spin-coats of a fluoruous solvent described above.

Graphene transferred on TPBi was then analyzed via Raman Spectroscopy in a Renishaw Invia Raman Microscope using a 532 nm laser and by
15 SEM in a Hitachi 5000. OLED devices were driven by a Keithley 2400 sourcemeter and current-voltage data was collected.

To evaluate the presence and quality of transferred graphene on the above organic substrate, Raman spectroscopy was performed. The Raman signature of the background thin-film without graphene was also measured, and the background
20 corrected Raman signature is shown in Figure 3a. The presence of a strong signal from the G and 2D peaks, located at 1590.54 cm^{-1} and 2683.0 cm^{-1} respectively, indicate that graphene is successfully transferred by the disclosed method onto organic small-molecule substrates. The small D-peak, located at 1352.5 cm^{-1} , demonstrates that the transfer process does not induce significant defects in the
25 transferred graphene film.

Graphene was also transferred onto Si substrates and Raman was measured for comparison (Figure 3b). Peak position and full-width-half-maximum (FWHM) for G and 2D peaks of graphene transferred on both substrates are listed in Table 1 below. Broadening of the peak FWHMs on organic substrate versus Si can be
30 attributed to increased substrate-induced disorder in graphene films on organic substrate versus silicon. Deviations in the G and 2D peak positions between the two substrates can be due to transfer-induced local dopant concentrations and local strain. The close agreement of the data demonstrates the effectiveness of the disclosed

graphene transfer process of graphene onto both high energy substrate (Si) and low energy substrate (organic substrate).

Table 1: Peak characteristics of graphene transferred onto organic substrate as compared with graphene transferred onto Si substrate

Sample		D Peak	G Peak	2D Peak
Graphene on Organic Substrate	FWHM	28.0cm ⁻²	19.1cm ⁻²	54.5cm ⁻²
	Position	1352.5cm ⁻²	1590.54cm ⁻²	2683cm ⁻²
Graphene on Si	FWHM		12.6cm ⁻²	32.4cm ⁻²
	Position	1346.7cm ⁻²	1594.2cm ⁻²	2685.2cm ⁻²

In order to probe surface morphology and transfer cleanliness, transferred films were inspected via SEM. Figure 4 shows SEM images taken at 10,000 times magnification at an 2 kV. Figure 4b shows graphene transferred on silicon using the disclosed method, including its morphology and a high level of cleanliness. Figure 4a shows graphene transferred on an organic thin-film of TPBi, illustrating the high fidelity transfer of graphene onto a low-energy surface with a transfer quality similar to that on silicon.

As a further demonstration of the quality and capabilities of the disclosed graphene transfer techniques, an organic LED was fabricated with graphene transferred serving as the cathode. OLED devices can be fabricated with an Aluminum cathode, which gives a good match to the Lowest Unoccupied Molecular Orbital (LUMO) of the electron transporting material (in this case, TPBi). An Aluminum cathode also reflects light with high efficiency, increasing the external quantum efficiency of the device when viewed through the anode, but resulting in an opaque device. In contrast, a graphene transferred onto organic substrate can serve as a transparent electrode and provide different architectures and devices.

Figure 5a shows the Current-Voltage characteristics of the graphene OLED device in comparison to a control device with an Aluminum cathode. The graphene device requires higher voltage to turn on. As a result, the device requires significant current density before voltage can drop over the diode. This can be ameliorated by process iteration and refinement to transfer graphene with a lower roughness. Figure 5b shows an image of the functional graphene OLED. The

transparency of the device can be attributable to the presence of graphene in conjunction with an ITO anode.

The above results demonstrate that the graphene transfer techniques disclosed herein can allow large-scale, patternable transfer to various substrates of choice, thereby enabling flexible and transparent electronics devices such as OLEDs, OPVs, as well as providing an integration process for tandem organic photovoltaics.

The description herein merely illustrates the principles of the disclosed subject matter. Various modifications and alterations to the described embodiments will be apparent to those skilled in the art in view of the teachings herein.

Accordingly, the disclosure herein is intended to be illustrative, but not limiting, of the scope of the disclosed subject matter.

WHAT IS CLAIMED IS:

1. A method for transferring graphene to a receiving substrate, comprising:
 - adhering graphene to a surface of a transfer stamp, the surface of the transfer stamp including a fluorinated polymer;
 - positioning the transfer stamp on a receiving substrate with the graphene contacting a surface of the receiving substrate;
 - applying pressure on the transfer stamp against the receiving substrate; and
 - removing the fluorinated polymer, thereby leaving the graphene attached to the surface of the receiving substrate.
2. The method of claim 1, further comprising, prior to the removing the fluorinated polymer:
 - removing the transfer stamp from the receiving substrate, thereby leaving the graphene attached to the surface of the receiving substrate, with the fluorinated polymer adhering to the graphene.
3. The method of claim 1, wherein removing the fluorinated polymer is performed while the transfer stamp is positioned on the receiving substrate.
4. The method of claim 1, wherein adhering graphene to the surface of the transfer stamp comprises adhering graphene having a metallic backing, the method further comprising removing the metallic backing.
5. The method of claim 1, wherein the fluorinated polymer comprises a polymer soluble in a segregated hydrofluoroether.
6. The method of claim 1, wherein the receiving substrate comprises an inorganic material.
7. The method of claim 1, wherein the surface of the receiving substrate comprises a non-fluorinated organic material

8. The method of claim 1, wherein the transfer stamp comprises a pliant polymer material.
9. The method of claim 1, wherein removing the fluorinated polymer comprising using a fluorous solvent.
10. The method of claim 10, wherein the fluorinated solvent comprises a segregated hydrofluoroether.
11. The method of claim 1, wherein removing the fluorinated polymer comprising using supercritical CO₂.
12. An electronic device including;
 - an anode,
 - a cathode comprising graphene, and
 - an organic material disposed between the anode and the cathode.
13. The electronic device of claim 12, wherein the electronic device is an OLED.

1/6

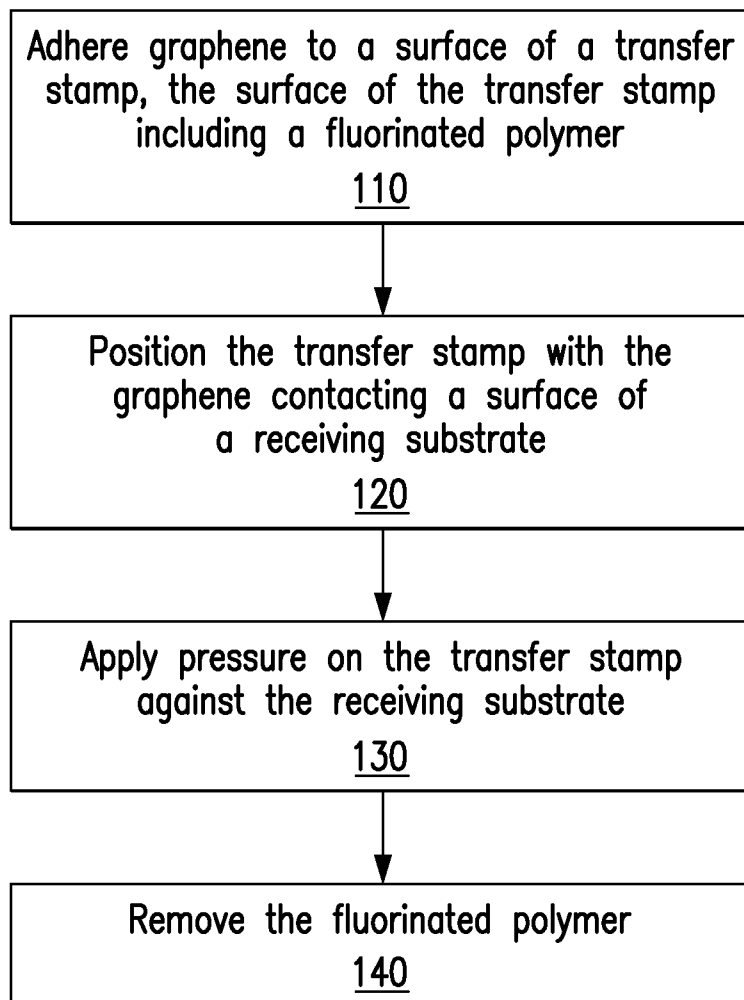


FIG. 1

2/6

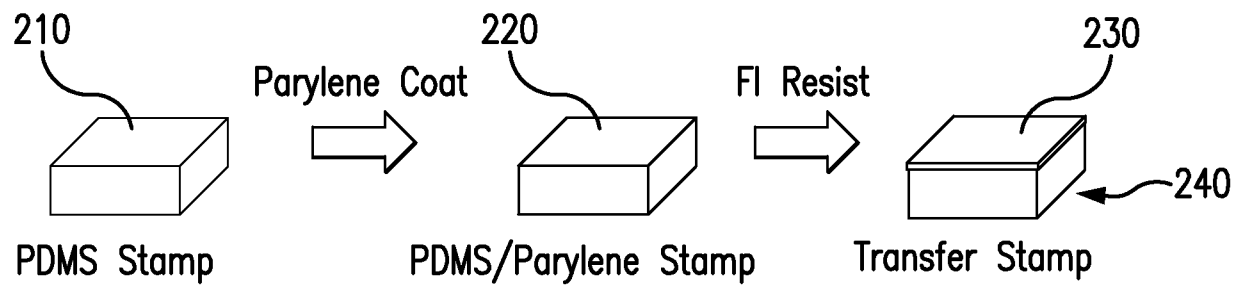


FIG. 2a

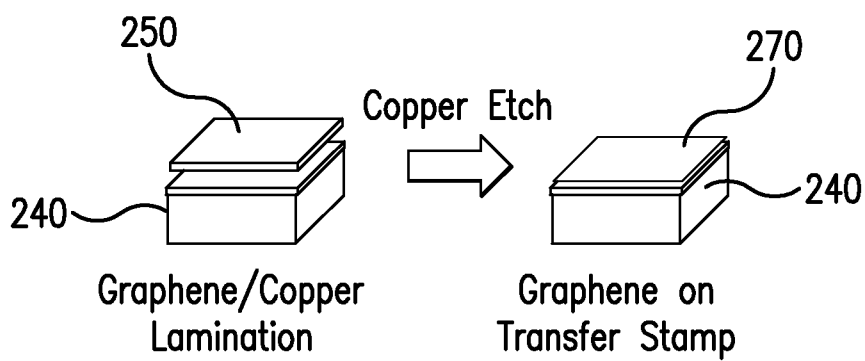


FIG. 2b

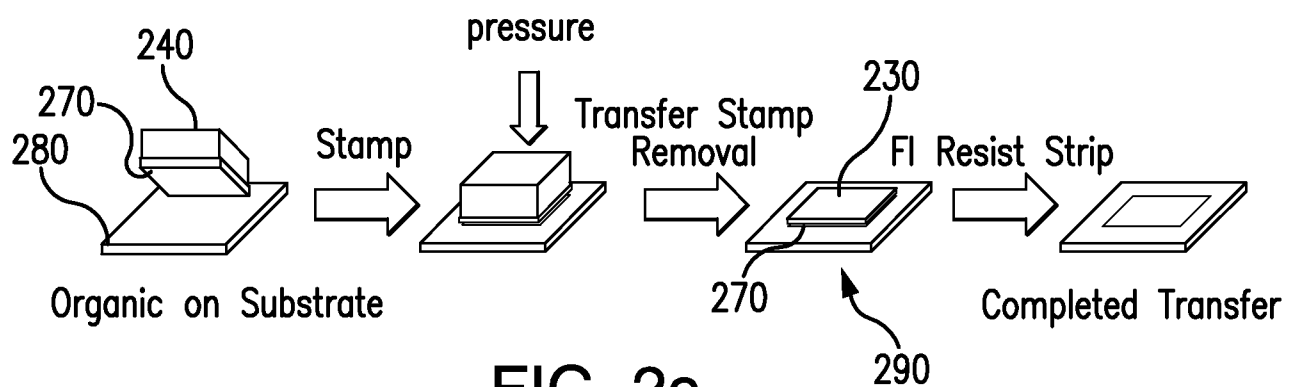


FIG. 2c

3/6

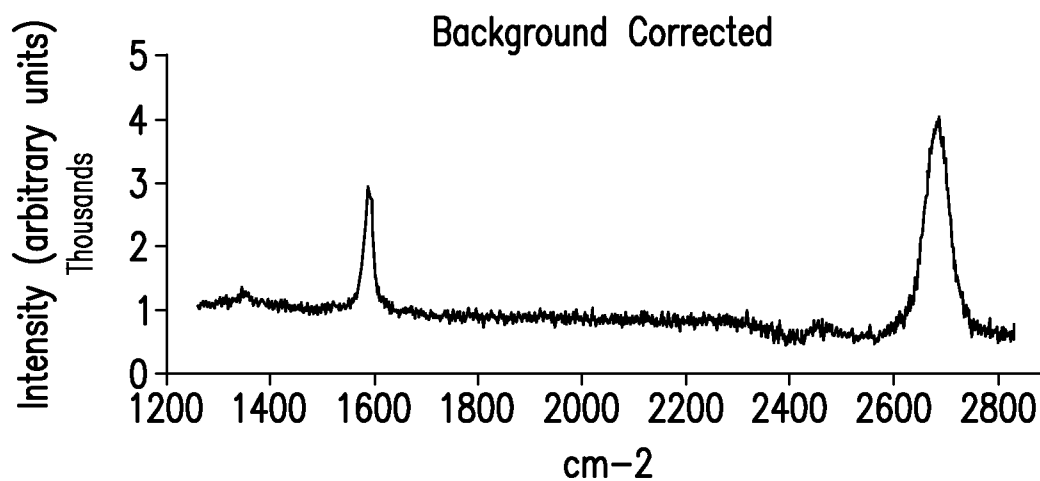


FIG. 3a

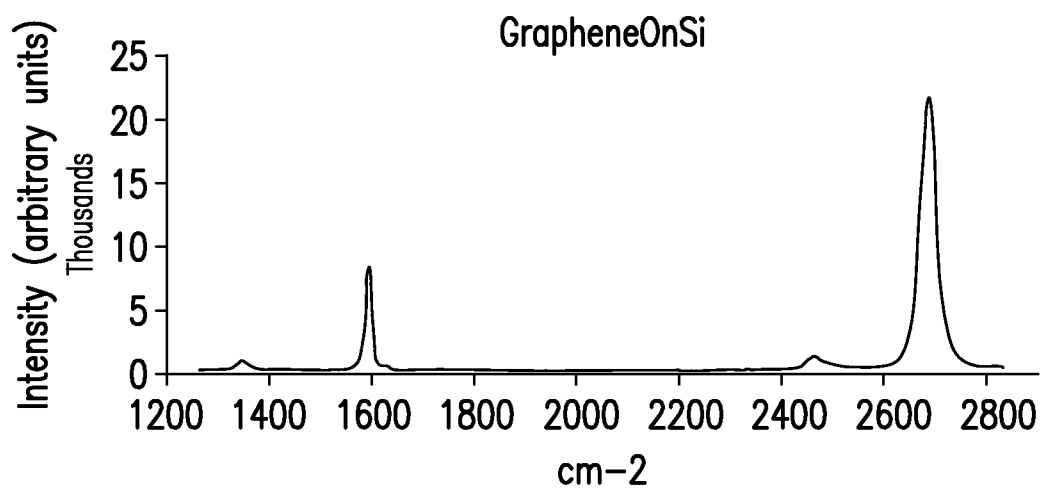


FIG. 3b

4/6

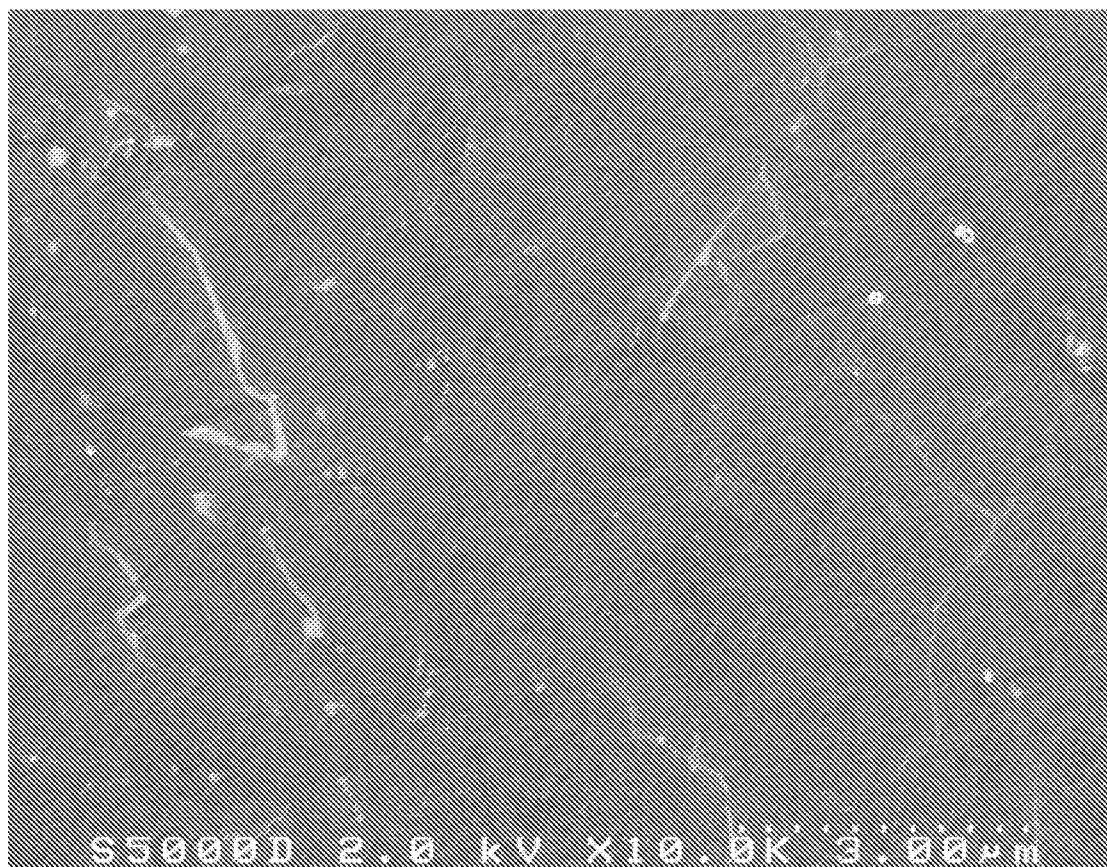


FIG. 4a

5/6

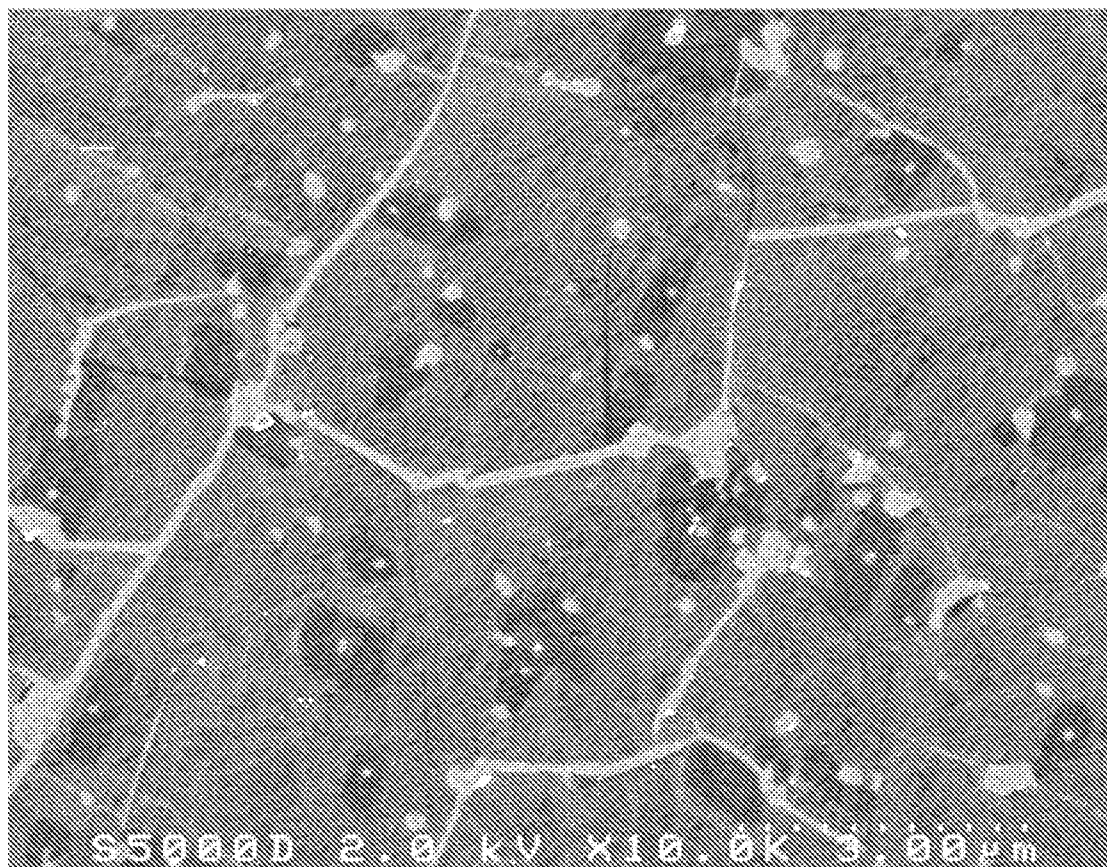


FIG. 4b

6/6

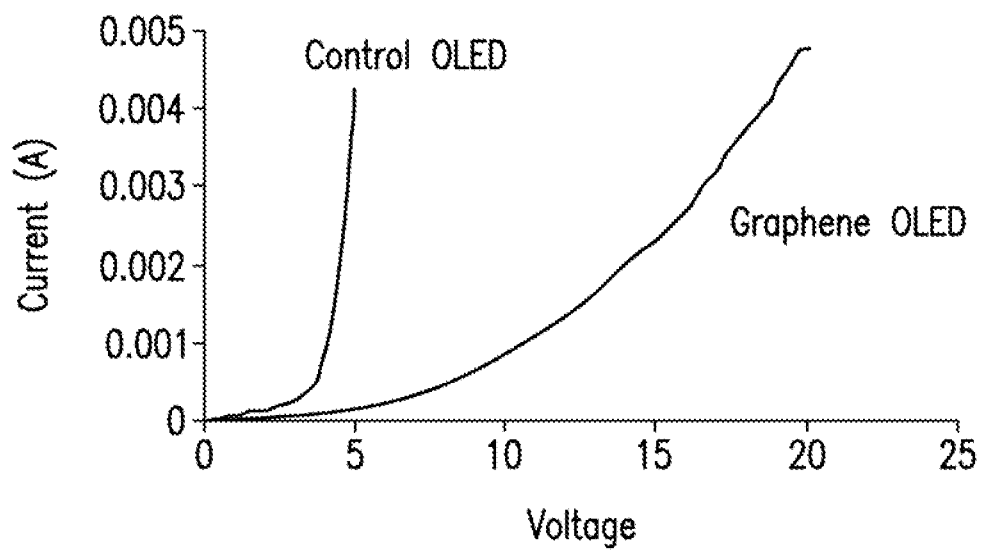


FIG. 5a

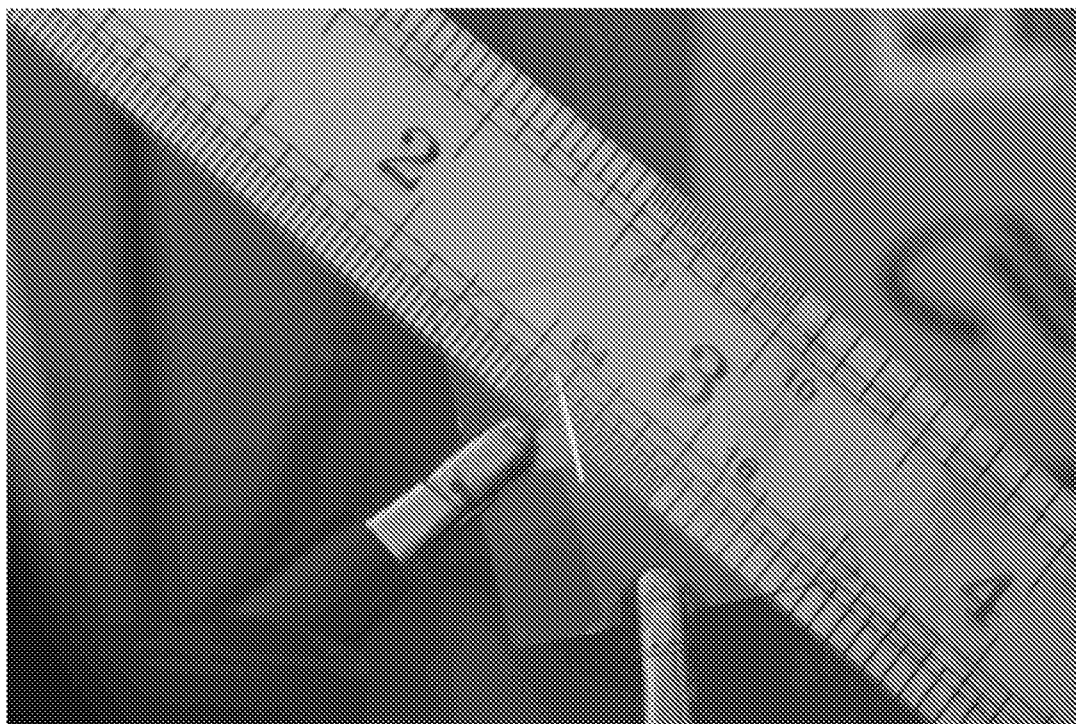


FIG. 5b

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/71377

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B31 B 1/60; B32B 37/00 (2013.01)

USPC - 156/60; 156/248; 156/249

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)

USPC - 156/60; 156/248; 156/249

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

USPC - all classes; NPL (key word limited)

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

PatBase, Google Scholar

Search terms - Meitl, "Nature Materials", transfer, stamp, graphene, KYMISSIS w2 Ioannis, COX w2 Marshall, esorcinarene, perfluorodecyl methacrylate, pdma, polydimethylP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/0101710 A1 (Choi et al.) 29 April 2010 (29.04.2010); para [0025], [0028], [0059]	1-1 1
Y	US 201 1/0159252 A1 (Ober et al.) 30 June 201 1 (30.06.201 1); abstract; para [0004], [0008], [001 1] - [0013]	1-1 1
A	US 2010/0143726 A1 (Golzhauser et al.); 10 June 2010 (10.06.2010); para [0020]-[0026]	1-1 1
A	WO 2010/132552 A1 (Rogers et al.) 18 November 2010 (18.11.2010); para [047]	1-1 1



Further documents are listed in the continuation of Box C.



* Special categories of cited documents:

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

"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

05 April 2013 (05.04.2013)

Date of mailing of the international search report

30 APR 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/71377

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group 1: claims 1-1 1, drawn to a method for transferring graphene to a receiving substrate, comprising:
- adhering graphene to a surface of a transfer stamp, the surface of the transfer stamp including a fluorinated polymer;
- positioning the transfer stamp on a receiving substrate with the graphene contacting a surface of the receiving substrate;
- applying pressure on the transfer stamp against the receiving substrate; and
- removing the fluorinated polymer, thereby leaving the graphene attached to the surface of the receiving substrate.

— See Sheet Below —

1. ☐ As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-1 1

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Box No III Observations where unity is lacking - continued

Group II: claims 12 and 13, drawn to an electronic device including:

- an anode,
- a cathode comprising graphene, and
- an organic material disposed between the anode and the cathode.

The inventions listed as Groups I and II do not relate to a single special technical feature under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not include the special technical features of the electronic device, the anode, and the cathode of Group II.

Group II does not include the special technical feature of a method for transferring graphene to a substrate comprising the steps of adhering graphene to a surface of a transfer stamp having a fluorinated polymer, positioning the transfer stamp on the receiving substrate, applying pressure, and removing the fluorinated polymer of Group I.

The inventions of Groups I and II share the technical feature of a graphene. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by reference WO 2010/132552 A1 (18 November 2010) at para [047]. As this technical feature was known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups.

Therefore, Groups I and II lack unity under PCT Rule 13 because they do not share the same or corresponding special technical feature.