

(51) International Patent Classification:
H01L 21/02 (2006.01)

(21) International Application Number:

PCT/GB2015/051146

(22) International Filing Date:

15 April 2015 (15.04.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1406788.8

15 April 2014 (15.04.2014)

GB

(71) Applicant: **THE UNIVERSITY OF MANCHESTER**
[GB/GB]; Oxford Road, Manchester Greater Manchester
M13 9PL (GB).(72) Inventors: **MONTEVERDE, Umberto**; School of Electrical and Electronic Engineering, University of Manchester, Oxford Road, Manchester Greater Manchester M13 9PL (GB). **PAL, Joydeep**; School of Electrical and Electronic Engineering, University of Manchester, Oxford Road, Manchester Greater Manchester M13 9PL (GB). **MIGLIORATO, Max**; School of Electrical and Electronic Engineering, University of Manchester, Oxford Road, Manchester Greater Manchester M13 9PL (GB). **MIS-SOUS, Mohamed**; School of Electrical and Electronic Engineering, University of Manchester, Oxford Road, Manchester Greater Manchester M13 9PL (GB). **BANGERT, Ursel**; Department of Physics and Energy, University of Limerick, Limerick (IE).(74) Agent: **HGF LTD**; Document Handling - HGF
(Manchester), Belgrave Hall, Belgrave Street, Leeds Yorkshire LS2 8DD (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: GRAPHENE-BASED ELECTRONIC STRUCTURE

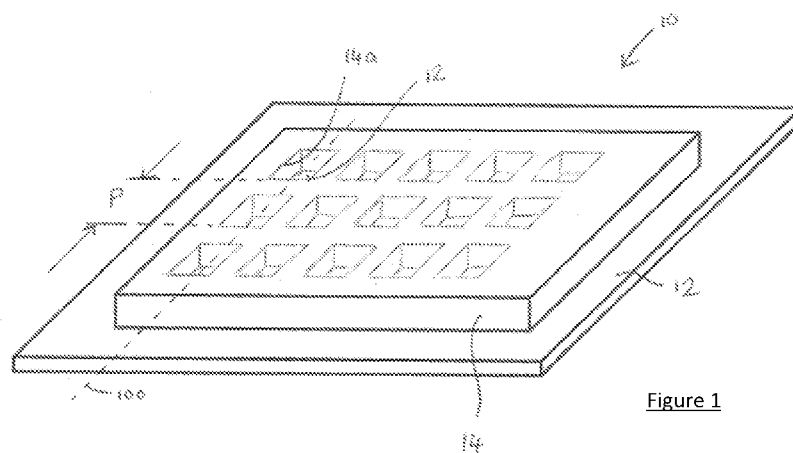


Figure 1

(57) Abstract: An electronic structure comprising a layer of graphene, and a constraining element arranged to constrain the layer of graphene, for example a periodic structure disposed on the layer of graphene. The constraining element (e.g. the periodic structure) is arranged to constrain the graphene and thereby induce strain in the layer of graphene such that the layer of graphene is morphologically rippled and includes semiconducting regions.

Graphene-based Electronic Structure

[0001] This invention relates to an electronic structure, and, more particularly, to an electronic structure that includes graphene, and electronic devices incorporating the electronic structure.

5

BACKGROUND

[0002] Since the first measurements and confirmation of the unique properties of graphene, it has been suggested that graphene may have applications in a huge variety of fields including digital electronics. However, graphene does not have a band gap opening which severely limits the on-off ratio of graphene-based electronic devices.

10

[0003] Attempts have been made to modify graphene to create a band gap opening so as to increase its usefulness in electronic applications. In particular, recent academic reports^{1,2} have showed that the Dirac point of the band structure of graphene may be tuned away from its natural 0 eV band gap state. One example of band gap opening in graphene is described in Balog et al. (2010)³ and involves the hydrogenation of a graphene lattice. Another example is described in US Patent No. US 8,044,472 (Kurtz et al.) where a force is applied to a substrate that supports the graphene in order to manipulate the electronic characteristics of the graphene.

15

[0004] To date, proposed methods for tuning the Dirac point band gap are cumbersome (e.g. subjecting the graphene lattice to shear strain), impractical (e.g. relying on atomic substitution of the graphene lattice sites) and incompatible with large area fabrication making such approaches unsuitable for commercial use in electronics applications.

20

[0005] It is an object of certain embodiments of the present invention to mitigate at least some of the disadvantages associated with the prior art.

25

BRIEF SUMMARY OF THE DISCLOSURE

[0006] In accordance with a first aspect of the present invention there is provided an electronic structure comprising:

a layer of graphene; and

¹ Pereira, V. M., Castro Neto, A. H. and Peres, N. M. R., Tight-binding approach to uniaxial strain in graphene, Phys. Rev. B 80, 045401-1-8 (2009).

² Guinea, F., Katsnelson, M. I. and Geim, A. K., Energy gaps and a zero-field quantum Hall effect in graphene by strain engineering, Nature Phys. 6, 30-33 (2010).

³ Balog, R. et al. (2010) Bandgap opening in graphene induced by patterned hydrogen adsorption. *Nature Materials*. Vol 9 (April 2010), 315-319.

a periodic structure disposed on the layer of graphene and arranged to induce strain in the layer of graphene such that the layer of graphene is morphologically rippled and includes semiconducting regions.

[0007] The periodic structure may have a periodicity of at least 8 nm along a single direction, and may have a periodicity of at least 10 nm along a single direction.

[0008] The morphologically rippled layer of graphene may have a periodicity of at least 8 nm along a single direction, and may have a periodicity of at least 10 nm along a single direction.

[0009] Ripples of the morphologically rippled layer of graphene may have amplitudes of at least 0.4 nm, and may have amplitudes of between 0.4 nm and 0.6 nm.

[0010] The semiconducting regions of the layer of graphene may be strained by 0.6% or more by the periodic structure.

[0011] The periodic structure may be arranged so as to define enclosed regions of the layer of graphene.

[0012] The induced strain may include shear strain.

[0013] The semiconducting regions may have a band gap opening of at least 0.1 eV. The semiconducting regions may have a band gap opening of at least 0.15 eV, and preferably at least 0.2 eV.

[0014] Alternatively, the Fermi Energy of the semiconducting regions may be shifted relative to the Dirac point thereby spontaneously producing an excess population of electrons in the conduction band of the layer of graphene. The shift of the Fermi Energy relative to the Dirac point may be at least 50 meV, and may be about 65 meV.

[0015] The periodic structure may comprise one or more of gold, aluminium, copper, TiAu, SiO₂, CH₄, and Al-PMGI.

[0016] The periodic structure may be bonded to the layer of graphene by direct chemical bonding and/or by Van der Waals interaction.

[0017] The periodic structure may include a first periodic structure disposed on a first side of the layer of graphene and a second periodic structure disposed on a second side of the layer of graphene.

[0018] The electronic structure may further comprise additional layers of graphene. In other words, the "layer" of graphene discussed above may include one or more sheets of graphene.

[0019] In accordance with a second aspect of the present invention, there is provided an electronic device including the electronic structure of the first aspect of the present invention.

[0020] In accordance with a third aspect of the present invention, there is provided a complementary-metal-oxide semiconductor (CMOS) device including the electronic structure of the first aspect of the present invention.

[0021] In accordance with a fourth aspect of the present invention, there is provided an optical detector including the electronic structure of the first aspect of the present invention. The optical detector may be an infra-red detector.

[0022] In accordance with a fifth aspect of the present invention, there is provided a pressure sensor including the electronic structure of the first aspect of the present invention.

[0023] In accordance with a sixth aspect of the present invention, there is provided a method of making an electronic structure, comprising the steps:

providing a layer of graphene; and

inducing strain in the layer of graphene by providing a periodic structure on the layer of graphene, wherein the strain induced by the periodic structure causes the layer of graphene to be morphologically rippled and include semiconducting regions.

[0024] The periodic structure may be deposited on the layer of graphene. The periodic structure may be deposited on the layer of graphene by lithography, and may be deposited on the layer of graphene by electron-beam lithography.

[0025] In an alternative embodiment, the periodic structure may be transferred onto the layer of graphene.

[0026] In an alternative embodiment, the layer of graphene may be deposited on the periodic structure.

[0027] In an alternative embodiment, the layer of graphene may be transferred onto the periodic structure.

[0028] The periodic structure may comprise one or more of gold, aluminium, copper, TiAu, SiO₂, CH₄, and Al-PMGI.

[0029] In a yet further aspect of the invention there is provided an electronic structure comprising

a layer of graphene

a constraining member

wherein the layer of graphene is constrained by the constraining member to cause one or more morphological ripples in the layer of graphene thereby to generate semi-conducting regions in the layer of graphene.

[0030] Preferably, there will be plural constraining members. More preferably, there will be a layer of graphene between plural constraining members. Even more preferably, there will be plural sets of constraining members, each set constraining a layer of graphene having said morphological ripples.

5 **[0031]** The constraining member may comprise a pair of constraining elements, between which the layer of graphene is located. The constraining elements may be separated by a distance of 40, 30 or 20 microns or less, for example 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 microns or less, for example in the nanometer range. Additionally or alternatively, the area defined by the graphene, that is the
10 area defined by the constraining member may be less than $400\mu\text{m}^2$, say less than $350\mu\text{m}^2$, for example less than 340, 330, 320, 310, 300, 290, 280, 270, 260, 250, 240, 230, 220, 210, 200, 150, 100, 75, 50, 25, 10, 5, 4, 3, 2, $1\mu\text{m}^2$.

[0032] The constraining member may be located on a substrate. The constraining member may define a pore, aperture or other region of partially or totally unsupported free space, for
15 example a holy carbon (or other material) grid, net or reticulated body.

[0033] The constraining member may comprise an electrode, for example a pair of constraining elements may each comprise an electrode.

[0034] Plural constraining elements may be provided on a substrate, each constraining element providing an electrode with a layer of graphene located and constrained between
20 successive constraining elements.

[0035] The one or more ripple may be up to 100nm high and/or have a width (at the base of the ripple) of 100nm. For example a height of up to 90nm, 80, 70, 60, 50, 40, 30, 20, 10, 5, 4, 3, 2, 1 nm. The width (at the base of the ripple) may be up to 90nm, 80, 70, 60, 50, 40, 30, 20, 10, 5, 4, 3, 2, 1 nm. The dimensions of the ripples may be outside this range.

25 **[0036]** In certain embodiments, the layer of graphene may be produced directly on the constraining member, for example by by chemical vapour deposition. Alternatively, constraining member may be deposited onto the graphene layer, or a precursor thereof. The layer of graphene may be transferred to the constraining member or *vice versa*.

[0037] In alternative embodiments, the layer of graphene may be produced by mechanical
30 exfoliation of graphite.

[0038] The periodic structure may have a periodicity of at least 8 nm along a single direction, and may have a periodicity of at least 10 nm along a single direction.

[0039] The morphologically rippled layer of graphene may have a periodicity of at least 8 nm

along a single direction, and may have a periodicity of at least 10 nm along a single direction.

[0040] Ripples of the morphologically rippled layer of graphene may have amplitudes of at least 0.4 nm, and may have amplitudes of between 0.4 nm and 0.6 nm.

5 **[0041]** The semiconducting regions of the layer of graphene may be strained by 0.6% or more by the periodic structure.

[0042] The periodic structure may be arranged so as to define enclosed regions of the layer of graphene.

[0043] The induced strain may include shear strain.

10 **[0044]** The semiconducting regions may have a band gap opening of at least 0.1 eV, and may have a band gap opening of at least 0.15 eV, and preferably at least 0.2 eV.

[0045] Alternatively, the Fermi Energy of the semiconducting regions may be shifted relative to the Dirac point thereby spontaneously producing an excess population of electrons in the conduction band of the layer of graphene. The shift of the Fermi Energy relative to the Dirac point may be at least 50 meV, and/or may be about 65 meV.

15 **[0046]** The periodic structure may be bonded to the layer of graphene by direct chemical bonding and/or by Van der Waals interaction.

[0047] The periodic structure may include a first periodic structure disposed on a first side of the layer of graphene and a second periodic structure disposed on a second side of the layer of graphene.

20 **[0048]** The method may further comprise providing additional layers of graphene to the electronic structure. As noted above, in other words, the "layer" of graphene discussed above may include one or more sheets of graphene.

BRIEF DESCRIPTION OF THE DRAWINGS

25 **[0049]** Embodiments of the invention are further described hereinafter with reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic representation of an electronic structure in accordance with an embodiment of the present invention;

30 Figure 2 shows predicted phonon dispersion curves for (a) C-diamond and (b) graphene, calculated using the MMP potential;

Figure 3(a) shows the band structure at the Dirac points of the sheet of graphene shown in Figure 3(c) in a strained and unstrained condition, as calculated by tight binding;

Figure 3(b) shows the phonon dispersion curve for the sheet of graphene of Figure 3(c) in a strained and unstrained condition;

Figure 3(c) shows a graphical representation of the strained sheet of graphene, as predicted by a Molecular Dynamics simulation using the MMP potential, that is the subject of
5 Figures 3(a) and 3(b);

Figure 4(a) shows the band structure at the Dirac points of a first region of the sheet of graphene shown in Figure 4(c) in a strained and unstrained condition, as calculated by tight binding;

Figure 4(b) shows the phonon dispersion curve for the first region of the sheet of
10 graphene of Figure 4(c) in a strained and unstrained condition;

Figure 4(c) shows a graphical representation of the strained sheet of graphene, as predicted by a Molecular Dynamics simulation using the MMP potential, that is the subject of Figures 4(a), 4(b), 4(d) and 4(e);

Figure 4(d) shows the band structure at the Dirac points of a second region of the sheet
15 of graphene shown in Figure 4(c) in a strained and unstrained condition, as calculated by tight binding;

Figure 4(e) shows the phonon dispersion curve for the second region of the sheet of graphene of Figure 4(c) in a strained and unstrained condition;

Figure 5(a) shows a high-resolution electron microscopy (HREM) image of a single layer
20 of graphene with a ripple surrounded by hydrocarbon contamination;

Figure 5(b) shows a Fast Fourier Transform (FFT) of the image of Figure 5(a);

Figures 5(c) to 5(j) each show an Inverse Fast Fourier Transform (IFFT) with a filter chosen to either match the exact a-plane spacing (Figures 5(c) to 5(f)) or spacings smaller than those of the a-planes (Figures 5(g) to 5(j));

Figure 6 shows a schematic cross-sectional view of an electronic structure in
25 accordance with another embodiment of the present invention;

Figure 7 shows an image of a test structure having contacts with varying spacings disposed on graphene;

Figure 8 shows a plot of Raman measurements of a test structure in accordance with
30 that shown in Figure 7;

Figure 9 shows a plot of Raman measurements of further test structures in accordance with that shown in Figure 7;

Figure 10 shows a key indicating tensile strain and compressive strain in respect of the plots shown in Figures 11 and 12;

Figure 11 shows an plot of strain measured across an electronic structure in accordance
35 with that shown in Figure 6;

Figure 12 shows a further plot of strain measured across an electronic structure in accordance with that shown in Figure 6,

Figure 13a shows a silica surface with four layers of graphene between two parallel electrodes;

5 Figure 13b is a cross sectional view along line A of Figure 13a;

Figure 13c is a cross sectional view along line B of Figure 13a;

Figure 13d is a three dimensional height image of Figure 13a;

Figure 14a is a three dimensional height image of part of four layers of graphene suspended across a hole in a substrate;

10 Figure 14b is a cross sectional view along line C of Figure 14a; and

Figure 14c is an enlarged view of a part of the four layers of graphene of Figure 14a..

DETAILED DESCRIPTION

[0050] Figure 1 shows an example of an electronic structure 10 in accordance with an embodiment of the present invention. The electronic structure 10 of Figure 1 is not drawn to scale and exaggerated dimensions are used to improve the reader's understanding. The electronic structure 10 comprises a layer of graphene 12 with a periodic structure 14 disposed thereon. The layer of graphene 12 may include one or more sheets of graphene. The periodic structure 14 has features in the form of apertures 14a that are repeated such that the periodic structure has a periodicity P along a first axis 100. The periodic structure 14 overlays the graphene but the graphene 12 is exposed (i.e. not overlaid) in the areas beneath the apertures 14a. Thus, the apertures 14a define enclosed regions of the layer of graphene 12.

[0051] It is found that the presence of the periodic structure 14 on the layer of graphene 12 gives rise to strain in the graphene 12. In response, morphological ripples form in the graphene 12 to counter the external strain induced by the periodic structure 14. However, the formed ripples do not result in a full relaxation and are found to exhibit a different strain component (shear) to the ones externally applied (by the periodic structure 14), together with internal relaxation. There is therefore a breaking of the hexagonal symmetry of the graphene 12 into two sublattices. Such induced strain results in a modification of the band gap around the Dirac point. That is, in contrast to unstrained graphene which exhibits a zero band gap and is metallic in nature, strained graphene having morphological ripples exhibits regions with a significant band gap opening in the proximity of the Dirac point and thus exhibits semiconducting behavior. Therefore, the morphological ripples include semiconducting regions as a result of the strain induced in the graphene 12 by the periodic structure 14.

35 [0052] The present invention is not limited to an electronic structure including a periodic

structure having the precise form shown in Figure 1. Indeed, any suitable periodic structure 14 may be disposed on the layer of graphene 12 for inducing the strain required to generate the formation of ripples and hence result in the graphene having semiconducting regions. In some embodiments, the periodic structure 14 is arranged so as to define enclosed regions of graphene 12. Such enclosed regions may be entirely bound by the periodic structure 14 or they may be bound about a discontinuous perimeter by the periodic structure 14. The periodic structure 14 may have a periodicity in any direction, irrespective of the symmetry of the pattern. The symmetry of the periodic structure 14 need not necessarily have square, rectangular or circular symmetry on the surface of the layer of graphene 12 and could have any repeatable design involving any geometrical form involving any number of sides and angles. The periodic structure 14 may be defined by a combination of a plurality of patterns where the plurality of patterns may or may not have the same periodicities.

[0053] In certain embodiments, the periodic structure 14 may have a periodicity of at least 8 nm along a single direction, and in some preferable embodiments the periodic structure 14 may have a periodicity of at least 10 nm along a single direction. The periodicity of the morphological ripples may preferably be at least 8 nm, and further preferably may be at least 10 nm along a single direction. The morphological ripples may each have an amplitude of at least 0.4 nm, and preferably may each have an amplitude of between 0.4 nm and 0.6 nm. The amplitude of the morphological ripples is defined as the height and depth of the hills and troughs formed by the ripples, respectively. The strain induced by the periodic structure is preferably greater than 0.6% so as to produce semiconducting regions with large band gaps.

[0054] The described preferable embodiments may exhibit strong morphological ripples that include semiconducting regions having a band gap which may be at least 0.1 eV. Alternatively, the described preferable embodiments may exhibit strong morphological ripples that include semiconducting regions wherein the Fermi Energy is shifted compared to the Dirac point thereby spontaneously producing an excess population of electrons in the conduction band of the graphene. This effect is equivalent to n-doping in semiconductor materials. The shift of the Fermi Energy relative to the Dirac point may be at least 50 meV, and may preferably be about 65 meV.

[0055] Electronic structures in accordance with embodiments of the present invention may have semiconducting regions having a band gap opening of at least 0.1 eV, at least 0.15 eV or at least 0.2 eV.

[0056] The distribution and band gap of the semiconducting regions may be tuned by the selection and/or modification of the form and periodicity of the periodic structure 14 disposed on the layer of graphene 12.

[0057] The periodic structure 14 may be deposited or transferred onto the layer of graphene 12. For example, the periodic structure 14 may be deposited on the layer of graphene 12 by lithography (electron beam lithography, for example). Alternatively, the layer of graphene 12 may be deposited or transferred onto the periodic structure 14 by any suitable method. The periodic structure may be made of any atomic species and compounds that may or may not contain carbon atoms. Examples of suitable materials for the periodic structure include (but are not limited to) any one or more of gold, aluminium, copper, TiAu, SiO₂, CH₄, and Al-PMGI. Indeed, we believe that metals, non-metals, insulators, semiconductors (organic and inorganic) and combinations of two or more may be deployed as the periodic structure.

[0058] . Unlike prior art methods where the graphene structure is modified by atomic substitution or the inclusion of different atoms from that of carbon (i.e. doping), the periodic structure 14 of the present invention is bonded to the layer of graphene 12 by direct chemical bonding (e.g. ionic or covalent bonding) and/or by Van der Waals interaction.

[0059] The layer of graphene 12 of the electronic structure 10 may be produced by any suitable method. In certain embodiments, the layer of graphene 12 may be produced by chemical vapour deposition (CVD). In other embodiments, the layer of graphene 12 may be produced by mechanical exfoliation of graphite. In certain embodiments within the scope of the present invention, multiple layers of graphene may be provided and the periodic structure is disposed on a top layer of the multiple layers.

[0060] In accordance with certain embodiments of the present invention, the electronic structure 10 may form part of an electronic device. For example, the electronic structure 10 may include electrical contacts suitable for incorporating the electronic structure in a wider electronic system. In accordance with embodiments of the present invention, the electronic structure 10 may form part of a complementary-metal-oxide semiconductor (CMOS) device.

The electronic structure 10 of the present invention may be fabricated in a manner that is CMOS compatible. This is in contrast to prior art methods for modifying the band structure of graphene.

[0061] In accordance with embodiments of the present invention, the electronic structure 10 may form part of an optical detector, which may, for example, be an infra-red (IR) detector.

[0062] In accordance with embodiments of the present invention, the electronic structure 10 may form part of a pressure sensor where external pressure applied to the electronic structure may result in further alteration of the band structure, where such alterations may be detected and attributed to an applied external pressure.

[0063] Figure 6 shows an electronic structure 10' according to an alternative embodiment of

the present invention. The electronic structure 10' includes a substrate layer 16 which may be made of silicon, for example, and a layer of graphene 12. The layer of graphene 12 may include one or more sheets of graphene. The layer of graphene 12 has a first side 12a and an opposing second side 12b, and has a first periodic structure 14 disposed on the first side 12a and a second periodic structure 14' disposed on the second side 12b. The second periodic structure 14' is disposed on the substrate 16 and may serve to support the layer of graphene 12 thereon.

[0064] The first periodic structure 14 includes a first material 18 and a second material 20 that is dissimilar to the first material 18. In one embodiment, the first material 18 may be a metal such as gold and/or the second material 20 may be a metal such as titanium. In other embodiments, any suitable one or more materials may form the first periodic structure 14. The second periodic structure 14' includes a first material 22 and a second material 24 that is dissimilar to the first material 22. In one embodiment, the first material 22 may be a polymer such as a polymethylglutarimide (PMGI) resist and/or the second material 24 may be a metal such as aluminium. In other embodiments, any suitable one or more materials may form the second periodic structure 14'.

[0065] In certain embodiments, either or both of the first periodic structure 14 and second periodic structure 14' may be made of multiple materials which may additionally be formed in layers. In the embodiment shown in Figure 6, the first periodic structure 14 has a periodicity P1 and the second periodic structure 14' has a periodicity P2 that is not equal to P1. In alternative embodiments, the first periodic structure 14 and the second periodic structure 14' may have the same periodicities (i.e. P1 may equal P2).

[0066] The first periodic structure 14 defines first apertures 14a on the first side 12a of the layer of graphene 12, i.e. areas on the first side 12a of the layer of graphene 12 where no first periodic structure 14 is disposed. Similarly, the second periodic structure 14' defines second apertures 14a' on the second side 12b of the layer of graphene 12, i.e. areas on the second side 12b of the layer of graphene 12 where no second periodic structure 14' is disposed. That is, in the regions of the second apertures 14a', the layer of graphene 12 is suspended over the substrate 16.

[0067] In order to reveal the strain-ripple formation mechanism, molecular dynamics (MD) simulations were used with a recently proposed interatomic many-body empirical potential⁴ (MMP potential) which has been extensively tested for Group IV Silicon and Germanium

⁴ Monteverde, U., Migliorato, M. A., Pal, J. and Powell, D., Elastic and vibrational properties of group IV semiconductors in empirical potential modelling, J. Phys.: Condens. Matter 25, 425801-1-10 (2013).

semiconductors. The MMP potential overcomes the classic shortcomings observed in short range pair potentials, i.e. the impossibility of obtaining a satisfactory representation of elastic and vibrational properties with a single set of parameters. This adversely impacts on the ability to model thermodynamic properties such as the coefficient of thermal expansion.

5 **[0068]** The MMP for carbon-based crystals was used. Further to satisfying the criteria of correctly and simultaneously predicting vibrational and elastic properties of diamond, the same parameter set was also able to correctly predict the essential features of other crystal phases such as graphene.

10 **[0069]** Figures 2(a) and 2(b) show predicted phonon dispersion curves for C-diamond (Figure 2(a)) and graphene (Figure 2(b)), respectively, calculated using the MMP potential. Experimental data are represented by open circles in C-diamond and Graphene. The MMP potential, with a single set of parameters fitted to the C-Diamond phase also accurately reproduces the vibrational spectrum of 2D graphene, indicating that π -bonding, which is not included in the MMP separately from σ -bonding, is sufficiently well described in the force field equations.

15 **[0070]** Using MD, ripple formation of a graphene sheet was investigated under different strain conditions to include tensile and compressive pressures. Both hydrostatic strain and strain along the ZigZag/Armchair directions were considered, which are respectively referred to hereinafter as x and y since such is the alignment of the model structure in respect of the Cartesian axes.

20 **[0071]** The MD simulations, comprising around 4000 atoms, started from an atomically flat single graphene sheet. Pressure was simulated by rigidly displacing the atoms on the plane and taking the resulting increase/decrease of the simulation box into account. Energy minimization then took place. The initial small movement of the atoms in and out of the ideal plane was soon replaced by larger movements and ultimately a visible change in the morphology of the overall structure. Eventually ripples spontaneously formed and exhibited a regular pattern.

25 **[0072]** Two specific cases were considered for a 10 x 10 nm graphene sheet. Firstly, compressive strain in the x direction of 3.5% together with tensile strain in the y direction of 3.5% (Figure 3(c)), and secondly, compressive strain of 3.5% in both the x and y directions (Figure 4(c)).

30 **[0073]** In the first case, static and wave front ripples orthogonal to the x direction were formed with around 0.5 nm (5 Å) height or depression for hills and troughs respectively. The expected wavelength of the ripples was around 10nm (one ripple every 10nm). In the second case a

more complex morphology was observed. Ripples appeared in a regular pattern, sinusoidal in nature, with fluctuation, again, of around 0.5 nm (5 Å) height or depression for hills and troughs respectively. The expected wavelength of the ripples was, again, around 10nm. Such peculiar sinusoidal shape is a direct response to hydrostatic compressive pressure and can be thought of as resulting from two colliding wave fronts orthogonal to each other. Scanning Tunneling Microscopy imaging has reported ripples in suspended graphene with a characteristic V-shape which matches the result of this simulation, suggesting that hydrostatic pressure was present in the experimental sample.

[0074] The distortion of the atomic bonds on the ripples was also analysed. In Figures 3(c) and 4(c) bonds are coloured from red to blue to represent tensile to compressive strain, compared to the equilibrium bond length of a flat graphene sheet ($LC/\sqrt{3} = 1.73\text{\AA}$). Green indicates low (or zero) strain.

[0075] It is clear from the inset in Figures 3(c) and 4(c) that a non-uniform strain distribution is predicted, the presence of which has been experimentally observed by Raman spectroscopy mapping of strain effects on a graphene sheet deposited on a flexible substrate.

[0076] The non-direct correspondence between ripples and stress can be explained by a loss of hexagonal symmetry in graphene, which produces the 2D equivalent of the Kleinman displacement for a 3D diamond structure (e.g. the rigid displacement of the two face centered cubic (fcc) sublattices with respect to each other in a diamond structure). In the sp^3 tetrahedral bonding, when uniaxial shear strain exists, the central atom relaxes causing the compression of one bond and the stretching of the other three bonds. What was observed and shown in the insets of Figures 3(c) and 4(c) is an equivalent behaviour for the sp^2 triangular bonding system. Such non-uniformity is verified as being a function of the applied external pressure, albeit as a threshold-activated process only for strains larger than $0.7\pm0.1\%$. A further non-intuitive observation is that while in the wave front ripple stretched and compressed bonds coexist throughout the sheet, strain switches from predominantly tensile to compressive along the ridge of the ripple (Figure 4(c)) which intuitively provides localised graphene areas (nanostructures) adjacent to each other but with very different strain and hence induced changes to the band structure as is shown further below.

[0077] In Figures 3(a), 4(a) and 4(d) the tight binding calculated band structure in the proximity of the Dirac point for particular areas of the graphene sheet is shown. The red lines are compared to the unstrained case (black lines). Non hydrostatic strain (e.g. shear or internal displacement) introduces non equivalencies in the high symmetry points, so that the K and M points are no longer degenerate and both the band structure and phonon dispersions need to be described with the addition of the K' and M' points.

[0078] Significant shear strain induced band gap opening has been predicted, measured and also deliberately introduced as result of patterned hydrogenation.

[0079] For both types of ripples the band gap opens. The opening is of 0.22eV (0.11eV) near the K' (K) point for the wave front ripple and 0.21eV (0.12eV) at the K (K') point for the sinusoidal ripple, albeit in this case only in the regions with predominantly tensile strain. In the compressive strain regions the band gap opening is negligible and the only difference compared to the unstrained case is that the Dirac point is found below the Fermi energy by 69 meV, thus exhibiting strain activated spontaneous n-doping characteristics.

[0080] It is also noticeable that for the wave front ripple the phonon dispersion is very different compared to the unstrained case, with a distinct change in the density of states for the optical phonon modes. This is not observed in the sinusoidal ripples where the density of states remains similar to that of unstrained graphene (black line).

[0081] One possible source of strain while performing electron microscopy is most likely imposed by the fabrication method (suspension over holey carbon grids) and the hydrocarbon (CH₄) contamination (pinning), which covers ~50% of the graphene.

[0082] Of the various techniques available to analyse these ripples in freestanding graphene, the most direct method is to reveal them directly through focus changes in electron microscopy images. In the present case, the non-flatness of the graphene sheet was observed by analysis of colour differences. In particular, these colour differences can be related to physical heights which correspond to undulations with wavelengths of typically around 10 nm and amplitude up to 0.5 nm (5 Å), identical to the height/depression predicted in the simulations of Figures 3(c) and 4(c). In this way it is common to observe the wave front type ripples. However, this requires corrected scanning transmission electron microscopes with very small distances over which to achieve focus changes.

[0083] Another method is to apply a precise and narrow bandwidth filter to the Fast Fourier Transform (FFT) (i.e., the computationally derived electron diffraction pattern) of a high-resolution lattice image. In the present case a ring filter corresponding to a width, in real space, of 0.0002 nm (0.002 Å) was applied to high resolution electron microscopy phase contrast images obtained in a Jeol ARM200F transmission electron microscope. The filter radius was changed corresponding to fractions of an Angstrom, down to steps of 0.0002 nm (0.002 Å) around the diffraction spot maxima. The shortening of the graphene a-lattice spacing arising from lattice projections of undulated regions is of the order of 0.0002-0.0005 nm (0.002-0.005 Å), so colour images in Figures 5(c)-(j) represent top/bottom and flanks of undulations in focus. The brighter colours (yellow/orange) indicate higher intensity in places where the

chosen/filtered-out lattice spacing is most clearly seen in the images, whereas less pronounced intensity (blurring, blue hues) can be seen places where the lattice spacings are not precisely congruent with the filter frequency. Additionally, in order to demonstrate the undulation effects, it is less important to identify the exact position of hills and troughs in the images, than to demonstrate the change in colour in a given location from yellow to blue with change of the corresponding filter frequency; this colour change is proof of the change in the projected lattice plane distance arising due to, in the graphene sheet of Figure 5(a), ripples of ~ 0.2 nm height/depth. Lattice plane distances can also change due to compressive/tensile strain, and hence the overall effect has a twofold origin. However, it is possible, to a large extent, to identify and separate the two origins by studying Inverse Fast Fourier Transforms (IFFTs) of individual sets of lattice planes as shown in Figures 5(c) to 5(j). All lattice spacings of planes, which have directions with a component parallel to the ripple front will show some contraction at the ripple flank due to the projection. On the other hand, if regions where lattice planes cross a curved ripple front/flank perpendicularly show high filter passes (e.g. in Figure 5(g)), this indicates tensile strain. Also, if regions with lattice plane spacings larger than the a-plane spacing are detected, this implies tensile strain in these areas. Hence combining data of the filtered intensity and the direction in which the corresponding lattice planes cross the ripple front/flank can provide information, further to the mere existence and shape of ripples and their shape, about tension/compression within this shape.

[0084] Figures 5(c)-(j) show the hill, trough and flank of a ripple, which is a mixture of wave front and sinusoidal type. The flank direction is indicated in the high-resolution electron microscopy (HREM) image of Figure 5(a). This suggests, in accordance with the simulated results, that the hydrocarbon contaminants, visible in the micrograph of Figure 5(a) as surface platelets, result in a uniaxial strain, in this case, predominantly in the (xy)-direction. The ripple is observed to curve at the bottom left of the image, which introduces tensile strain (circled region in Figure 5(e)) as well as compressive strain (circled regions in Figures 5(g)-(h)) along the 'bend', again, in accordance with the strain calculation for the sinusoidal ripple (Figure 4(a)). The blue colouration along the wave front (straight) part in Figure 5(c) and Figure 5(g) as well as in the combined-effect image in Figure 5(f), arises from the projection shortening of the inclined bonds. From this analysis, it can be concluded that both uniaxial strain and hydrostatic strain are introduced by the hydrocarbons and their respective directions can be inferred by the resulting shape of the ripples (as indicated by the arrows shown in Figure 5(a)).

[0085] In summary, the molecular dynamics simulation of graphene has highlighted two major types of ripples: wave front and sinusoidal. Examples and strain patterns of both types of ripples are supported by transmission electron microscopy.

[0086] Ripples appear to arise in the presence of compressive strain in a single direction orthogonal to the wave front, or hydrostatic compression for the sinusoidal type. This suggests that manipulating strain on the surface of graphene can lead to control of the type of generated ripple.

- 5 [0087] The wavefront ripple leads to an appreciable band gap opening of 0.22 eV and a simultaneous detectable change in the phonon dispersion.

[0088] The sinusoidal case presents the most interesting strain pattern. Tensile and compressive strain is found on the opposite sides of the V-shape. Compressive and tensile strain results in opposite types of band structures, as the tensile strain region is the only one that exhibits a band gap opening of around 0.19 eV together with spontaneous n-doping characteristics. The surface of graphene therefore results in a sequence of doped and undoped semiconducting/metallic regions of nanoscale dimension, in close proximity to each other, and obtainable on demand by application of hydrostatic compression. Experimental electron microscopy shows how impurities can produce strain in the graphene structure.

- 15 [0089] The present invention exploits this phenomenon in a controllable and tunable manner by inducing strain so as to form morphological ripples and thereby manipulate the band structure of graphene in the proximity of the ripples. Electronic structures in accordance with the present invention may have a large surface area thereby increasing their usefulness, effectiveness and suitability for integration into electronic systems. Furthermore, fabrication methods in accordance with embodiments of the present invention are scalable and CMOS compatible thereby providing huge commercial potential.

[0090] Experimental evidence demonstrating the creation of strain due to periodic structures on graphene is set out below in relation to Figures 7 to 12. In particular, Figure 7 shows an optical image of a test structure made up of contacts 14 forming a test “periodic structure” 14 disposed on graphene 12. The contacts 14 are disposed at varying distances apart from one another and define a 1 μm gap, a 3 μm gap, a 5 μm gap and a 10 μm gap. Raman measurements of the strain (the commonly known as G peak in Raman measurements is widely known to exhibit blue/red shift towards higher energies in response to compressive/tensile strain, respectively) of the graphene 12 were obtained within the gaps at points 1 to 4 shown in Figure 7 and an additional measurement of the strain of the graphene 12 was obtained away from the contacts 14 to provide control data relating to an unstrained condition. Figure 8 shows the results of Raman measurements for Graphene (4 monolayers) deposited on a GaAs substrate with PdAu contacts on a layer of graphene 12 that included four sheets of graphene (i.e. “four layer graphene”, or 4LG). As can be seen from Figure 8, the graphene 12 exhibits strain in the gaps between the contacts 14 (relative to the unstrained

condition as determined by the control measurement).

[0091] Figure 9 shows the results of Raman measurements for Graphene (1 and 4 monolayers) deposited on a SiO₂ substrate with PdAu contacts on a layer of graphene 12 that included four sheets of graphene (i.e. "four layer graphene", or 4LG) and, separately for SiO₂ contacts 14 on a layer of graphene 12 that included one sheet of graphene (i.e. "one layer graphene", or 1LG). As can be seen from Figure 9, the graphene 12 exhibits strain in the gaps between the contacts 14 (relative to the unstrained condition as determined by the control measurement).

[0092] Figures 11 and 12 show images produced from Raman measurements that show the strain distribution on graphene 12 in the region of an aperture 14a formed by a periodic structure 14. Figure 10 shows a key demonstrating that green colour indicates an unstrained condition, whereas red indicates the presence of tensile strain, and blue indicates the presence of compressive strain. In both of Figures 11 and 12, within the region of the aperture 14a, regions 202 of compressive strain are exhibited and regions of tensile strain 200 are exhibited. This demonstrates that the periodic structure 14 has induced strain in the graphene 12 and indicates that the graphene 12 includes morphological ripples due to the presence of the periodic structure 14.

[0093] Turning now to Figures 13a to 13d, there is shown, in Figure 13a, an enlarged view of the 1 micron gap channel of Figure 7. Thus, a silica surface (not shown) has deposited or otherwise located thereon a pair of facing electrodes E1, E2 with a channel G therebetween. Located within the channel G are four layers of graphene, being constrained by the facing edges of the electrodes E1, E2.

[0094] Referring to Figures 13b and 13c the rippling of the graphene is clearly illustrated in Figure 13d. As the width of the channel G decreases (i.e. from Figure 13b to Figure 13c) the ripples become more densely packed and the total proportion of the channel which shows the rippling effect increases. In Figure 13b, the central ripple has an amplitude of about 60 nm and a width at the base of about 100 nm. In figure 13c, the central ripple has an amplitude of about 40 nm and a base width of about 160 nm, meaning that the areas under each central ripple are approximately equal. However, in Figure 13c the density of ripples has increased, and hence the proportion of the channel in which the rippling effect is demonstrated.

[0095] From our studies we believe that as the width of the channel decreases, and as the extent of rippling increases (in terms of the proportion of the area effected by the rippling phenomenon) the graphene layer will or may increase its semiconducting behavior.

[0096] Of course, this leads to the possibility of providing a patterned electrode array on a

substrate and depositing or otherwise locating graphene layers between the electrodes to generate an electronic structure.

[0097] Although we do not wish to be bound by any particular theory, we believe that the facing edges of the electrodes constrain the graphene layer, thereby generating the intralayer stresses which lead to the rippling effect. As we have convincingly shown above, the rippling leads to semiconducting regions in the graphene layer.

[0098] In our experiments the evidence of rippling diminished as the width of the channel increased to and beyond 10 microns, suggesting that on silica substrates at least there may be a limit to the width of the channel which allows for graphene to display the behavior.

[0099] In order to investigate the effect that the substrate had on the provision of the ripples we suspended layers of graphene across an aperture of dimensions 10 x 30 μ m. In this experiment the aperture was provided by optical lithography to create holes in a PMGI layer which was spincoated on to a silicon-containing substrate. We also believe that a lacey carbon grid or other materials could equally be used. Figure 14a shows a proportion of the suspended graphene layer GL bounded by the material of the grid GD by which it is constrained.

[00100] Figure 14b shows a cross sectional profile along the line C of Figure 14a and clear evidence of the rippling effect is indicated by the arrows. The scale of the cross section is such that the size of rippling is not immediately apparent but our measurements show that when constrained between a 10 micron gap (as in the case of Figure 14, a, b, c) the rippling effect is substantially greater than when the graphene layers are deposited or otherwise located on a substrate. Hence the substrate appears to be damping the rippling effect, at least at relatively large (e.g. up to and over 10 micron) channel widths, as compared to locating the layer of graphene over a hole or other region of free space.

[00101] Figure 14c provides further evidence of the rippling effect as indicated by the arrows.

[00102] Accordingly, our work convincingly shows that electronic structures comprising graphene having semiconducting regions can be fabricated, and have the ability to be scaled to commercially useful applications.

[00103] Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of them mean "including but not limited to", and they are not intended to (and do not) exclude other moieties, additives, components, integers or steps. Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

[00104] Features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

[00105] The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

19
CLAIMS

1. An electronic structure comprising:
a layer of graphene; and
5 a constraining member
wherein the layer of graphene is constrained by the constraining member to cause one or more morphological ripples in the layer of graphene thereby to generate semi-conducting regions in the layer of graphene.
- 10 2. An electronic structure according to Claim 1, wherein the constraining member induces strain in the layer of graphene.
3. An electronic structure according to Claim 1 or 2, wherein the constraining member is or comprises at least a part of a periodic structure.
- 15 4. An electronic structure according to Claim 3, wherein the periodic structure is arranged to induce strain in the layer of graphene such that the layer of graphene is morphologically rippled and includes semiconducting regions.
- 20 5. An electronic structure according to any preceding Claim, wherein the constraining member comprises one or more constraining elements.
6. An electronic structure according to any preceding Claim, wherein the constraining member and/or a constraining element comprises an electrode.
- 25 7. An electronic structure according to any preceding Claim in which the layer of graphene is located upon a substrate or is located above an aperture, hole or other region of free space.
- 30 8. An electronic structure according to any preceding Claim, wherein the constraining member comprises one or more constraining elements which elements are separated by a distance of of 40, 30 or 20 microns or less, for example 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 microns or less, for example in the nanometer range and/or the area defined by the area defined by
35 the constraining member may be less than $400\mu\text{m}^2$, say less than $350\mu\text{m}^2$, for example less than 340, 330, 320, 310, 300, 290, 280, 270, 260, 250, 240, 230, 220, 210, 200,

150, 100, 75, 50, 25, 10, 5, 4, 3, 2, $1\mu\text{m}^2$.

- 5 9. An electronic structure according to any preceding Claim, wherein said one or more ripples has an amplitude in excess of 0.1nm, for example in excess of 0.5nm, 1nm or 5nm, preferably in excess of 7.5 nm and most preferably in excess of 10nm, say from 5, 7.5 or 10 nm to 200nm.
10. An electronic structure comprising:
a layer of graphene, and
10 a periodic structure disposed on the layer of graphene and arranged to induce strain in the layer of graphene such that the layer of graphene is morphologically rippled and includes semiconducting regions.
- 15 11. The electronic structure of claim 3, 4 or 10, wherein the periodic structure has a periodicity of at least 8 nm along a single direction.
12. The electronic structure of claim 11, wherein the periodic structure has a periodicity of at least 10 nm along a single direction.
- 20 13. The electronic structure of claim 10, 11 or 12, wherein the morphologically rippled layer of graphene has a periodicity of at least 8 nm along a single direction.
14. The electronic structure of claim 13, wherein the morphologically rippled layer of graphene has a periodicity of at least 10 nm along a single direction.
- 25 15. The electronic structure of any of claims 10 to 14, wherein ripples of the morphologically rippled layer of graphene have amplitudes of at least 0.4 nm.
16. The electronic structure of claim 15, wherein ripples of the morphologically rippled layer of graphene have amplitudes of between 0.4 nm and 0.6 nm.
- 30 17. The electronic structure of any preceding claim, wherein the semiconducting regions of the layer of graphene are strained by 0.6% or more by the constraining element or the periodic structure.

18. The electronic structure of any preceding claim, wherein the constraining element or periodic structure is arranged so as to define enclosed regions of the layer of graphene.
- 5 19. The electronic structure of any preceding claim, wherein the induced strain includes shear strain.
20. The electronic structure of any preceding claim, wherein the semiconducting regions have a band gap opening of at least 0.1 eV.
- 10 21. The electronic structure of claim 20, wherein the semiconducting regions have a band gap opening of at least 0.15 eV, and preferably at least 0.2 eV.
- 15 22. The electronic structure of any of claims 1 to 19, wherein the Fermi Energy of the semiconducting regions is shifted relative to the Dirac point thereby spontaneously producing an excess population of electrons in the conduction band of the layer of graphene.
- 20 23. The electronic structure of claim 22, wherein the shift of the Fermi Energy relative to the Dirac point is at least 50 meV.
- 25 24. The electronic structure of claim 23, wherein the shift of the Fermi Energy relative to the Dirac point is about 65 meV.
- 30 25. The electronic structure of any preceding claim, wherein the constraining element or periodic structure comprises one or more of gold, aluminium, copper, TiAu, SiO₂ and CH₄.
26. The electronic structure of any preceding claim, wherein the constraining element or periodic structure is bonded to the layer of graphene by direct chemical bonding and/or by Van der Waals interaction.
- 35 27. The electronic structure of any preceding claim, wherein the constraining element or periodic structure includes a first periodic structure or constraining element disposed on a first side of the layer of graphene and a second periodic structure or constraining element disposed on a second side of the layer of graphene.

28. The electronic structure of any preceding claim, further comprising additional layers of graphene.

29. An electronic device including the electronic structure of any preceding claim.

5

30. A complementary-metal-oxide semiconductor (CMOS) device including the electronic structure of any of claims 1 to 29.

31. An optical detector including the electronic structure of any of claims 1 to 29.

10

32. The optical detector of claim 31, wherein the optical detector is an infra-red detector.

33. A pressure sensor including the electronic structure of any of claims 1 to 29.

15

34. A method of making an electronic structure, comprising the steps:

providing a layer of graphene; and

inducing strain in the layer of graphene by constraining the layer of graphene with a constraining member, for example by providing a periodic structure on the layer of graphene, wherein the strain induced by the constraining member or periodic structure causes the layer of graphene to be morphologically rippled and include semiconducting regions.

20

35. The method of claim 34, wherein the periodic structure is deposited on the layer of graphene.

25

36. The method of claim 35, wherein the periodic structure is deposited on the layer of graphene by lithography.

37. The method of claim 36, wherein the periodic structure is deposited on the layer of graphene by electron-beam lithography.

30

38. The method of claim 34, wherein the periodic structure is transferred onto the layer of graphene.

39. The method of claim 34, wherein the layer of graphene is deposited on the periodic structure.

35

40. The method of claim 34, wherein the layer of graphene is transferred onto the periodic structure.
- 5 41. The method of any of claims 34 to 40, wherein the periodic structure comprises one or more of gold, aluminium, copper, TiAu, SiO₂ and CH₄.
42. The method of any of claims 34 to 41, wherein the layer of graphene is produced by chemical vapour deposition.
- 10 43. The method of any of claims 34 to 41, wherein the layer of graphene is produced by mechanical exfoliation of graphite.
44. The method of any of claims 34 to 43, wherein the periodic structure has a periodicity of at least 8 nm along a single direction.
- 15 45. The method of claim 44, wherein the periodic structure has a periodicity of at least 10 nm along a single direction.
- 20 46. The method of any of claims 34 to 45, wherein the morphologically rippled layer of graphene has a periodicity of at least 8 nm along a single direction.
47. The method of claim 46, wherein the morphologically rippled layer of graphene has a periodicity of at least 10 nm along a single direction.
- 25 48. The method of any of claims 34 to 47, wherein ripples of the morphologically rippled layer of graphene have amplitudes of at least 0.4 nm.
49. The method of claim 48, wherein ripples of the morphologically rippled layer of graphene have amplitudes of between 0.4 nm and 0.6 nm.
- 30 50. The method of any of claims 34 to 49, wherein the semiconducting regions of the layer of graphene are strained by 0.6% or more by the periodic structure.

51. The method of any of claims 34 to 50, wherein the periodic structure is arranged so as to define enclosed regions of the layer of graphene.
52. The method of any of claims 34 to 51, wherein the induced strain includes shear strain.
53. The method of any of claims 34 to 52, wherein the semiconducting regions have a band gap opening of at least 0.1 eV.
54. The method of claim 53, wherein the semiconducting regions have a band gap opening of at least 0.15 eV, and preferably at least 0.2 eV.
55. The method of any of claims 34 to 52, wherein the Fermi Energy of the semiconducting regions is shifted relative to the Dirac point thereby spontaneously producing an excess population of electrons in the conduction band of the layer of graphene.
56. The method of claim 55, wherein the shift of the Fermi Energy relative to the Dirac point is at least 50 meV.
57. The method of claim 56, wherein the shift of the Fermi Energy relative to the Dirac point is about 65 meV.
58. The method of any of claims 34 to 57, wherein the periodic structure is bonded to the layer of graphene by direct chemical bonding and/or by Van der Waals interaction.
59. The method of any of claims 34 to 58, wherein the periodic structure includes a first periodic structure disposed on a first side of the layer of graphene and a second periodic structure disposed on a second side of the layer of graphene.
60. The method of any of claims 34 to 59, further comprising providing additional layers of graphene.

1/8

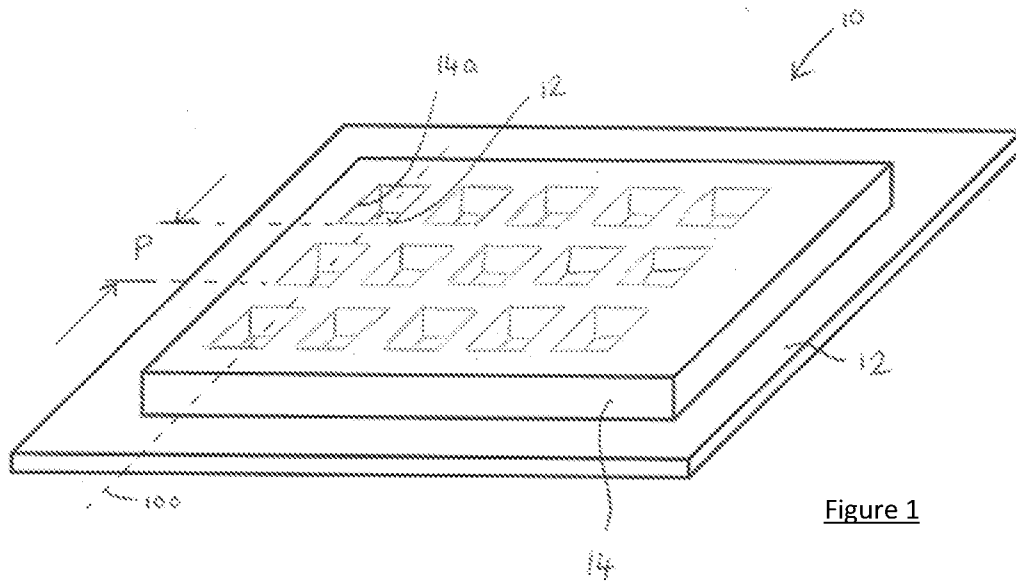


Figure 1

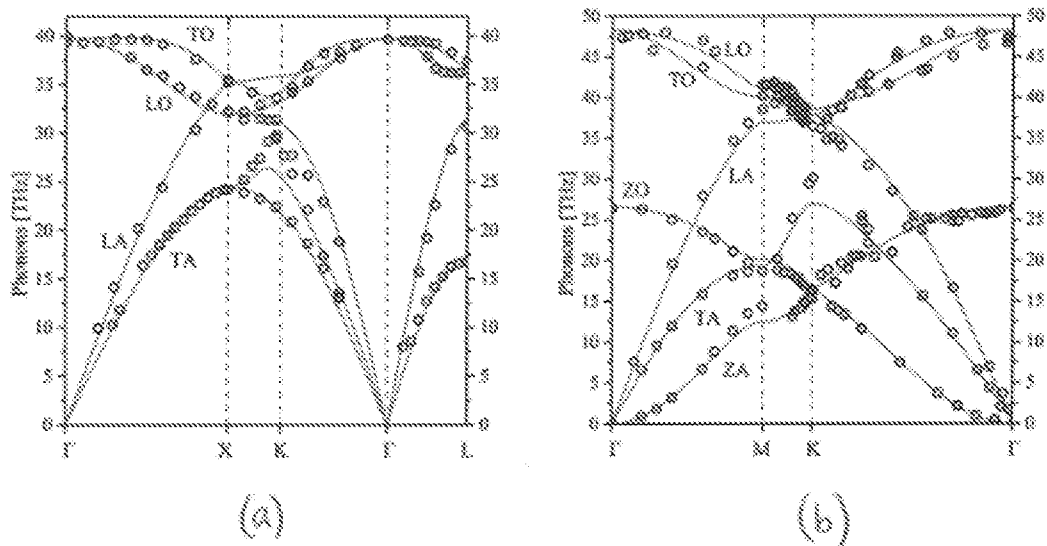


Figure 2

2/8

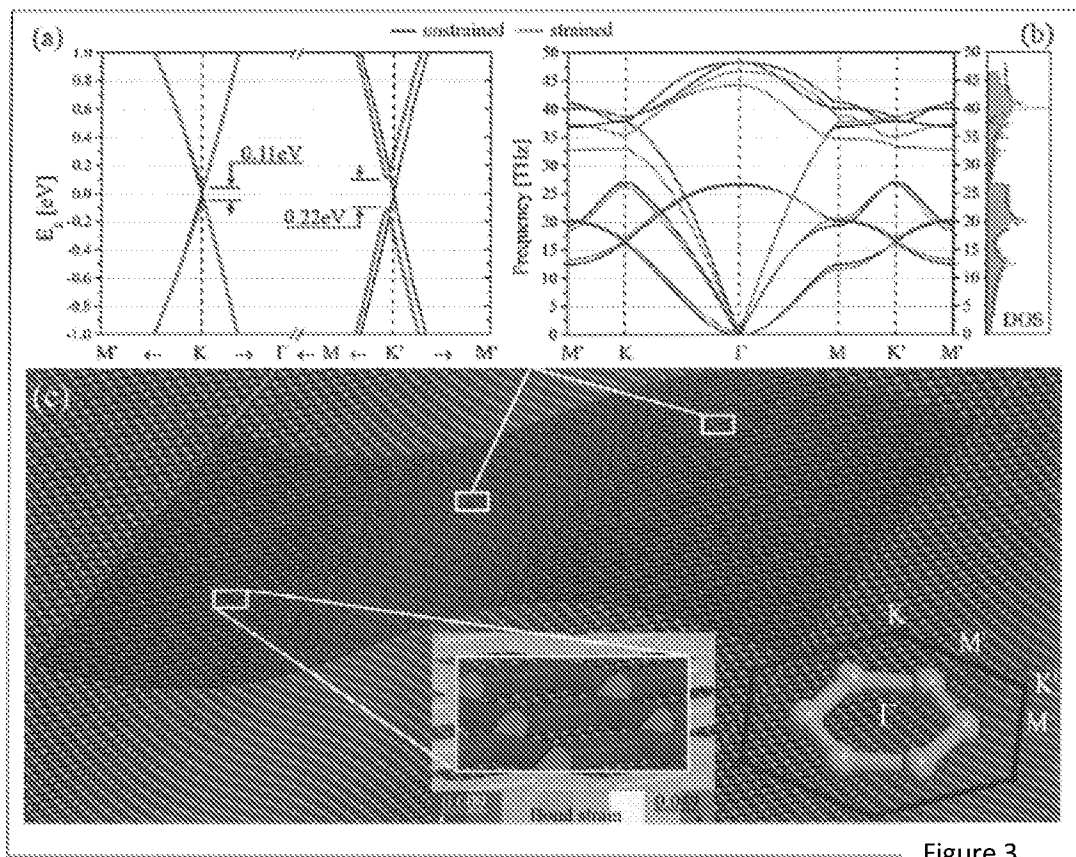


Figure 3

3/8

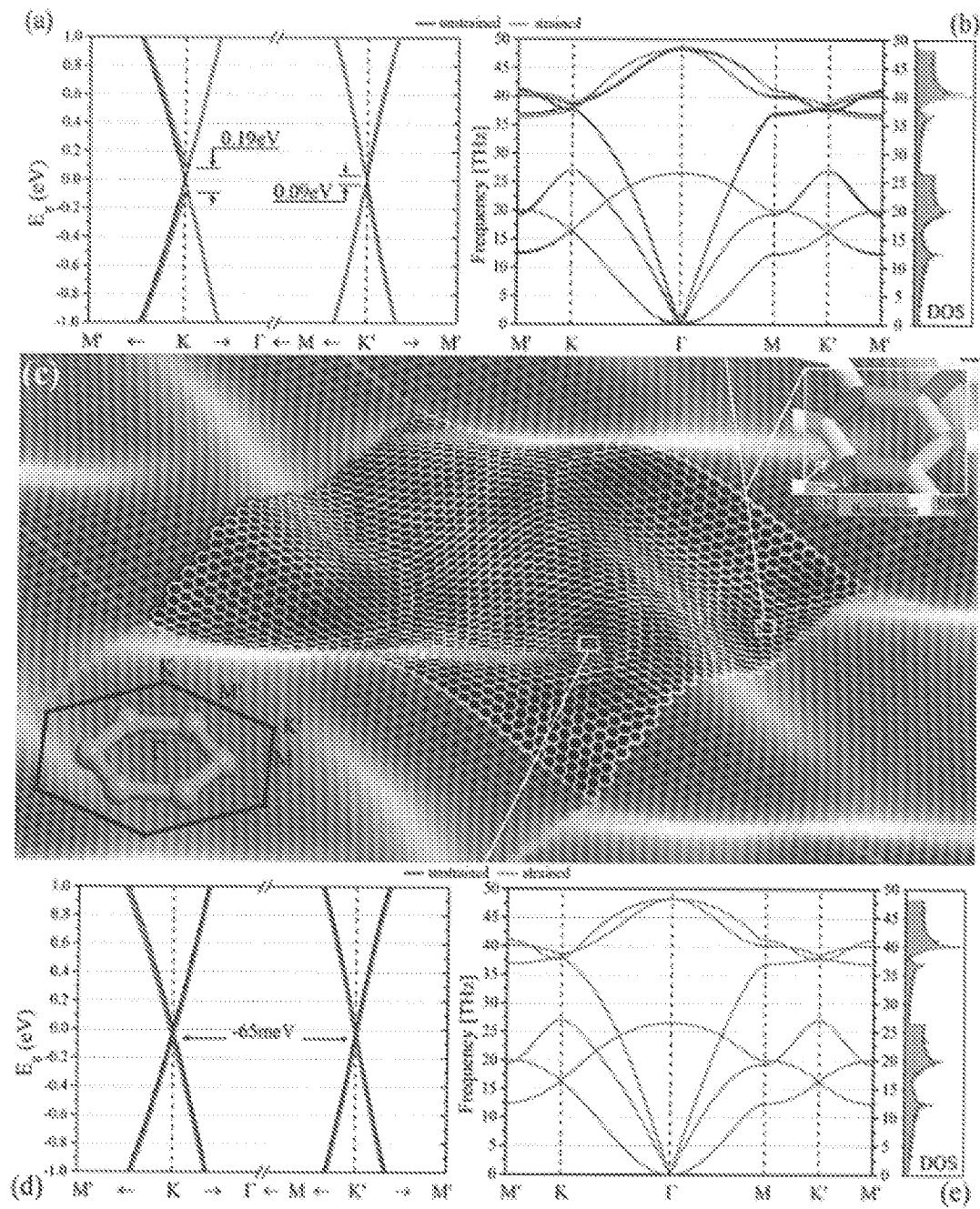


Figure 4

4/8

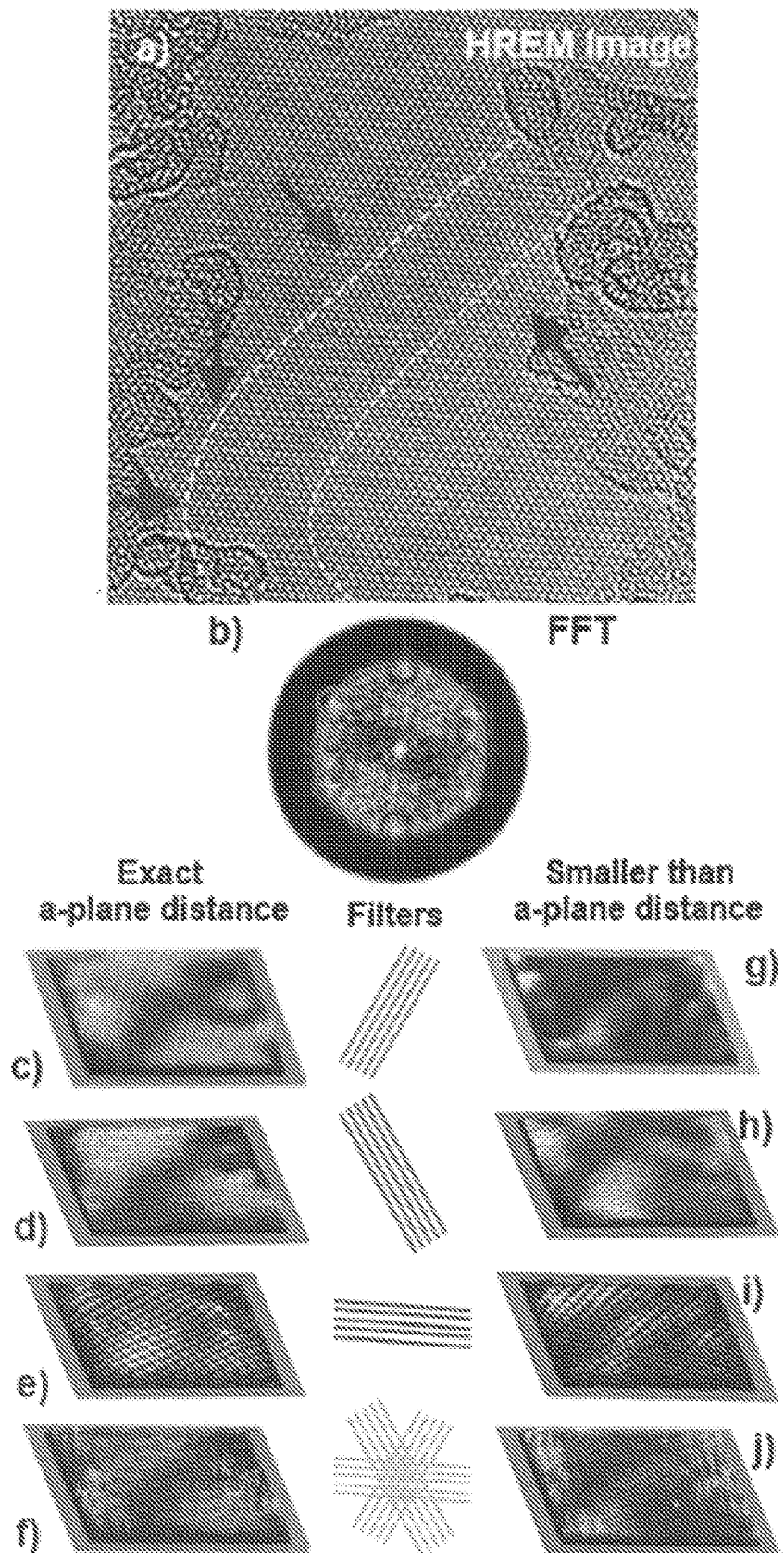


Figure 5

5/8

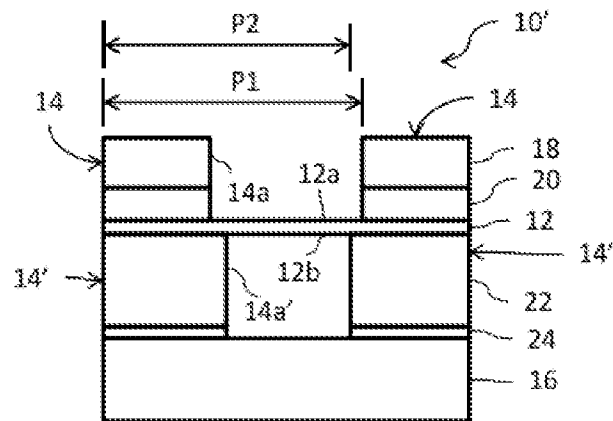


FIGURE 6

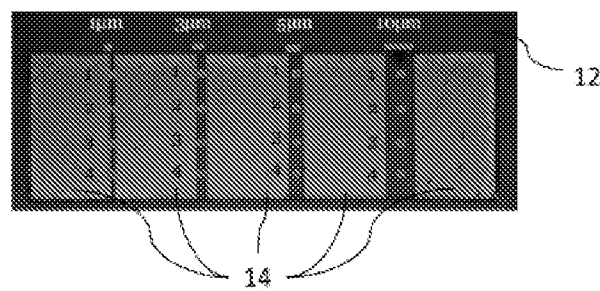


FIGURE 7

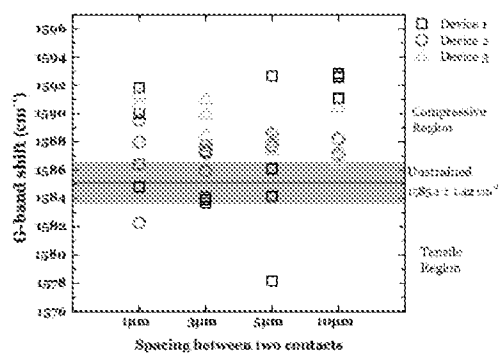


FIGURE 8

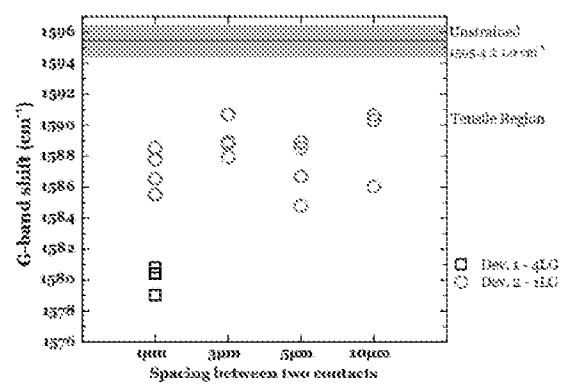


FIGURE 9

6/8

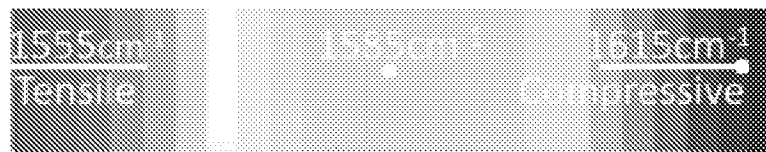


FIGURE 10

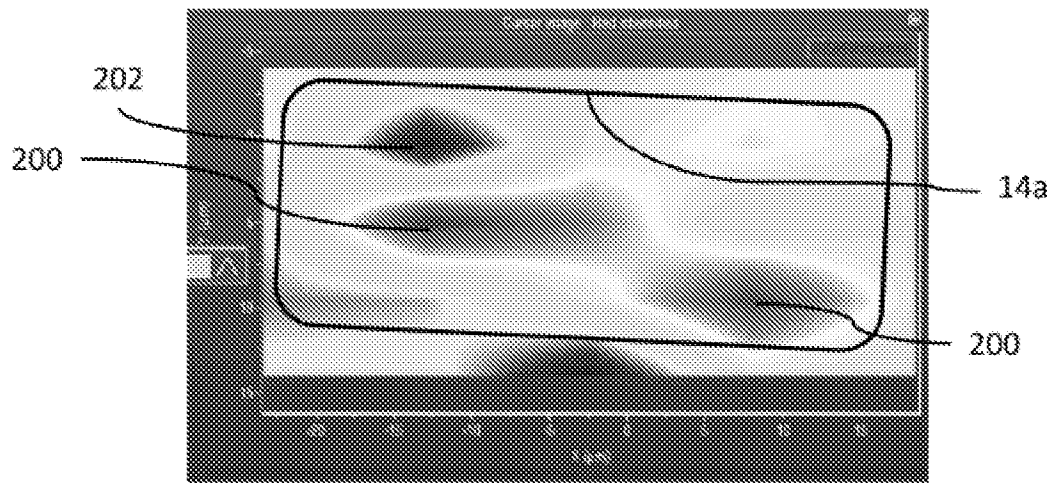


FIGURE 11

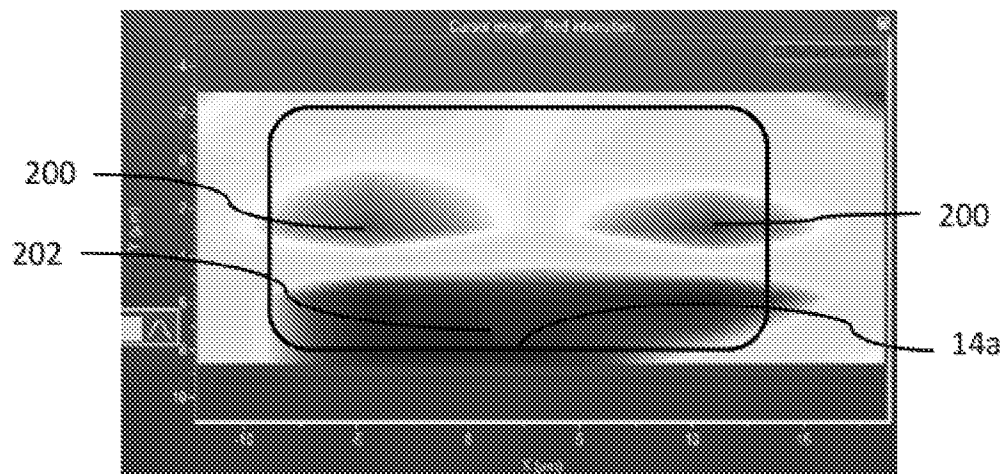


FIGURE 12

7/8

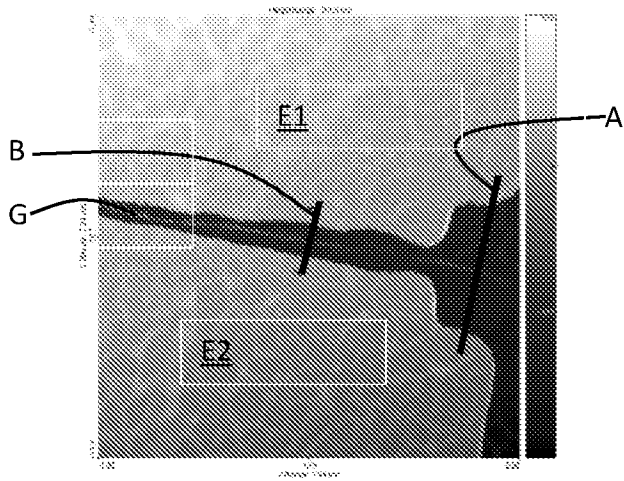


Figure 13a

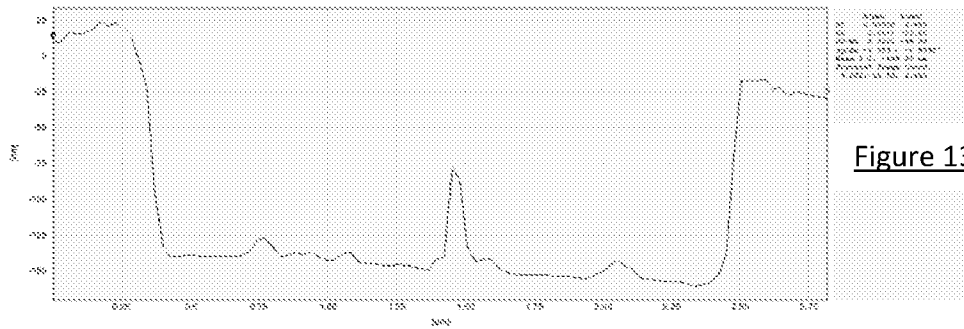


Figure 13b

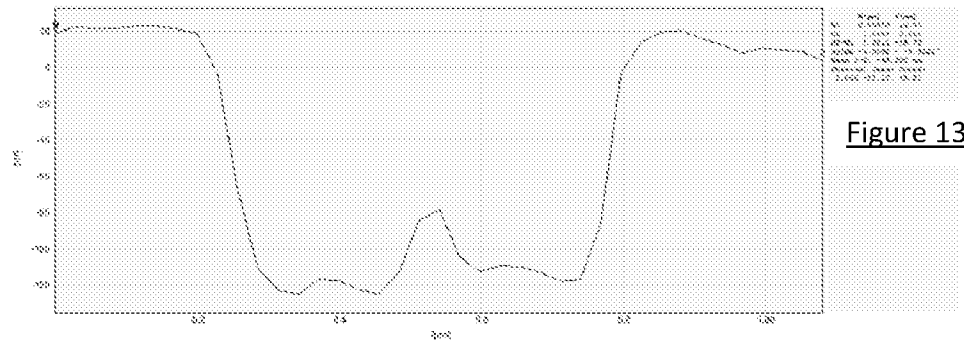


Figure 13c

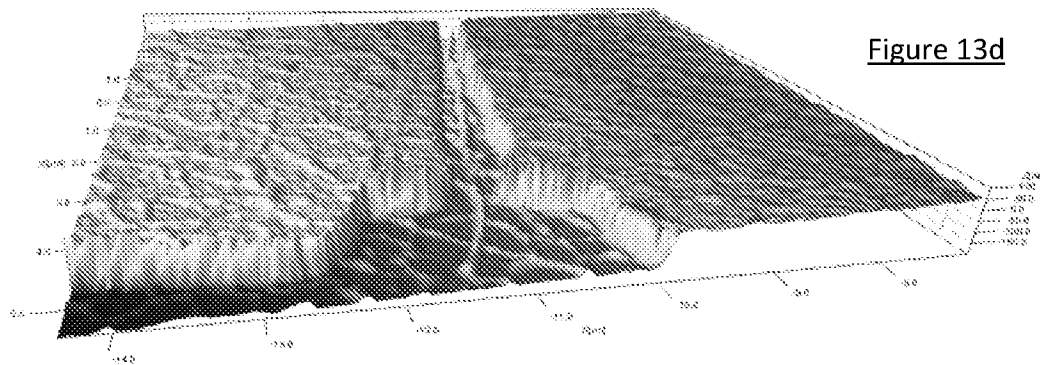


Figure 13d

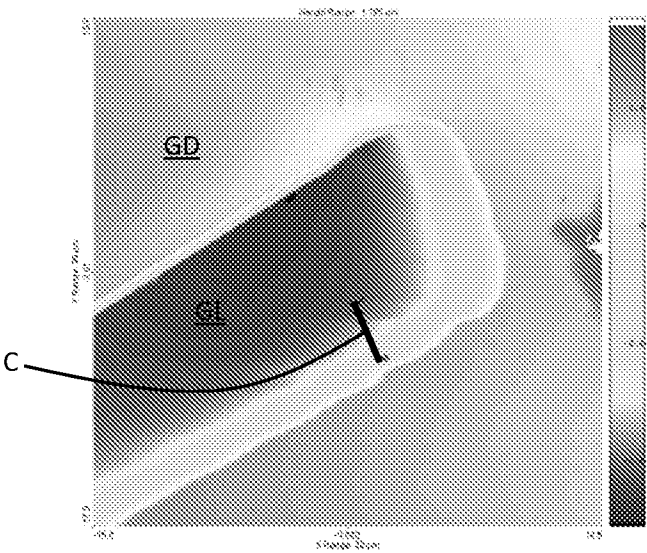


Figure 14a

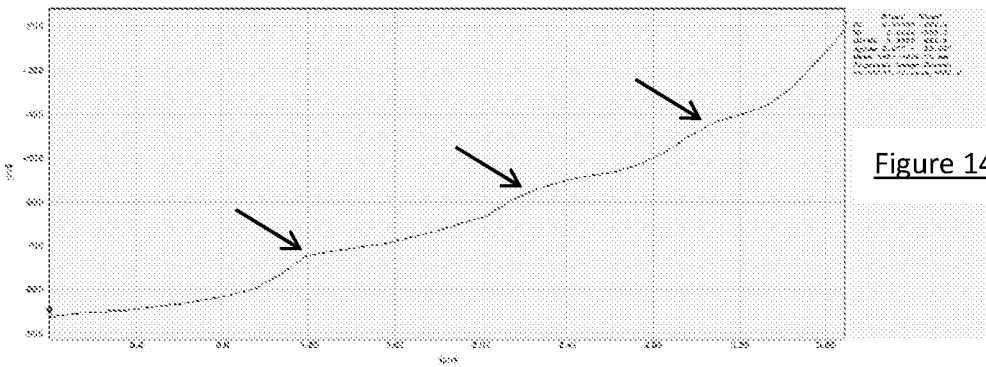


Figure 14b

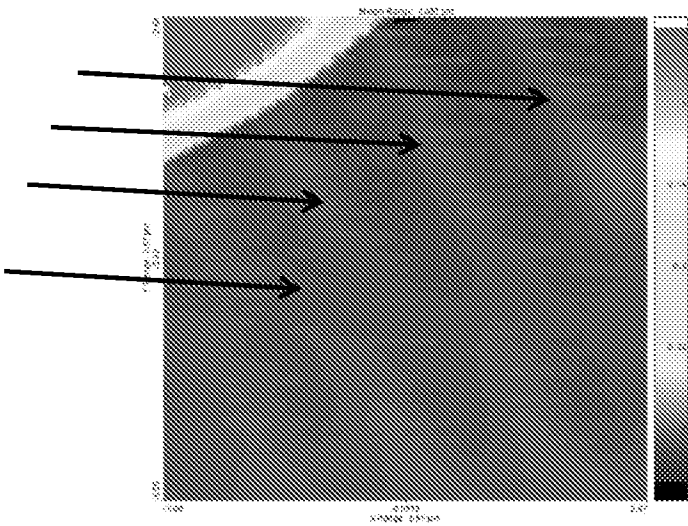


Figure 14c

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/051146A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L21/02
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)
H01L

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, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GUI GUI ET AL: "Electronic properties of rippled graphene", JOURNAL OF PHYSICS: CONFERENCE SERIES, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 402, no. 1, 20 December 2012 (2012-12-20), page 12004, XP020235605, ISSN: 1742-6596, DOI: 10.1088/1742-6596/402/1/012004 the whole document ----- -/--	1-9, 17-25, 28-32, 34,42, 43, 46-50, 52-57,60



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

"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

10 June 2015

Date of mailing of the international search report

17/06/2015

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

Meister, Martin

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2015/051146

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BAO W ET AL: "Controlled ripple texturing of suspended graphene and ultrathin graphite membranes", NATURE NANOTECHNOLOGY, NATURE PUBLISHING GROUP, LONDON, GB, vol. 4, no. 9, 1 January 2009 (2009-01-01) , pages 562-566, XP007916453, ISSN: 1748-3387, DOI: 10.1038/NNANO.2009.191 [retrieved on 2009-07-26] the whole document -----	1-9, 17-25, 28-32, 34,42, 43, 46-50, 52-57,60