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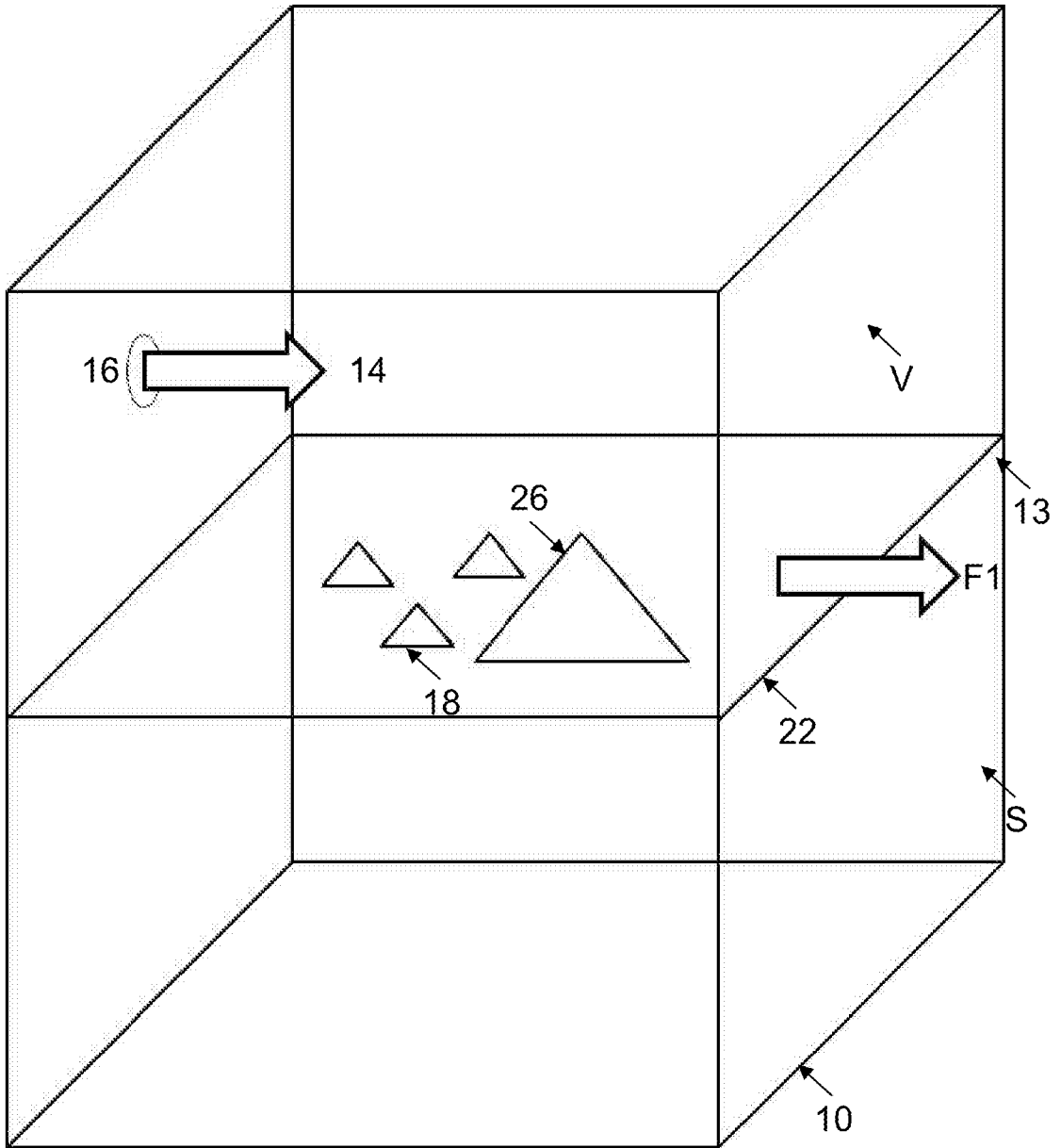


Fig. 1

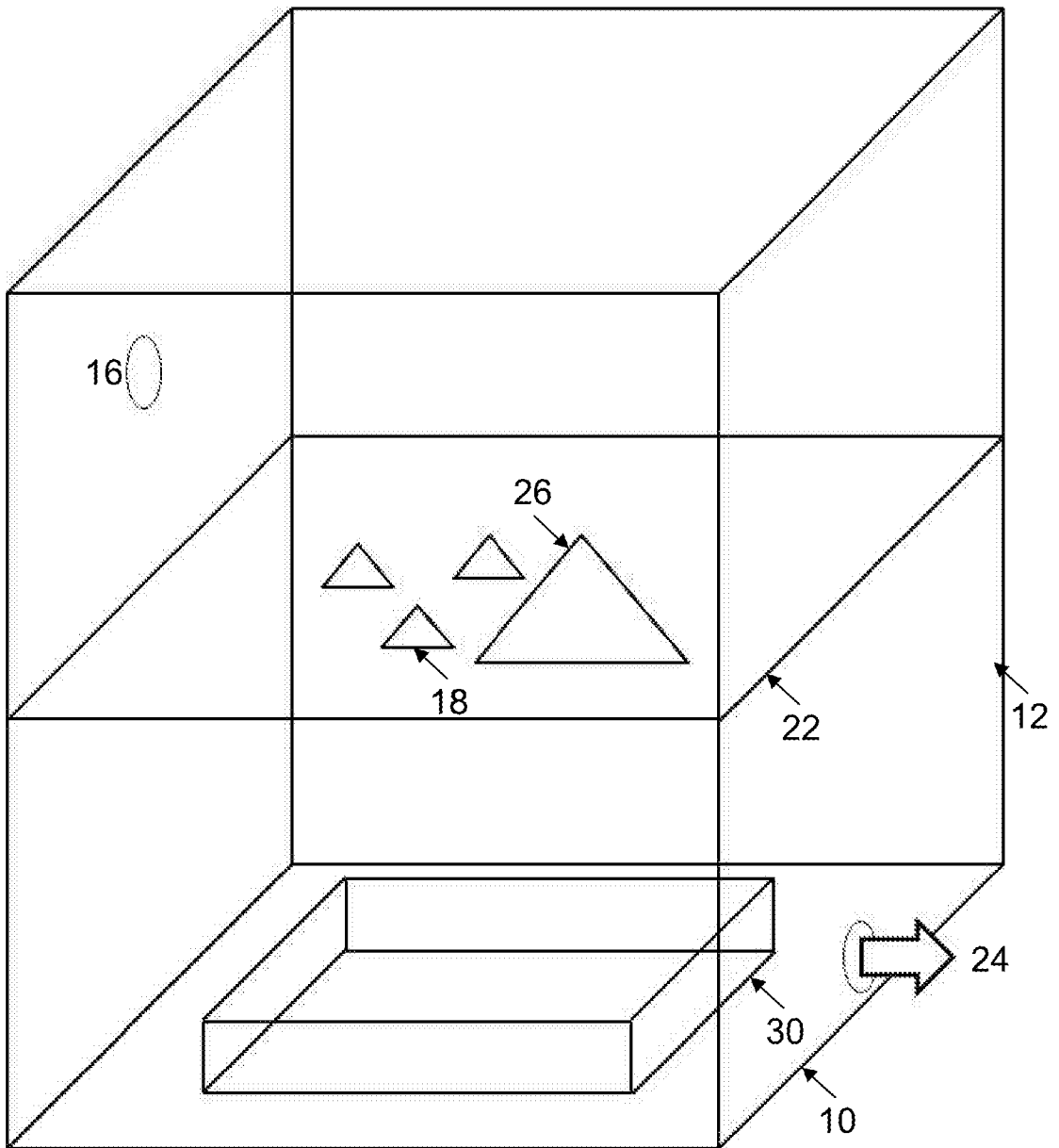


Fig. 2

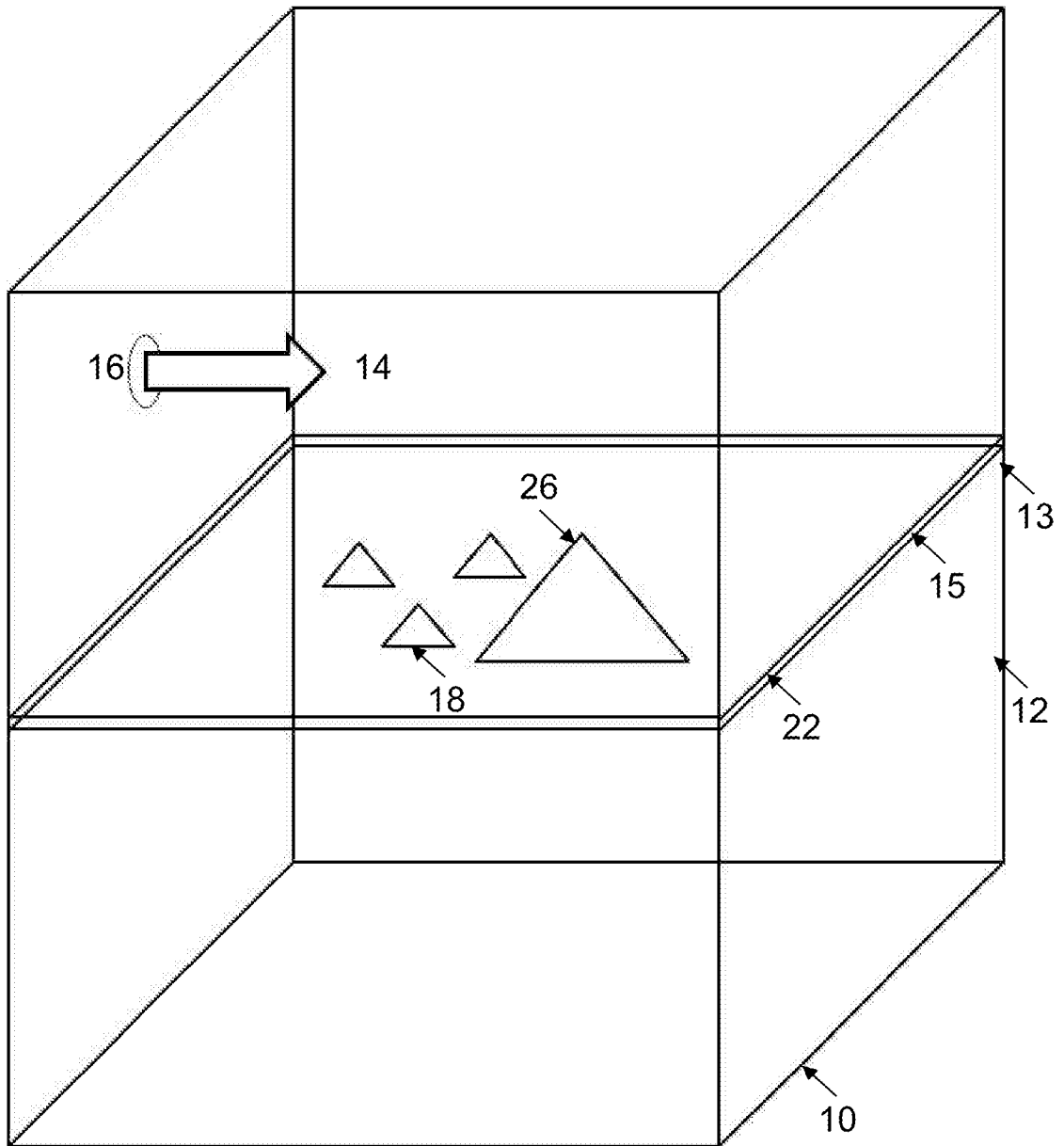


Fig. 3

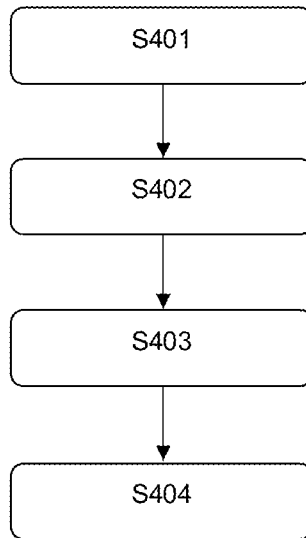


Fig. 4

Method and apparatus

Field

- 5 The present invention relates to a method of, and an apparatus for, manufacturing a sheet of a two-dimensional, 2D, material.

Background to the invention

- 10 Two-dimensional, 2D, materials (also known as single layer materials), are crystalline materials composed of a single layer of atoms. Generally, 2D materials may be categorised either as 2D allotropes (suffix –ene, for example graphene) or as compounds (suffix –ane or –ide). Generally, layered combinations of different 2D materials are called van der Waals
- 15 heterostructures. Generally, 2D materials may have properties superior to those of corresponding 3D materials. For example, graphene is a crystalline allotrope of carbon in the form of a nearly transparent (to visible light) one atom thick sheet. Graphene is hundreds of times stronger than most steels by weight and has the highest known thermal and electrical conductivities, displaying current
- 20 densities a factor of 1,000,000 greater than that of copper.

- Some 2D materials have found use in applications such as photovoltaics, semiconductors, electrodes and water purification. However, realisation of the properties of 2D materials in other applications, for example structural
- 25 applications, is limited. Particularly, sheets, for example pristine sheets, of 2D materials are limited in size to generally fragments (also known as platelets or chips).

- For example, graphene is material comprised of carbon just one atom thick.
- 30 Graphene is tougher than diamond and possesses many remarkable and desirable properties. For example, graphene has high thermal conductivity,

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electrical conductivity and a high strength to weight ratio. Graphene also exhibits remarkable optical properties. Graphene may be used in flexible touchscreens for mobiles, super-light batteries, aerospace composite materials and medical uses. However, conventional manufacturing methods only allow for small chips or platelets of graphene to be created, with large platelets suffering from lower quality, defects in structure or no longer monatomic layers since layers often end up stacked atop one another. These small chips of graphene often measure less than a few millimetres. It is evident that larger sheets of graphene will be needed to fulfil the potential applications of graphene. This is a difficult task generally, because 2D materials are of higher energy than corresponding three-dimensional, 3D, materials. Additionally, phonon density of states increases with increasing physical size, which acts to force 2D materials into a three dimensional configurations.

15 Hence, there is a need to improve manufacturing of sheets of 2D materials.

Summary of the Invention

It is one aim of the present invention, amongst others, to provide a method of, and an apparatus for, manufacturing a sheet of a 2D material which at least partially obviates or mitigates at least some of the disadvantages of the prior art, whether identified herein or elsewhere.

A first aspect provides a method of manufacturing a first sheet of a first two-dimensional, 2D, material, for example graphene, the method comprising:

- providing a container containing a substrate, comprising a set of layers including a solid layer, and a volume above the substrate;
- supplying precursor species to the volume, wherein the precursor species comprise atoms, for example carbon atoms, of the first 2D material;
- allowing the precursor species to settle on a surface of the substrate;

applying a first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material; and

5 withdrawing, at least in part, the substrate after allowing the precursor species to settle on the surface of the substrate.

A second aspect provides an apparatus for manufacturing a first sheet of a first two-dimensional, 2D, material, for example graphene, the apparatus comprising: a container containing a substrate, comprising a set of layers including a solid
10 layer, and a volume above the substrate;

a source arranged to supply precursor species to the volume, wherein the precursor species comprise atoms of the 2D material, wherein the source is configured such that the precursor species settle on a surface of the substrate; and

15 a means for applying a first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material.

A third aspect provides a sheet of a two-dimensional, 2D, material manufactured
20 according to the first aspect.

Detailed Description of the Invention

According to the present invention there is provided a method of manufacturing
25 a sheet of a 2D material, as set forth in the appended claims. Also provided is an apparatus for manufacturing a sheet of a 2D material. Other features of the invention will be apparent from the dependent claims, and the description that follows.

30 ***Method***

The first aspect provides a method of manufacturing a first sheet of a first two-dimensional, 2D, material, for example graphene, the method comprising:
providing a container containing a substrate, comprising a set of layers including a solid layer, and a volume above the substrate;

- 5 supplying precursor species to the volume, wherein the precursor species comprise atoms, for example carbon atoms, of the first 2D material;
allowing the precursor species to settle on a surface of the substrate;
applying a first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first
10 sheet of the first 2D material; and
withdrawing, at least in part, (e.g fully withdrawing) the substrate after allowing the precursor species to settle on the surface of the substrate.

In this way, the applied first force induces and/or promotes coalescing of the
15 precursor species to form the first sheet of the 2D material on and/or proximal to the surface of the substrate. That is, the applied first force reduces mutual separations between the precursor species settled on the surface of the substrate and/or between the precursor species settled on the surface of the substrate and the forming first sheet of the first 2D material, for example
20 coalesced precursor species and/or fragments of the first sheet. In other words, the applied first force results in movement and/or relative movement of the precursor species, coalesced precursor species and/or fragments of the first sheet that results in coalescing thereof. In this way, manufacture of the first sheet of the 2D material is improved, allowing relatively large sheets of 2D materials
25 to be formed and removed.

Sheet

The method is of manufacturing the first sheet of the first 2D material. It should
30 be understood that a size, for example a length and/or a width, of the first sheet is not limited in principle, bounded only by a size of the container. Particularly,

the method according to the first aspect seeks to provide a method of manufacturing large sheets of 2D materials, up to metres in length and/or width.

In one example, the first sheet of the first 2D material comprises and/or is a
5 pristine sheet (i.e. a continuous sheet having no defects therein). In one
example, the first sheet of the first 2D material has a width and/or a length in a
range from 1 cm to 100 m, preferably in a range from 10 cm to 10 m, more
preferably in a range from 1 m to 5 m.

10 In one example, the method comprises forming a second sheet of the first 2D
material above the first sheet of the first 2D material, for example by repeating
the steps of supplying the precursor species to the volume, allowing the
precursor species to settle on the surface of the first sheet of the first 2D material
and applying the first force on the precursor species, parallel to the surface of
15 the substrate, to coalesce, at least in part, the precursor species to form the
second sheet of the first 2D material. In this way, a layered structure composed
of multiple sheets of the first 2D material may be manufactured.

In one example, the method comprises forming a first sheet of a second 2D
20 material above the first sheet of the first 2D material, for example by supplying
precursor species to the volume, wherein the precursor species comprise atoms
of the second 2D material; allowing the precursor species to settle on the surface
of the first sheet of the first 2D material and applying the first force on the
precursor species, parallel to the surface of the substrate, to coalesce, at least
25 in part, the precursor species to form the second sheet of the second 2D
material. In this way, a layered heterostructure composed of sheets of the first
2D material and the second 2D material may be manufactured.

In one example, the method comprises forming a first set of M sheets, including
30 the first sheet, of the first 2D material and a second set of N sheets, including a
first sheet, of a second 2D material, wherein M and N are natural numbers

greater than or equal to 1. In one example, respective sheets of the first 2D material and the second 2D material are layered, for example alternately.

Two-dimensional material

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The method is of manufacturing the first sheet of the first 2D material, for example graphene.

10 In one example, the first 2D material comprises and/or is a 2D allotrope, for example graphene, graphyne, borophene, germanene, silicone, Si₂BN, stanine, plumbene, phosphorene, antimonene, bismuthene and/or molybdenite. Other 2D allotropes are known. Preferably, the first 2D material comprises and/or is graphene.

15 In one example, the first 2D material comprises and/or is a compound, for example graphene, hexagonal boron nitride, borocarbonitride, germanane, a transition metal di-chalcogenide (TMDC) and/or a MXene. Other 2D compounds are known.

20 In one example, the first 2D material comprises and/or is a metal, for example Pt, Pd or Rh, or an alloy, for example of Pb and Sn and/or Bi.

In one example, the method comprises forming a first sheet of a second 2D material. The second 2D material may be as described with respect to the first
25 2D material. In one example, the first 2D material and the second 2D material are different 2D materials.

Container

30 The method comprises providing the container (also known as a chamber or a vessel) containing the substrate and the volume above the substrate. It should

be understood that since the substrate comprises the first liquid layer below the solid layer, the container is thus suitable for retaining the first liquid layer therein.

In one example, the container comprises a plurality of walls including a lower wall, a set of side walls and optionally, an upper wall. In one example, the
5 container comprises an outlet, or a plurality of outlets, for withdrawing at least liquid therethrough, for example arranged in the lower wall. In one example, the outlet is a closeable outlet. In one example, the container comprises an inlet, or a plurality of inlets, for supplying the precursor species therethrough. In one
10 example, the container comprises a door, or a plurality of doors, provided in the plurality of walls, for extracting the first sheet therethrough. In one example, the plurality of walls comprise no additional perforations therethrough (i.e. in addition to the inlet, the inlet and/or the door and/or the respective pluralities thereof).

15 It should be understood that the volume is a region above the substrate, within the container. In one example, the method comprises evacuating the volume, thereby providing a vacuum for example at a desired pressure, in the volume. In one example, the desired pressure is dependent, at least in part, on a partial pressure of the substrate. In one example, the method comprises introducing a
20 gas into the volume and optionally, controlling a pressure and/or a temperature of the gas in the volume, thereby providing a gaseous atmosphere in the volume. In one example, the gas comprises an inert gas for example a noble gas such as Ar or He, and/or a reactive gas.

25 In one example, providing the container comprises including therein a source arranged to supply the precursor species to the volume, wherein the source is configured such that the precursor species settle on the surface of the substrate and coalesce to form the first sheet of the first 2D material. In one example, the source comprises a directional source of the precursor species, such as a
30 source which produces an output beam of the precursor species. The source

arranged to supply the precursor species to the volume may be as described below.

5 *Substrate*

The substrate comprises the set of layers including the solid layer. In one example, the surface of the substrate comprises and/or is an upper surface of the solid layer.

10

Supplying the precursor species

15 The method comprises supplying the precursor species to the volume, wherein the precursor species comprise atoms, for example carbon atoms, of the first 2D material. It should be understood that the precursor species are generally mutually isolated in the volume (i.e. mutually spaced apart).

20 Methods of supplying precursor species comprising atoms are known. In one example, supplying the precursor species comprises creating the atoms, for example carbon atoms, by photolysis, by electrical discharge, by decomposition, by cracking and/or by fracking. In one example, creating the atoms by photolysis comprises photodissociation and/or multi-photon dissociation of a precursor using electromagnetic radiation of a suitable wavelength or wavelengths. The wavelength used may be in the ultraviolet region of the electromagnetic spectrum, or of a shorter wavelength. In one example, creating the atoms by
25 electrical discharge is by electrical arcing, for example between rods of a material corresponding to the first 2D material, for example carbon rods. In one example, creating the atoms comprises obtaining the atoms from a precursor gas. For example, carbon atoms may be created using a carbon containing
30 precursor gas, such as a hydrocarbon gas. The hydrocarbon gas may be an alkane, such as methane or ethane. Alternatively, the carbon containing

precursor gas may be a per or partially halogenated hydrocarbon. The term 'gas' as used herein refers to any species in the gas phase, including vapours and sublimates. In one example, creating the atoms comprises obtaining the atoms from a precursor solid. For example, carbon atoms may be created using particulate graphite as a precursor. For example, carbon atoms may be created using a carbohydrate precursor. For example a sugar precursor, such as sucrose, may be decomposed to create the carbon atoms.

In one example, supplying the precursor species to the volume comprises creating the atoms in the container. It may be possible to create the atoms outside of the container and to introduce the atoms into the container. In general, this is less preferred owing to the reactivity of the atoms.

In one example, the precursor species comprise clusters of the atoms, for example 2D clusters thereof, and/or 2D fragments of the first 2D material. In one example, the precursor species comprise fragments of the first 2D material. These 2D clusters and/or the 2D fragments may provided seeds for growth of the first sheet. In one example, the method comprises generating the 2D clusters and/or the 2D fragments, at least in part, in the volume from the atoms. In one example, supplying the precursor species to the volume comprises adding the 2D clusters and/or the 2D fragments, at least in part, into the volume. That is, the 2D clusters and/or the 2D fragments may be generated in advance and supplied together with the atoms.

In one example, supplying the precursor species to the volume comprises controlling a distribution of the precursor species in the volume and/or on the surface of the substrate. In one example, supplying the precursor species to the volume comprises controlling a volume density of the precursor species, for example of the atoms, in the volume. Generally, a sufficiently low volume density of the precursor species and a sufficiently large interatomic distance therebetween (i.e. a mutual spacing between the precursor species) is required

so that the precursor species do not interact before reaching the surface of the substrate, and/or so that stacking of the precursor species on the surface of the substrate is reduced. However, generally, it is also desirable to use as high a volume density of the precursor species as possible within these constraints so that a rate of formation of the first sheet of the first 2D material is increased.

Settling and coalescing

The method comprises allowing the precursor species to settle on the surface of the substrate and applying the first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material.

Since the first sheet of the first 2D material is formed on and/or proximal to the surface of the substrate, planar movement of the precursor species, for example atoms and/or coalesced atoms such as fragments of the first sheet, is enabled by the applied first force. This planar movement is thus directional (i.e. not random) and may be at a suitable temperature and pressure to allow bonds between the atoms to form.

In one example, allowing the precursor species to settle on the surface of the substrate is effected, at least in part, by gravity, condensation, interatomic forces, such as van der Waals forces, between the precursor species and the surface of the substrate, a gaseous atmosphere in the volume and/or control of the conditions in the container such as temperature and pressure therein.

In one example, applying the first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material comprises applying the first force on the precursor species to form a plurality of fragments of the first sheet on and/or proximal to the surface of the surface and optionally, applying the first force on

the precursor species to at least some of the plurality of the fragments to coalesce to form the first sheet.

Forces

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The method comprises applying the first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material. It should be understood that a component of the first force is parallel to the surface of the substrate and hence parallel to a plane of the first sheet of the first 2D material. In this way, the applied first force moves the precursor species in a direction thereof.

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In one example, the first force comprises and/or is a centripetal force, a gravitational force, an electromagnetic force and/or an electrostatic force.

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In one preferred example, the first force comprises and/or is a centripetal force, such as provided by centrifuging the container. In one example, applying the first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material comprises centrifuging the container. In this way, the centripetal force moves the precursor species proximal to and/or on the surface of the substrate radially outwards.

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In one example, applying the first force on the precursor species comprises controlling a magnitude, a direction and/or a duration of the first force.

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In one example, the method comprises opposing, at least in part, the first force, for example by attractive forces (for example, intramolecular bonding such as covalent, ionic and/or metallic and/or intermolecular forces such as electrostatic, ion-dipole and/or van der Waals forces including hydrogen bonding, dipole-dipole and/or dispersion (London) forces) and/or frictional forces between the

precursor species proximal to and/or on the surface of the substrate and the surface of the substrate. In this way, a rate of coalescing of the precursor species may be controlled. In this way, the precursor species, coalesced precursor species, fragments of the first sheet and/or the first sheet may be retained on the surface of the substrate.

In one example, the method comprises controlling an attractive force and/or a frictional force between the precursor species and the surface of the substrate, for example by selecting, modifying and/or activating the surface of the substrate. In this way, a rate of coalescing of the precursor species may be controlled. In this way, the precursor species, coalesced precursor species, fragments of the first sheet and/or the first sheet may be retained on the surface of the substrate.

In one example, the method comprises controlling a repulsive force between the precursor species and the surface of the substrate, for example by selecting, modifying and/or activating the surface of the substrate. In this way, a rate of coalescing of the precursor species may be controlled. In this way, the precursor species, coalesced precursor species, fragments of the first sheet and/or the first sheet may be retained on the surface of the substrate.

In one example, the method comprises applying a second force on the precursor species, transverse to the first force. In this way, an attractive force and/or a frictional force between the precursor species and the surface of the substrate may be controlled.

In one example, the method comprises controlling a frictional force between the precursor species and the surface of the substrate, for example by selecting, modifying and/or activating the surface of the substrate. In this way, a rate of coalescing of the precursor species may be controlled.

Removing the substrate

In one example, the method comprises removing, at least in part, the first sheet of the first 2D material, for example from the container.

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The method comprises withdrawing, at least in part, the substrate after allowing the precursor species to settle on the surface of the substrate, for example by melting the solid layer and draining the substrate, including the liquefied solid layer, from the container, for example through an outlet thereof. It should be understood that withdrawing, at least in part, the substrate after allowing the precursor species to settle the surface of the substrate is after coalescing, at least in part, the precursor species to form the first sheet of the first 2D material. In one example, removing, at least in part, the first sheet of the first 2D material comprises withdrawing, at least in part, the substrate after allowing the precursor species to settle on the surface of the substrate, for example by draining the substrate, including the liquefied solid layer, from the container and collecting the first sheet remaining in the container.

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In one example, removing, at least in part, the first sheet of the first 2D material comprises gasifying, at least in part, the substrate, after forming the first sheet of the first 2D material and collecting the first sheet of the first 2D material. In one example, gasifying, at least in part, the substrate comprises subliming the substrate and/or successive phase transitions of the substrate from solid to liquid to gas.

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In one example, removing, at least in part, the first sheet of the first 2D material comprises removing the first sheet of the first 2D material from the surface of the substrate, after forming the first sheet of the first 2D material, using a roller device and/or a skimming device.

30

In one example, providing the container comprises introducing a target (also known as a preform or a mould) below and/or in the substrate. In this way, the first sheet of the first 2D material may be collected on the target, which may act as a support for the first sheet of the first 2D material, once the substrate is withdrawn from the container. In one example, the target comprises and/or is a liquid-porous target. In one example, target is removable from the container.

In one example, the method comprises draping the first sheet, at least in part, over the target, thereby collecting the first sheet of the first 2D material thereupon, for example after withdrawing the substrate, as described above.

In one example, the method comprises replenishing the substrate in the container.

In this way, by repeating the steps of supplying the precursor species to the volume; allowing the precursor species to settle on the surface of the substrate; and applying the first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material; withdrawing, at least in part, the substrate; draping the sheet over the target and replenishing the substrate in the container, a layered structure composed of multiple sheets of the 2D material may be collected in the target. Similarly, layered heterostructures may be manufactured.

First liquid layer

In one example, the method comprises including a first liquid layer in the set of layers, above the solid layer. That is, in the absence of the first liquid layer, the solid layer is the uppermost layer and the method comprises allowing the precursor species to settle on the surface of the solid layer. In contrast, in the presence of the first liquid layer, the first liquid layer is the uppermost layer and

the method comprises allowing the precursor species to settle on the surface of the first liquid layer. Hence, the first liquid layer provides a temporary substrate.

Particularly, the second liquid layer affords enhanced planar mobility of the precursor species and/or fragments of the first sheet of the first 2D material,
5 improving coalescing and formation of the first sheet of the first 2D material.

In one example, the method comprises:

including a first liquid layer in the set of layers, above the solid layer;
10 wherein allowing the precursor species to settle on the surface of the substrate comprises allowing the precursor species to settle on the surface of the first liquid layer; and
solidifying the first liquid layer before applying the first force on the precursor species.

15 In this way, the precursor species settle on the surface of the first liquid layer, thereby providing greater lateral mobility thereof compared with the precursor species settled on the surface of the solid layer. In this way, mutual separation (i.e. lateral separation) between the precursor species may be reduced by
20 agitation, as described below, before then solidifying the first liquid layer and subsequently applying the first force on the precursor species, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material.

In one example, an upper surface of the solid layer contacts, for example
25 directly, a lower surface of the first liquid layer. In one example, the surface of the substrate comprises and/or is the upper surface of the first liquid layer. In one example, the substrate includes no further layers between the first liquid layer and the solid layer. In one example, a density of the solid layer is less than a density of the first liquid layer.

30

In one example, the first liquid layer and the solid layer are liquid and solid phases, respectively, of the substrate. In one example, the first liquid layer and the liquefied solid layer are miscible. For example, the first liquid layer may be provided by a polar liquid, such as water, and the solid layer may be provided by solidifying another polar liquid. For example, the first liquid layer may be provided by a non-polar liquid, such as an oil or a wax, and the solid layer may be provided by solidifying another non-polar liquid. In one example, the first liquid layer and the liquefied solid layer are immiscible. For example, the first liquid layer may be provided by a polar liquid, such as water, and the solid layer may be provided by solidifying a non-polar liquid, such as an oil or a wax, or vice-versa. In one example, the first liquid layer comprises water, an acid, a base, another polar liquid or a non-polar liquid, for example an organic liquid, such as a hydrocarbon. In one example, the first liquid layer comprises and/or is water and the solid layer comprises and/or is ice.

15

In one example, providing the container comprises preparing, at least in part, the solid layer by solidifying, at least in part, the first liquid layer. In one example, solidifying, at least in part, the first liquid layer comprises cooling, at least in part, the first liquid layer, for example below a melting point thereof. In one example, solidifying, at least in part, the first liquid layer comprises reacting, at least in part, the first liquid layer with a solidifying agent.

20

The first liquid layer may be any suitable liquid which allows the precursor species to settle on a surface thereof and the first sheet of the first 2D material to float on the surface due to surface tension, repulsive forces and/or through temporary bond formation between the first liquid layer and the precursor species. The first liquid layer is held at a predetermined temperature and pressure to allow the first sheet of the first 2D material to form and to float. This enables the nascent first sheet of the first 2D material to retain its 2D structure, overcoming any tendency for the structure to fold up. The first liquid layer is held in the container which can be heated and/or pressurised to ensure the correct

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conditions for formation of the first sheet of the first 2D material. The first liquid layer may be water, an acid, a base, another polar liquid or a non-polar liquid, for example an organic liquid, such as a hydrocarbon. The first liquid layer may be generally as described with respect to the first liquid layer.

5

In one example, including the first liquid layer comprises melting, at least in part, the solid layer before allowing the precursor species to settle on the surface of the substrate. That is, the first liquid layer is provided from the solid layer, for example having a same composition thereof.

10

In one example, the method comprises controlling a thickness of the first liquid layer. In this way, the thickness of the first liquid layer may be controlled to a desirable thickness, for example to balance constraining, at least in part, movement of the precursor species downwards, in use, due to the temporary solid surface of the solid layer beneath the first liquid layer with the enhanced planar mobility of the precursor species and/or fragments of the first sheet of the first 2D material afforded by the first liquid layer. For example, some of the precursor species may dissolve, disperse and/or settle in the first liquid layer. In one example, the thickness of the first liquid layer is in a range from 0.1 nm to 1,000 μm , preferably in a range from 10 nm to 500 μm , more preferably in a range from 100 nm to 100 μm .

15

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Agitating the substrate

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In one example, the method comprises agitating the substrate while applying the first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material. In this way, a likelihood of bonding of the precursor species, for example of the atoms, is increased.

30

In one example, agitating the substrate comprises mechanically agitating the substrate, for example ultrasonically and/or by shaking. For example, ultrasonic vibrational transducers may be applied directly onto the solid layer and/or attached to the container, such as on side walls thereof at an appropriate height, and vibrations therefrom conducted through the container. For example, the
5 container may be mounted on a conventional shaker table. In one example, the substrate comprises a second liquid layer, above the solid layer, and agitating the substrate comprises mechanically agitating the substrate by stirring the second liquid layer, for example using a magnetic stirrer.

10

In one example, the method comprises agitating the precursor species and/or fragments of the first sheet of the first 2D material on the surface of the substrate by directing a gas across and/or through the surface of the substrate. For example, blowing devices may produce a gross turbulent atmosphere and/or
15 have high directionality. For example, multiple narrow bore blowers may blow across the surface of the substrate.

In one example, the method comprises:

including a first liquid layer in the set of layers, above the solid layer;

20

wherein allowing the precursor species to settle on the surface of the substrate comprises allowing the precursor species to settle on the surface of the first liquid layer;

agitating the first liquid layer to coalesce, at least in part, the precursor species; and

25

solidifying the first liquid layer before applying the first force on the precursor species.

In one example, the method comprises sublimating, at least in part, the solid layer while applying the first force on the precursor species, parallel to the
30 surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material, thereby agitating the precursor

species and/or fragments of the first sheet of the first 2D material due to the sublimate rising from the solid layer.

Monitoring

5

In one example, the method comprises monitoring, for example in situ monitoring, of the forming of the first sheet of the 2D material, for example by reflected high-energy electron diffraction (RHEED) and/or an optical technique, such as reflectometry, ellipsometry, reflectance anisotropy or Raman scattering.

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Apparatus

The second aspect provides an apparatus for manufacturing a first sheet of a first two-dimensional, 2D, material, for example graphene, the apparatus comprising:

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a container containing a substrate, comprising a set of layers including a solid layer, and a volume above the substrate;

a source arranged to supply precursor species to the volume, wherein the precursor species comprise atoms of the 2D material, wherein the source is configured such that the precursor species settle on a surface of the substrate; and

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a means for applying a first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material.

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In one example, the means for applying the first force on the precursor species provides a centripetal force (for example, via a centrifuge), a gravitational force (for example, via an inclined substrate), an electromagnetic force and/or an electrostatic force.

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In one example, the apparatus comprises means for solidifying, at least in part, the first liquid layer for preparing, at least in part, the solid layer therefrom. In one example, the means for solidifying at least in part, the first liquid layer comprises a cooler. For example, heat may be withdrawn above the first liquid layer causing at least a part of a surface thereof to solidify. For example, cold refrigerated elements may be arranged a periphery, for example a circumference, of the container, for example at a height corresponding to an upper surface of the first liquid layer.

10 In one example, the apparatus comprises an agitator.

The third aspect provides a sheet of a two-dimensional, 2D, material manufactured according to the first aspect.

15 ***Definitions***

Throughout this specification, the term “comprising” or “comprises” means including the component(s) specified but not to the exclusion of the presence of other components. The term “consisting essentially of” or “consists essentially of” means including the components specified but excluding other components except for materials present as impurities, unavoidable materials present as a result of processes used to provide the components, and components added for a purpose other than achieving the technical effect of the invention, such as colourants, and the like.

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The term “consisting of” or “consists of” means including the components specified but excluding other components.

Whenever appropriate, depending upon the context, the use of the term “comprises” or “comprising” may also be taken to include the meaning “consists

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essentially of” or “consisting essentially of”, and also may also be taken to include the meaning “consists of” or “consisting of”.

5 The optional features set out herein may be used either individually or in combination with each other where appropriate and particularly in the combinations as set out in the accompanying claims. The optional features for each aspect or exemplary embodiment of the invention, as set out herein are also applicable to all other aspects or exemplary embodiments of the invention, where appropriate. In other words, the skilled person reading this specification
10 should consider the optional features for each aspect or exemplary embodiment of the invention as interchangeable and combinable between different aspects and exemplary embodiments.

Brief description of the drawings

15 For a better understanding of the invention, and to show how exemplary embodiments of the same may be brought into effect, reference will be made, by way of example only, to the accompanying diagrammatic Figures, in which:

20 Figure 1 schematically depicts an apparatus and a method according to an exemplary embodiment;

Figure 2 schematically depicts an apparatus and a method according to an exemplary embodiment;

25 Figure 3 schematically depicts an apparatus and a method according to an exemplary embodiment; and

30 Figure 4 schematically depicts a method according to an exemplary embodiment.

Detailed Description of the Drawings

Figure 1 schematically depicts an apparatus and a method according to an exemplary embodiment. In this example, the apparatus is for, and the method is of, manufacturing graphene.

A substrate S, comprising a set of layers including a solid layer 13, and a volume V above the substrate S, are provided in a container 10. Precursor species 14 are supplied to the volume V, wherein the precursor species comprise atoms, in this example carbon atoms, of the first 2D material. The precursor species 14 are allowed to settle on a surface 22 of the substrate S. A first force F1 is applied on the precursor species 14, parallel to the surface of the substrate S, to coalesce, at least in part, the precursor species 14 to form the first sheet 26 of the first 2D material. Removal of the first sheet 26 of the first 2D material may be as described below with respect to Figure 2.

In this example, the solid layer 13 is the uppermost layer and the method comprises allowing the precursor species 14 to settle on the surface 22 of the solid layer 13 and to coalesce to form the first sheet 26 of the first 2D material.

In this example, the container 10 may be heated and/or pressurised to ensure the substrate S is at the optimum temperature and pressure to allow the formation of the graphene sheet 26. The source of carbon atoms 14 is created in the volume V of the container 10 above the substrate S. The carbon atoms may be created from a precursor which is introduced through an inlet 16. Carbon atoms 14 from the source settle on the surface 22 of the substrate S. Subsequently, carbon-carbon bonding results in the deposition of graphene fragments 18. Carbon-carbon bonding can occur through random motion of the carbon atoms on the surface 22 of the substrate S. The applied first force F1 promotes carbon-carbon bonding of the carbon atoms on the surface 22 of the substrate S. Additionally and/or alternatively, the applied first force F1 promotes

graphene fragments 18 to assemble into the graphene sheet 26. The surface 22 of the substrate acts to retain the 2D structure of the graphene sheet 26.

The container 10 may comprise a translating source of atomic carbon which is
5 configured to be translatable across the container 10. The flow of the carbon atoms 14 from the source of the atomic carbon may be to some extent directional. The movement of the source of atomic carbon across the container 10 allows the production of a relatively even distribution of carbon atoms 14 on the surface of the substrate S. The carbon atoms 14 coalesce to form a plurality
10 of graphene fragments 18. Suitable agitation of the substrate S by an agitator (not shown) may enhance this process. The essentially planar nature of the surface 22 of the substrate S encourages the formation and retention of a two dimensional structure. The graphene fragments 18 can be regarded as discrete floating islands. Continuing agitation by the agitator results in the graphene
15 fragments 18 moving and bonding with other graphene fragments 18 to eventually form the large graphene sheet 26 on the surface of the substrate S. The graphene sheet 26 can then be separated from the liquid S, for example using the techniques described in relation to Figure 2.

20 Figure 2 schematically depicts an apparatus and a method according to an exemplary embodiment, generally as described with respect to Figure 1.

A liquid-porous target 30 is provided in the first liquid layer 12. The solid layer 13 is liquefied. Thus, the substrate S is a liquid. The container 10 comprises an
25 outlet 24 for draining the substrate therethrough.

As the liquid level within the container 10 drops as the substrate drains through the outlet 24, so does the graphene sheet 26 until it comes to rest on the liquid-porous substrate 30. The liquid-porous substrate 30 can then be removed from
30 the container 10 and the graphene sheet 26 can be removed from the liquid-porous substrate 30 by any suitable method.

Figure 3 schematically depicts an apparatus and a method according to an exemplary embodiment.

5 In this example, the substrate S comprises a first liquid layer 15 included the set of layers, above the solid layer 13. In this example, the first liquid layer 15 is the uppermost layer and the method comprises allowing the precursor species 14 to settle on the surface 22 of the first liquid layer 15 and solidifying the first liquid layer 15 before applying the first force F1 on the precursor species 14.

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Figure 4 schematically depicts a method according to an exemplary embodiment. The method is of manufacturing a first sheet of a first two-dimensional, 2D, material, for example graphene.

15 At S401, a container containing a substrate, comprising a set of layers including a solid layer, and a volume above the substrate is provided.

At S402, precursor species are supplied to the volume, wherein the precursor species comprise atoms, for example carbon atoms, of the first 2D material.

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At S403, the precursor species are allowed to settle on a surface of the substrate.

25 At S404, a first force is applied on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material.

The method may include any of the steps described herein.

30 Although a preferred embodiment has been shown and described, it will be appreciated by those skilled in the art that various changes and modifications

might be made without departing from the scope of the invention, as defined in the appended claims and as described above.

5 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.

10 All of the features disclosed in this specification (including any accompanying claims 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 most some of such features and/or steps are mutually exclusive.

15 Each feature disclosed in this specification (including any accompanying claims, and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

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CLAIMS

1. A method of manufacturing a first sheet of a first two-dimensional, 2D, material, the method comprising:
- 5 providing a container containing a substrate, comprising a set of layers including a solid layer, and a volume above the substrate;
- supplying precursor species to the volume, wherein the precursor species comprise atoms of the first 2D material;
- allowing the precursor species to settle on a surface of the substrate;
- 10 applying a first force on the precursor species, parallel to the surface of the substrate, to coalesce, at least in part, the precursor species to form the first sheet of the first 2D material; and
- withdrawing, at least in part, the substrate after allowing the precursor species to settle on the surface of the substrate.
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2. The method according to any previous claim, wherein the first force comprises and/or is a centripetal force, a gravitational force, an electromagnetic force and/or an electrostatic force.
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3. The method according to any previous claim, comprising applying a second force on the precursor species, transverse to the first force.
4. The method according to any previous claim, comprising controlling an attractive force between the precursor species and the surface of the substrate.
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5. The method according to any previous claim, comprising removing, at least in part, the first sheet of the first 2D material.
6. The method according to claim 5, wherein removing, at least in part, the first sheet of the first 2D material comprises gasifying, at least in part, the substrate, after forming the first sheet of the first 2D material and collecting the first sheet of the first 2D material.
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7. The method according to any previous claim, comprising:
including a first liquid layer in the set of layers, above the solid layer;
wherein allowing the precursor species to settle on the surface of the substrate
comprises allowing the precursor species to settle on the surface of the first
5 liquid layer; and
solidifying the first liquid layer before applying the first force on the precursor
species.

8. The method according to claim 7, comprising melting, at least in part, the first
10 liquid layer and/or the solid layer after forming the first sheet of the first 2D
material.

9. The method according to any of claims 7 to 8, comprising controlling a
15 thickness of the first liquid layer.

10. The method according to claim 9, wherein the thickness of the first liquid
layer is in a range from 0.1 nm to 1,000 μm , preferably in a range from 10 nm to
500 μm , more preferably in a range from 100 nm to 100 μm .

20 11. The method according to any previous claim, wherein the precursor species
comprise fragments of the first 2D material.

12. The method according to any previous claim, comprising sublimating, at
least in part, the solid layer while applying the first force on the precursor
25 species, parallel to the surface of the substrate, to coalesce, at least in part, the
precursor species to form the first sheet of the first 2D material.

13. The method according to any previous claim, comprising agitating the
substrate while applying the first force on the precursor species, parallel to the
30 surface of the substrate, to coalesce, at least in part, the precursor species to
form the first sheet of the first 2D material.

14. The method according to any previous claim, comprising forming a first sheet of a second 2D material above the first sheet of the first 2D material.

5 15. The method according to any preceding claim wherein the first two-dimensional, 2D, material is graphene.

16. The method according to any preceding claim, wherein the atoms are carbon atoms.