Gas sensor comprising graphene and a method to sense gases

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Abstract: The present invention relates to a sensing device for sensing polar molecules, such as H₂S, and a method of quantitative sensing of polar molecules.
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GAS SENSOR COMPRISING GRAPHENE AND A METHOD TO SENSE GASES

FIELD OF THE INVENTION
The present invention relates to a sensing device for polar molecules sensing and a method of quantitative sensing of polar molecules.

BACKGROUND OF THE INVENTION
Gas sensors play a significant role in numerous application fields, such as environmental monitoring, medical diagnosis, military and aerospace.

Solid state gas sensors possess advantages such as small size, low power, high sensitivity and low cost for detecting very low concentrations of a wide range of gases in the range of parts-per-million (ppm). In particular, solid state sensors composed of 2D materials are of high interest in this emerging field due to their high sensitivity.

However, so far, sensors made from 2D materials have the disadvantage that measurements are not reproducible from device to device as the measurements are mostly based on the change of the absolute value of resistivity when a gas is adsorbed on the material 2D plane. For this reason, due to inhomogeneity present in the monolayer material, such as charge puddles, point defects, it is difficult to have reproducibility from device to device. In addition, these measurements suffer from problems associated with long term stability and limited measurement accuracy.

Hence, an improved gas and liquids sensor and a method to sense gases and liquids would be advantageous, and in particular a more efficient and/or reliable gas and liquids sensor and a method to sense gases able to provide accurate and reproducible measurements, from device to device, would be advantageous.

OBJECT OF THE INVENTION
It may be seen as an object of the present invention to provide a sensing device for polar molecules sensing and a method of quantitative sensing of polar molecules able to provide accurate and reproducible measurements, from device to device.
In particular, it may be seen as a further object of the present invention to provide a sensing device for polar molecules sensing and a method of quantitative sensing of polar molecules that solve the above mentioned problems of the prior art based on statistical analysis of edge sensing.

5

An object of the present invention is to provide an alternative to the prior art.

SUMMARY OF THE INVENTION

10 Thus, the above described object and several other objects are intended to be obtained in a first aspect of the invention by providing a sensing device for polar molecules sensing, the sensing device comprising:

- at least one layer of conducting 2D material, such as an electrically continuous graphene film;
- covering means for covering the at least one layer of conducting 2D material configured to leave at least one edge of the at least one layer of conducting 2D material accessible;
- a bottom electrode located onto the covering means.

20 In some embodiments, all edges of the at least one layer of conducting 2D material are accessible.

The conducting 2D material should have a finite number of stable configurations for polar molecules adsorbed at an edge and the probability of occupation of those configurations should be electrically tuneable by altering a gate voltage.

The 2D basal plane of the conducting 2D material may have any 2D shape such as a square, a rectangle, a polygon, an oval, a circle or any regular or irregular 2D shape.

Electrically continuous graphene film comprises graphene compounds produced using a variety of fabrication techniques. For example, electrically continuous graphene film could be a thin film composed of multiple graphene nano-flakes or nano-sheets made from liquid exfoliation of graphite.
The term "graphene" is meant to include monolayer graphene, bilayer graphene, and graphene comprised of more than two layers. Preferably, the graphene will comprise less than 10 layers.

The covering means for covering the at least one layer of conducting 2D material may comprise at least one electrically insulating material. The covering means may comprise a coating.

The covering means may comprise or be an electrically insulating material such as Boron Nitride (BN), SiC2, SiN, aluminium oxides or a combination thereof.

The Boron Nitride used as electrically insulating material may be any crystalline form of BN, preferably BN in its hexagonal form (hBN) having a layered structure similar to graphite.

In some embodiments, the covering means comprises more than one type of electrically insulating material.

By the covering means being configured to leave at least one edge of the at least one layer of conducting 2D material accessible is meant that at least one edge is not covered by the covering means and is exposed to the surroundings. By exposed to the surroundings is meant exposed to any polar molecules of interest in the surroundings.

The covering means should cover the entire surface of the 2D basal plane of the conducting 2D material to avoid errors in the measurement and interpretation of data due to contact between polar molecules and the 2D basal plane.

The covering means might also cover, at least partially, some edges leaving at least one edge uncovered.

By the term, "edge" is meant a 1D atomic edge of the conducting 2D material. The 1D edge of a 2D material is generally well-defined. Also, well-defined for a 2D material is the 2D basal plane.
In some further embodiments, the covering means comprises two or more layers. The two or more layers of the covering means may each be layers, where one side has the same or similar dimensions as a 2D basal plane of the at least one layer of conducting 2D material against which the covering means layer abuts.

In some embodiments, the sensing device comprises a stack of multiple, individually stacked layers of conducting 2D material separated by layers of electrically insulating material, wherein each of the layers of electrically insulating material partially covers any conducting 2D material layer above or below in the stack in such a way as to leave at least one edge of the partially covered conducting 2D material accessible.

In some further embodiments, the stack of multiple, individually stacked layers comprises n graphene layers separated by n+1 electrically insulating layers, wherein each of the electrically insulating layers partially covers any graphene layer above or below in the stack in such a way as to leave at least one edge of the partially covered graphene layer accessible.

In another embodiment, the stack of multiple, individually stacked layers comprises the layers: a Boron Nitride (BN) layer/a graphene layer/a BN layer/a graphene layer/a BN layer.

In some embodiments, the covering means comprises two layers having 2 sides that are significantly larger than the third side, the larger sides having dimensions equal to or similar to the 2D basal plane of the conducting 2D material.

In some embodiments, the covering means for covering the at least one layer of conducting 2D material is or comprises electrically insulating materials, such as a top layer and a bottom layer of electrically insulating materials located onto a top and a bottom surface of the at least one layer of conducting 2D material.

By top and bottom surface are meant the two largest surfaces of the basal plane of the at least one layer of conducting 2D material.
The electrically insulating material may comprise one or more of: Boron Nitride (BN), SiO2, BN, SiN, aluminium oxides or a combination thereof.

The bottom electrode may comprise or be an electrically conducting material, such as graphene or a metal. The bottom electrode may be a highly doped silicon-wafer.

In some embodiments, the bottom electrode is located onto the bottom layer of the electrically insulating materials.

In some other embodiments, the top layer and/or the bottom layer is or comprises electrically insulating materials such as BN, SiO2, SiN, aluminium oxides or a combination thereof.

In some further embodiments, the sensing device further comprises means for measuring electrical properties of the at least one layer of conducting 2D material, such as an electrical current, I, and a voltage, V, as a function of an applied gate voltage between the at least one layer of conducting 2D material and the bottom electrode, thereby allowing the measurement of the sensing device resistance while a potential sweep is performed.

By "sensing device resistance" is meant an electrical resistance of the conductive 2D material.

Measurement of the sensing device resistance comprises in-plane resistivity measurements of the at least one layer of conducting 2D material.

In some embodiments, the sensing device may comprise means for applying a gate voltage.

In a second aspect, the invention relates to a method of sensing polar molecules, the method comprising:

- exposing to polar molecules at least one edge of at least one layer of conducting 2D material confined between a top and a bottom layer of
electrically insulating materials covering a top and a bottom surface of the at least one layer of conducting 2D material;
- detecting a variation in ohmic resistance of the at least one layer of conducting 2D material while shifting a gate potential between a negative and a positive value, such as between -50 and +50 volts, the gate potential applied between the at least one layer of conducting 2D material and a bottom electrode located onto the bottom layer of electrically insulating materials.

10 The sensing of polar molecules may be a quantitative sensing of polar molecules.

The top and bottom surface of the at least one layer of conducting 2D material is the two sides of the 2D basal plane of the conducting 2D material.

15 In an embodiment, wherein the conducting 2D material comprises more than one layer of 2D material, e.g. bilayer graphene, the top and bottom surface of the at least one layer of conducting 2D material is the two 2D basal planes not abutting another layer of conducting 2D material.

20 The electrically insulating materials covering a top and a bottom surface of the at least one layer of conducting 2D material may fully cover the top and a bottom surface of the at least one layer of conducting 2D material.

In a third aspect, the invention relates to a method of sensing polar molecules using a sensing device according to the first aspect, the method comprising:
- exposing to polar molecules at least one edge of the at least one layer of conducting 2D material confined between the top and the bottom layer of electrically insulating materials;
- detecting a variation in ohmic resistance of the at least one layer of conducting 2D material while applying a gate voltage sweep between a negative and a positive value, such as between -50 and +50 volts, the gate voltage sweep applied between the at least one layer of conducting 2D material and the bottom electrode.

35 The sensing of polar molecules may be a quantitative sensing of polar molecules.
The electrically insulating materials covering a top and a bottom surface of the at least one layer of conducting 2D material may fully cover the top and a bottom surface of the at least one layer of conducting 2D material.

5 In an embodiment, the method of sensing polar molecules further comprises:
- varying a temperature of the sensing device thereby changing the adsorption of the polar molecules onto the at least one edge of the at least one layer of conducting 2D material.

10 By varying a temperature is meant that the temperature is changed and/or adjusted.
Variation of the temperature of the sensing device changes the adsorption of the polar molecules onto the at least one edge of the at least one layer of conducting 2D material. An alternative operational method may comprise the application of vacum so as to control the adsorption of the polar molecules to the at least one layer of conducting 2D material.

In a fourth aspect, the invention relates to a method of monitoring orientation of polar molecules, the method comprising:

- changing an alignment of polar molecules at an edge of at least one layer of conducting 2D material confined between a top and a bottom layer of electrically insulating materials, the at least one layer of conducting 2D material having at least one edge accessible, by applying a gate voltage sweep between a negative and a positive value, the gate voltage sweep applied between the at least one layer of conducting 2D material and a bottom electrode located onto the bottom layer of electrically insulating materials.

By at least one edge of the at least one layer of conducting 2D material being accessible is meant that at least one edge is not covered and is exposed to the surroundings. By exposed to the surroundings is meant exposed to any polar molecules of interest in the surroundings.
By "changing an alignment of polar molecules" is meant changing the relative difference in the occupation of the finite number of stable configurations for polar molecules adsorbed at an edge.

5 In a fifth aspect, the invention relates to a method of monitoring orientation of polar molecules, using a sensing device according to the first aspect, the method comprising:
   - changing an alignment of polar molecules at the at least one edge of the at least one layer of conducting 2D material confined between the top and the bottom layer of electrically insulating materials, by applying a gate voltage sweep between a negative and a positive value, the gate voltage sweep applied between the at least one layer of conducting 2D material and the bottom electrode located onto the bottom layer of electrically insulating materials.

10 In a sixth aspect, the invention relates to the use of a sensing device according to the first aspect for quantitatively and selectively sensing polar molecules such as H2O, H2S, NH3 or NO2.

20 In a seventh aspect, the invention relates to a method of calculating the adsorption of polar molecules on a sensing device according to the first aspect, the method comprising:
   a) estimating a fraction \( f \) of binding sites with a molecule bound to them by statistical mechanical calculations;
   b) estimating a total dipolar moment \( p \) of the sensing device due to all the attached molecules by statistical mechanical calculations;
   where a calculation of the \( f \) and \( p \), depend on the temperature of the device \( \Gamma \), gate-voltage \( V_g \) sweep, dipolar moment of polar molecules in the mixture \( p_i \) and partial pressure of polar molecules in the mixture, \( P_i \).

30 As the calculation of the \( f \) and \( p \) depends on the temperature of the device, it may be beneficial the presence of a temperature sensor.

Thus, in one embodiment, according to the first aspect of the invention, the sensing device further comprises means for measuring the temperature of the sensing device, such as at least one temperature sensor.
In an eighth aspect, the invention relates to a method of producing a sensing device according to the first aspect, the method comprising the steps of:

a) encapsulating, e.g. by the process of lamination, the at least one layer of conductive 2D material between layers of electrically insulating material such that any layer of conductive 2D material is sandwiched between two layers of electrically insulating material,

b) placing the layers assembled in step a) on the bottom electrode,

c) shaping the desired device geometry, e.g. by one or more of the processes of lithography, etching and/or milling, in such a way that the at least one edge of the at least one layer of conducting 2D material is left accessible,

d) creating at least one electrical contact to the conductive 2D material using one or more conductive electrode(s) such that a small part of the at least one edge is covered by the conductive electrode.

In some embodiments, shaping the desired device geometry comprises removing unnecessary material from the layers assembled in step a) after assembly.

In further embodiments, shaping the desired device geometry comprises at least one reactive ion etch (RIE) etching step. The etching procedure may serve to reduce the edge disorder in the at least one edge.

In other embodiments, shaping the desired device geometry comprises an oxygen plasma etch of the graphene.

In some other embodiments, shaping the desired device geometry comprises a process, which will reduce the edge disorder in the at least one edge.

Creating at least one electrical contact to the conductive 2D material may be done using the process of lithography in combination with deposition of a thin metal film and a lift-off process.

In some further embodiments, creating at least one electrical contact to the conductive 2D material comprises using lithography, e.g. electron beam lithography (EBL), and/or deep UV and/or photolithography techniques, to define the at least one electrical contact.
The first, second and other aspects and embodiments of the present invention may be combined with any of the other aspects and embodiments. These and other aspects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.
BRIEF DESCRIPTION OF THE FIGURES

The sensing device for polar molecules sensing and a method of quantitative sensing of polar molecules according to the invention will now be described in more detail with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

Figure 1 shows schematically a sensing device for polar molecules sensing according to an embodiment of the present invention.

Figure 2 shows schematically a sensing device for polar molecules sensing according to an embodiment of the present invention.

Figure 3 shows schematically changing of an alignment of polar molecules at an edge of a layer of conducting 2D material.

Figure 4 is a scanning electron micrograph (SEM) image showing conductive electrodes in contact with part of the edge of a conducting 2D material.

Figure 5 is a flow-chart illustrating claim 6.

Figure 6 is a flow-chart illustrating claims 7 and 8.

Figure 7 is a flow-chart illustrating claim 12.

Figure 8 is a flow-chart illustrating claim 13.

Figure 9 is a graph of experimentally determined sensing device resistance for a sensing device of the present invention.

Figure 10 is a graph of theoretically calculated resistance for different net dipole moments at the graphene edge in a sensing device of the present invention.

Figure 11 is a graph of the sensing device resistance, \( R \), measured across a sensing device after fluorine or oxygen edge treatments and in an environment composed of dry air with 1% water vapour.

DETAILED DESCRIPTION OF AN EMBODIMENT

Figure 1 shows schematically a sensing device 1 for polar molecules sensing according to an embodiment of the present invention. In the embodiment shown in figure 1, the sensing device 1 has a layer of conducting 2D material 2, such as an electrically continuous graphene film. The 2D basal plane of the conducting 2D
material 2 is covered by a top layer 7 and a bottom layer 8 both made of one or more electrically insulating materials such as hexagonal Boron Nitride (hBN).

The top layer 7 and bottom layer 8 are part of covering means 3, which are configured to partially cover the conducting 2D material 2, while leaving at least one edge 4 of the conducting 2D material 2 accessible. Comprised in the covering means 3 is a further insulating layer, which is provided between the bottom layer 8 and a bottom electrode 5.

Leaving at least one edge 4 of the conducting 2D material 2 accessible, means that the edge 4 will be exposed to polar molecules 6 in the surroundings, which may adsorb at the edge 4. The conducting 2D material 2 should have a finite number of stable configurations for polar molecules 6 adsorbed at its edge 4 and the probability of occupation of those configurations should be electrically tuneable by altering a gate voltage, Vg.

The sensing device 1 has means for measuring an electrical current, I, and a voltage, V, as a function of an applied gate voltage, Vg, between the layer of conducting 2D material 2 and the bottom electrode 5, which allows measurement of the sensing device resistance while a potential sweep is performed.

The sensing device 1, when in operation, can trap and detect polar molecules at an edge 4 of the conducting 2D material 2. The sensing device resistance reflects (1) the occupation of adsorbed polar molecules 6 at the edge 4, N, and (2) the relative difference in the occupation of the finite number of stable configurations with those adsorbed polar molecules, η. Both depend on the dipole moment of the polar molecules 6 such that it is possible to achieve selective sensing of gasses comprising polar molecules 6. The sensing device may be used to quantitatively and selectively sense polar molecules 6 such as H2O, NH3 or NO2.

In some embodiments, the polar molecules may comprise H2S molecules.

In some other embodiments, the sensing device may be used to quantitatively and selectively sense H2S molecules in a mixture of polar and/or non-polar gases.
The sensing device of the invention allows to detect concentration of polar molecules between 5 ppm to 300 ppm.

The sensing device of the invention may be scaled up or down, thus modifying the concentration range of polar molecules that can be detected.

Figure 2 shows schematically a sensing device 1 for polar molecules sensing according to an embodiment of the present invention. In the embodiment shown in figure 2, the sensing device 1 has a layer of conducting 2D material 2, such as an electrically continuous graphene film. The 2D basal plane of the conducting 2D material 2 is covered by a top layer 7 made of hexagonal Boron Nitride (hBN) and a bottom layer 8 made of SiC.

The top layer 7 and bottom layer 8 are part of covering means 3, which are configured to partially cover the conducting 2D material 2, while leaving at least one edge 4 of the conducting 2D material 2 accessible. Provided on the bottom layer 7 is a bottom electrode 5, which in the embodiment shown in figure 2 is made of Si.

Leaving at least one edge 4 of the conducting 2D material accessible, means that the edge 4 will be exposed to polar molecules 6 in the surroundings, which may adsorb at the edge 4. The conducting 2D material 2 should have a finite number of stable configurations for polar molecules 6 adsorbed at its edge 4 and the probability of occupation of those configurations should be electrically tuneable by altering a gate voltage, Vg.

The sensing device 1 has means for measuring an electrical current, I, and a voltage, V, as a function of an applied gate voltage, Vg, between the layer of conducting 2D material 2 and the bottom electrode 5, which allows measurement of the sensing device resistance, \( R = \frac{V}{I} \), while a potential sweep is performed.

The sensing device 1, when in operation, can trap and detect polar molecules at an edge 4 of the conducting 2D material 2. The sensing device resistance reflects (1) the occupation of adsorbed polar molecules 6 at the edge 4, N, and (2) the relative difference in the occupation of the finite number of stable configurations.
with those adsorbed polar molecules, \( \eta \). As both depend on the dipole moment of the polar molecules 6 it is possible to achieve selective sensing of gasses comprising polar molecules 6. The sensing device may be used to quantitatively and selectively sense polar molecules 6 such as H2O, NH3 or NO2.

Figure 3 shows schematically changing of an alignment of polar molecules at an edge of a layer of conducting 2D material. In figure 3 is shown schematically a sensing device 1, which could be a sensing device 1 as shown in figures 1 or 2. By making a gate voltage sweep between a negative and a positive value of an applied gate voltage, \( V_g \), between the at least one layer of conducting 2D material 2 and the bottom electrode 5 the alignment of polar molecules 6 at the edge 4 may be changed as illustrated in figure 2.

Figure 4 is a scanning electron micrograph (SEM) image showing conductive electrodes 20 in contact with part of the edge of a conducting 2D material 2. The electrical contacts were created using electron beam lithography (EBL), in combination with deposition of a thin metal film and a lift-off process, but other techniques may be used for scalable fabrication. In the image shown in figure 4, the scale bar (white stripe in lower right corner) is 5\( \mu \)m.

Figure 5 is a flow-chart of a method of sensing polar molecules 6. The method comprises exposing 9 to polar molecules 6 at least one edge 4 of at least one layer of conducting 2D material 2 confined between a top 7 and a bottom 8 layer of electrically insulating materials covering a top and a bottom surface of the at least one layer of conducting 2D material 2. Further, the method comprises detecting 10 a variation in ohmic resistance of the at least one layer of conducting 2D material 2 while shifting a gate potential between a negative and a positive value, such as between -50 and +50 volts, the gate potential applied between the at least one layer of conducting 2D material 2 and a bottom electrode 5 located onto the bottom layer 8 of electrically insulating materials.

Figure 6 is a flow-chart of a method of sensing polar molecules 6 using a sensing device 1 as disclosed herein. The method comprises exposing 11 to polar molecules at least one edge 4 of said at least one layer of conducting 2D material 2 confined between the top and the bottom layer 8 of electrically insulating materials.
materials. Further, the method comprises detecting a variation in ohmic resistance of the at least one layer of conducting 2D material 2 while applying a gate voltage sweep between a negative and a positive value, such as between -50 and +50 volts, the gate voltage sweep applied between the at least one layer of conducting 2D material 2 and the bottom electrode 5. The method may further comprise the step of varying a temperature of the sensing device 1 thereby changing the adsorption of the polar molecules 6 onto the at least one edge 4 of the at least one layer of conducting 2D material 2.

Figure 7 is a flow-chart of a method of calculating the adsorption of polar molecules 6 on a sensing device 1 as disclosed herein. The method comprises the steps of:

a) estimating a fraction \( f \) of binding sites with a molecule bound to them by statistical mechanical calculations;

b) estimating a total dipolar moment \( p \) of said sensing device (1) due to all the attached molecules by statistical mechanical calculations;

where a calculation of \( f \) and \( p \) depend on the temperature \( T \), gate-voltage \( V_g \) sweep, dipolar moment of polar molecules 6 in the mixture \( p_i \) and partial pressure of polar molecules in the mixture, \( P_i \).

In the case of graphene as the conducting 2D material, polar molecules 6 are known to solely exhibit two equilibrium and symmetrically oriented positions with respect to the graphene plane. The population of these two confined states is regulated by the presence of an external local electric field, \( E_{loc} \), enabling the uniform alignment of polar molecules 6 at a graphene edge 4 in one of these two configurations. Collective orientated polar molecules at a graphene edge generates a net dipole moment in one of the two possible directions perpendicular to the graphene plane \( p_\Sigma \), which has a measurable effect on the electrical characteristics \( R(V_g, p_\Sigma) \) of the monolayer.

Due to the two possible directions of the net dipole perpendicular to the conductor (+-Pz) \( R \) will symmetrically shift in the x-axis \( (V_{gate}) \), in positive and negative directions. By doing a cyclic gate-sweep, and obtaining the shifts (in the x axis) of the resistance when molecules are at the edge \( (R(V_g, +-pz)) \) for the two orientations +-pz the sensing method of the invention does not depend on the absolute value of the device resistance.
This type of "differential" sensing is the one enabling the quantitative sensing with 2D materials of the invention, making the sensing independent from the material quality and avoiding any initial calibration stage.

To a first approximation, \( p_z \) is given by \( p_z = \mu d N \eta \), where \( \mu d \) is the dipolar moment of a single molecule, \( N \) is the total number of adsorbed molecules at the edges and \( \eta \) is the relative difference in the number of molecules above, \( N(\zeta > 0) \), and below, \( N(\zeta < 0) \), the graphene plane such that \( \eta = (N(\zeta > 0) - N(\zeta < 0))/N \). Above or below the graphene plane refers to the two stable, equally probable and symmetric configurations exhibited by polar molecules adsorbed at graphene edges.

Using statistical mechanics the fraction of binding sites with a molecule bound to them, \( f \), as a function of temperature, \( T \), and the partial pressure of the molecules of the gas in the atmosphere, \( P \), may be given by:

\[
f(T, P) = \frac{A(T) P}{e^{-\beta \varepsilon_b} + A(T) P},
\]

where \( e \) is Euler's number, \( \beta \) is the thermodynamic beta, \( \varepsilon_b \) is the chemical binding energy to the edge for the studied molecules, (possibly obtained from DFT calculations) and \( A(T) \) is the Langmuir isotherm result of a molecule with three distinct rotational degrees of freedom and three distinct vibrational degrees of freedom given by:

\[
A(T) = \frac{8\sigma(k_B T_{rot1} T_{rot2} T_{rot3})^{1/2}}{\sqrt{\pi}(k_B T)^4} \left( \frac{2\pi \hbar^2}{m} \right)^{3/2} \prod_{i=1}^{3} \sinh \left( \frac{T_{vib_i}}{2T} \right)
\]

The dependence on temperature means that the sensitivity of a sensing device may be increased by changing the temperature.

The descriptions, wherein graphene is the conducting 2D material, can be extended, with appropriate changes having been made, to other conducting 2D materials.
Figure 8 is a flow-chart of a method of producing a sensing device as disclosed herein. The method comprises the steps of:

a) encapsulating 16, e.g. by the process of lamination, the at least one layer of conductive 2D material 2 between layers of electrically insulating material such that any layer of conductive 2D material 2 is sandwiched between two layers of electrically insulating material,
b) placing the layers assembled in step a) on the bottom electrode 5,
c) shaping a desired device geometry, e.g. by one or more of the processes of lithography, etching and/or milling, in such a way that the at least one edge 4 of the at least one layer of conducting 2D material 2 is left accessible,
d) creating at least one electrical contact to the conductive 2D material 2 using one or more conductive electrode(s) 20 such that a small part of the at least one edge 4 is covered by the conductive electrode(s) 20.

As a working example, a device has been produced using the process of dry-pickup and encapsulation of graphene between hexagonal Boron Nitride (hBN) layers. Square devices were shaped from these heterostructures by electron beam lithography (EBL) and reactive ion etch (RIE) etching steps. The RIE process comprised an initial SF6 etch (of the top hBN layer), a brief oxygen plasma etch (of the graphene layer) and by a second SF6 etch (of the bottom layer). The usage of RIE steps as etching procedure reduced the edge disorder in the at least one edge of the graphene, which has been found to be beneficial to the function of the device. The creation of at least one electrical contact comprised a second EBL step performed to define the contacts of the device, followed by the evaporation of Cr/Pd/Au and a lift-off. An example of electrical contacts created is shown in figure 4.

Figure 9 is a graph of experimentally determined sensing device resistance for a single sensing device of the present invention. The device resistance was measured for three different environments: vacuum, dry air, and dry air with 1% water vapour and using the following two sweep sequences: +Vg,max → -Vg,max (continuous lines) and -Vg,max → +Vg,max (dashed lines). For both the vacuum and dry air curves the resistance \( R(V_g) \) is seen to be independent of sweep direction with a charge neutrality point (where the device resistance peaks) at -4V resulting from residual device doping. In contrast, the charge neutrality point in
$R(V_g)$ in an environment of 1% water vapour is shifted by about +7V or -7V when sweeping from $+V_{g\text{,max}}$ or from $-V_{g\text{,max}}$, respectively. These symmetric, reproducible and reversible incidents of p- or n-doping are surprising for a micron-sized hBN encapsulated graphene device and cannot be accounted for by common hysteretic effects such as charge transfer from adsorbed molecules at edges. Rather, the observed symmetrically switchable electrostatic behaviour is macroscopic evidence of a bi-stable charge-induction mechanism in an ensemble of polar molecules adsorbed at the graphene edge. Collective orientated polar molecules at graphene edges generates a net dipole moment in one of the two possible directions perpendicular to the graphene plane, $p_z$, which has a measurable effect on the sensing device resistance of the graphene monolayer, as seen in figure 9. The existence of such gate-controlled $p_z$ directly measured from the electrical characteristics, i.e. ambipolar resistance shift in the x axis, of the 2D conducting layer is the basis for the functioning of the sensing device disclosed herein.

Figure 10 is a graph of the theoretically calculated resistance for different net dipole moments at the graphene edge in a sensing device of the present invention. The three different configurations were:

- molecules above the graphene plane ($p_z = + \mu dN$),
- crown of molecules below the graphene plane ($p_z = - \mu dN$), and
- absence of crown of dipoles ($p_z = 0$).

The $p_z = + \mu dN$ and the $p_z = - \mu dN$ corresponds to fully occupied and oriented water molecules at the edges (thus, $\eta = 1$) in the two possible orientations for polar molecules at a graphene edge. In the calculation, $\mu d = 1.85D$ was used as the dipole moment of water and the total number of dipoles at the edge, $N$, was estimated as $N = (4L)/ab$, where $4L$ is the perimeter of the graphene layer and $ab$ is the distance between binding sites at the graphene edge. From statistical analysis it can be shown that the graphene edges of the experiments performed and shown herein are saturated (fully occupied) by molecules. Thus, $ab$ will approximately be given by the second nearest neighbour distance in a graphene lattice (about 0.25 nm).
In Figure 11 is shown a graph of the sensing device resistance, $R$, measured across a device after fluorine or oxygen edge treatments and in an environment composed of dry air with 1% water vapour. The edges of different graphene layers were treated with either oxygen (O$_2$) or fluorine-based (SF$_6$) plasmas to evaluate the adsorption of polar molecules with respect to the edge passivation of graphene. Fluorine decoration at the edge was achieved by a plasma treatment of the finalized device at room temperature with SF$_6$ as precursor gas. In contrast, oxygen decoration of the graphene edges was achieved by first annealing the device up to 400 degrees, in order to eliminate residual fluorine existent from the fabrication process, and then exposing the device to two seconds of oxygen plasma in order to have oxygen chemically bonded to the graphene edge.

As the shift in the peaks of the device resistance, $R$, across the device as a function of the gate-voltage, $V_g$, is dependent on $\eta$ (the relative difference in the number of molecules above and below the graphene plane) it can be seen from figure 11 that exposing the edges of a graphene layer to fluorine reduces $\eta$. This points to a reason why the effect has previously been unreported for similar devices. Typically, the final etching process in the fabrication of an hBN encapsulated graphene device is a fluorine-based etch of the substrate-contacted hBN layer, which would have the additional effect of fluorinating the exposed graphene edges and suppressing the behaviour utilised by the device of the present invention.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.
List of references

1 sensing device
2 conducting 2D material
3 covering means
4 edge
5 bottom electrode
6 polar molecules
7 top layer
8 bottom layer
9 method step: exposing to polar molecules
10 method step: detecting a variation in ohmic resistance
11 method step: exposing to polar molecules
12 method step: detecting a variation in ohmic resistance
13 method step: varying a temperature
14 method step: estimating a fraction $f$
15 method step: estimating a total dipolar moment $p$
16 method step: encapsulating
17 method step: placing layers on bottom electrode
18 method step: shaping a desired device geometry
19 method step: creating electrical contact(s)
20 conductive electrode
CLAIMS

1. A sensing device (1) for polar molecules sensing by adsorption, said sensing
device (1) comprising :
   - at least one layer of conducting 2D material (2), such as an electrically
     continuous graphene film;
   - covering means (3) for covering said at least one layer of conducting 2D
     material (2) configured to leave at least one edge (4) of said at least one layer of
     conducting 2D material (2) accessible;
   - a bottom electrode (5) located onto said covering means (3)
     wherein said covering means (3) for covering said at least one layer of conducting
     2D material (2) is or comprises electrically insulating materials, such as a top
     layer (7) and a bottom layer (8) of electrically insulating materials located onto a
     top and a bottom surface of said at least one layer of conducting 2D material (2),
   - means for measuring electrical properties of said at least one layer of
     conducting 2D material (2), such as an electrical current, I, and a voltage, V, as a
     function of an applied gate voltage between said at least one layer of conducting
     2D material (2) and said bottom electrode (5), thereby allowing the measurement
     of said sensing device resistance while a potential sweep is performed;

20 wherein the calculation of the adsorption of polar molecules on said sensing
device (1), is performed by:
   a) estimating a fraction \( f \) (14) of binding sites with a molecule bound to them
      by statistical mechanical calculations;
   b) estimating a total dipolar moment \( p \) (15) of said sensing device (1) due to
      all the attached molecules by statistical mechanical calculations;

25 where a calculation of said \( f \) and \( p \), depend on the temperature \( \Gamma \),
      gate-voltage \( V_g \) sweep, dipolar moment of polar molecules in the mixture \( p_i \) and
      partial pressure of polar molecules in the mixture, \( P_i \).

30 2. A sensing device (1) according to claim 1, wherein said polar molecules
 comprise H2S molecules.

3. A sensing device (1) according any of the preceding claims, said sensing device
 further comprising :
4. A sensing device (1) according to any of the preceding claims 1-3, wherein said bottom electrode (5) is located onto said bottom layer of said electrically insulating materials.

5. A sensing device (1) according to any of the preceding claims 1-4, wherein said top layer (7) and/or said bottom layer (8) is or comprises electrically insulating materials such as BN, SiO₂, SiN, aluminium oxides or a combination thereof.

6. A method of sensing polar molecules, said method comprising:
   - exposing (9) to polar molecules (6) at least one edge (4) of at least one layer of conducting 2D material (2) confined between a top (7) and a bottom (8) layer of electrically insulating materials covering a top and a bottom surface of said at least one layer of conducting 2D material (2);
   - detecting (10) a variation in ohmic resistance of said at least one layer of conducting 2D material (2) while shifting a gate potential between a negative and a positive value, such as between -50 and + 50 volts, said gate potential applied between said at least one layer of conducting 2D material (2) and a bottom electrode (5) located onto said bottom layer (8) of electrically insulating materials.

7. A method of sensing polar molecules using a sensing device (1) according to any of the preceding claims 1-5, said method comprising:
   - exposing (11) to polar molecules at least one edge (4) of said at least one layer of conducting 2D material (2) confined between said top and said bottom layer (8) of electrically insulating materials;
   - detecting (12) a variation in ohmic resistance of said at least one layer of conducting 2D material (2) while applying a gate voltage sweep between a negative and a positive value, such as between -50 and + 50 volts, said gate voltage sweep applied between said at least one layer of conducting 2D material (2) and said bottom electrode (5).
8. A method of sensing polar molecules according to claim 7, further comprising:

- varying (13) a temperature of said sensing device (1) thereby changing the adsorption of said polar molecules (6) onto said at least one edge (4) of said at least one layer of conducting 2D material (2).

9. A method of monitoring orientation of polar molecules (6), said method comprising:

- changing an alignment of polar molecules (6) at an edge (4) of at least one layer of conducting 2D material (2) confined between a top (7) and a bottom layer (8) of electrically insulating materials, said at least one layer of conducting 2D material (2) having at least one edge (4) accessible, by applying a gate voltage sweep between a negative and a positive value, said gate voltage sweep applied between said at least one layer of conducting 2D material (2) and a bottom electrode (5) located onto said bottom layer (8) of electrically insulating materials.

10. A method of monitoring orientation of polar molecules (6), using a sensing device (1) according to any of the preceding claims 1-5, said method comprising:

- changing an alignment of polar molecules (6) at said at least one edge (4) of said at least one layer of conducting 2D material (2) confined between said top (7) and said bottom layer (8) of electrically insulating materials, by applying a gate voltage sweep between a negative and a positive value, said gate voltage sweep applied between at least one layer of conducting 2D material (2) and said bottom electrode (5) located onto said bottom layer (8) of electrically insulating materials.

11. The use of a sensing device (1) according to any of the preceding claims 1-5 for quantitatively and selectively sensing polar molecules (6) such as H2O, NH3 or NO2.

12. A method of producing a sensing device according to any of the preceding claims 1-5, the method comprising the steps of:

a) encapsulating (16), e.g. by the process of lamination, said at least one layer of conductive 2D material (2) between layers of electrically insulating material such that any layer of conductive 2D material (2) is sandwiched between two layers of electrically insulating material,
b) placing said layers assembled in step a) on said bottom electrode (5, 17),

c) shaping a desired device geometry (18), e.g. by one or more of the processes of lithography, etching and/or milling, in such a way that said at least one edge (4) of said at least one layer of conducting 2D material (2) is left accessible,

d) creating at least one electrical contact (19) to said conductive 2D material (2) using one or more conductive electrode(s) (20) such that a small part of said at least one edge is covered by said conductive electrode(s) (20).
Fig. 9

Theory

\[ p_z = -\mu_d N \]

\[ p_z = 0 \]

\[ p_z = +\mu_d N \]

Fig. 10
Fig. 11
INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/062286

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/12
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)
B82Y G01N B01J

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search
5 September 2019

Date of mailing of the international search report
16/09/2019

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Ruchaud, Nicolas
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<td>X</td>
<td>L. WANG ET AL: &quot;One-Dimensional Electrical Contact to a Two-Dimensional Material&quot;,</td>
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<tr>
<td></td>
<td>ISSN: 0036-8075, DOI: 10.1126/science.1244358 abstract figures page 614, column 3, line 23 - page 617, column 2, line 15 -----</td>
<td>1-5,12</td>
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