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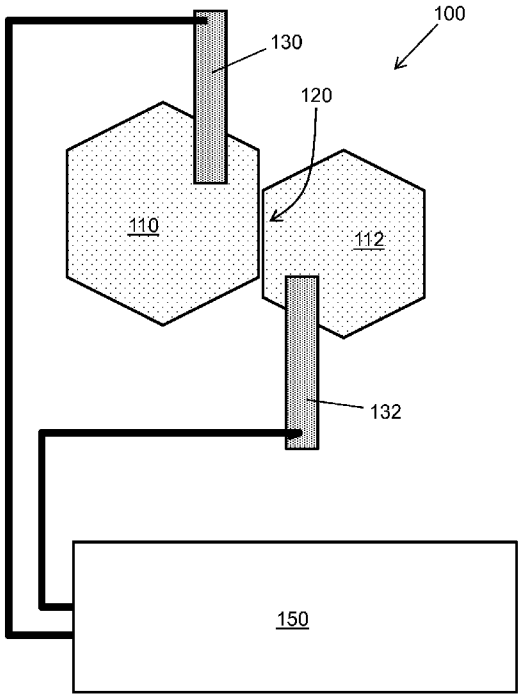

FIG. 1

(57) Abstract: The present invention relates generally to the field of chemical sensing. More specifically, in certain aspects the present invention relates to graphene -based devices and methods useful in chemical sensing. One aspect of the invention is a sensing device including a first graphene grain; a second graphene grain disposed in substantial contact with the first graphene grain, the first graphene grain and the second graphene grain having a grain boundary formed therebetween; a first electrode operatively coupled to the first graphene grain; a second electrode operatively coupled to the second graphene grain; and an electrical measurement system coupled to the first electrode and the second electrode, the electrical measurement system being configured to measure one or more electrical properties of the grain boundary.

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GRAPHENE-BASED CHEMICAL SENSING DEVICES AND METHODS FOR CHEMICAL SENSING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Patent Application serial no. 62/018,006, filed June 27, 2014, which is hereby incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates generally to the field of chemical sensing. More specifically, in certain aspects the present invention relates to graphene-based devices and methods useful in chemical sensing, such as gas sensing.

Technical Background

[0003] Graphene has been one of the most studied materials of the past decade, as a result of its exceptional electrical, mechanical and thermal properties. Despite its relatively short history, it has attracted significant scientific study for use in numerous advanced technological fields, such as photonics, high frequency electronics, nanoelectromechanical systems for mass detection, and biological sensing applications.

[0004] Graphene has also been studied for use as a sensing material in gas sensors, particularly due to its high specific surface area (~2600 m^2/g), high carrier mobility (~2500 to 40,000 $cm^2V^{-1}s^{-1}$ for supported graphene depending on temperature, carrier density, and substrate phonons) and low 1/f noise as compared to other solid state sensor materials. Such sensors depend on the fact that the electronic properties of graphene, such as the resistance, AC impedance or Hall resistance, can change when exposed to gaseous analytes.

[0005] However, conventional graphene-based chemical sensors can suffer from a variety of limitations. While graphene-based devices can advantageously be fabricated and using conventional state-of-the-art semiconductor fabrication techniques, the sensitivity of graphene can be lower than other carbon forms such as nanotubes or nanowires, especially when integrated onto a substrate into a device. Moreover, in many devices, at useful analyte concentrations, the resistance of the graphene itself is much less than the resistance between the electrical contacts and the graphene. In such devices, any change in resistance resulting from a change in analyte concentration can be difficult to measure as a result of the high contact resistance. One way that has been suggested to improve sensor response is

to eliminate defects from the graphene. See, e.g., U.S. Patent Application Publication no. 2010/0255984.

[0006] There remains a need for improved graphene-based chemical sensors.

SUMMARY OF THE INVENTION

[0007] In one aspect, the invention relates to a sensing device. The sensing device includes

a first graphene grain;

a second graphene grain disposed in substantial contact with the first graphene grain, the first graphene grain and the second graphene grain having a grain boundary formed therebetween;

a first electrode operatively coupled to the first graphene grain;

a second electrode operatively coupled to the second graphene grain; and

an electrical measurement system coupled to the first electrode and the second electrode, the electrical measurement system being configured to measure one or more electrical properties of the grain boundary.

[0008] As will be described in detail herein, the sensing device can be configured in a number of architectures. For example, the sensing device can be configured to measure the resistance across the grain boundary, i.e., as a chemiresistor device. In other aspects of the invention, the sensing device can be configured as a chemical sensing field effect transistor (chemFET).

[0009] In another aspect, the invention relates to a method for sensing an analyte. The method includes

contacting with the analyte a sensing device including

a first graphene grain; and

a second graphene grain disposed in substantial contact with the first graphene grain, the first graphene grain and the second graphene grain having a grain boundary formed therebetween; and

measuring one or more electrical properties of the grain boundary.

[0010] The devices, systems and methods of the present invention can result in a number of advantages over prior art devices, systems and methods. Notably, the grain boundary-based devices described herein can have significantly increased sensitivity as compared to single- or polycrystalline graphene-based devices. In certain aspects, the sensitivity of the

discussed grain boundary-based devices increases as the length of the device decreases (e.g., in an inversely proportional relationship), such that smaller devices can have increased sensitivity. In certain embodiments, this can lead to nanometer scale ultrasensitive sensors. Other advantages will become apparent to the person of skill in the art in view of the present disclosure.

Brief Description of the Drawings

[0011] The accompanying drawings are not necessarily to scale, and sizes of various elements may be re-scaled for clarity.

[0012] FIG. 1 is a schematic plan view of a sensing device according to one embodiment of the invention;

[0013] FIG. 2 is a schematic cross-sectional view of the sensing device of FIG. 1;

[0014] FIG. 3 is a schematic cross-sectional view of a sensing device according to another embodiment of the invention;

[0015] FIG. 4 is a schematic plan view of a sensing device according to another embodiment of the invention;

[0016] FIG. 5 is a picture of the sensing measurement setup used in the experiments described herein;

[0017] FIG. 6 is a close-up of the sensing measurement setup in FIG. 5;

[0018] FIG. 7 is an optical microscopy image of graphene after being transferred to a silicon dioxide-on-silicon substrate (scale bar = 100 μm);

[0019] FIG. 8 is a high-magnification image of the selected square region of FIG. 7 (scale bar = 20 μm);

[0020] FIG. 9 is a false color SEM image of an as-fabricated grain boundary-based sensor device (scale bar = 5 μm), annotated with an electrical circuit model of the device between the electrodes marked 3 and 4;

[0021] FIG. 10 is a D-band map of the graphene grains of the device of FIG. 9 (scale bar = 5 μm);

[0022] FIG. 11 is a 2D/G band ratio map of the graphene grains of the device of FIG. 9 (scale bar = 5 μm);

[0023] FIG. 12 is a set of selected area electron diffraction patters obtained from the left grain (G_L), the right grain (G_R) and the grain boundary region (GB);

[0024] FIG. 13 is a graph of the performance of the device of FIG. 9 in the grain and grain-boundary regions for dimethyl methylphosphonate (DMMP) and 1,2-dichlorobenzene (DCB), in which the top-to-bottom order of the legend is the same as the top-to-bottom order of the traces;

[0025] FIG. 14 is a false color scanning electron microscopy (SEM) image of a multi-electrode grain boundary sensor (scale bar = 5 μm);

[0026] FIG. 15 is a graph of the performance of the device of FIG. 14 as a function of the distance between the electrodes;

[0027] FIG. 16 is an annotated version of the image of FIG. 9;

[0028] FIG. 17 is a graph of the current-voltage (i-V) properties of the sensor of FIG. 9, in which the top-to-bottom order of the legend is the same as the top-to-bottom order of the traces at the right side of the figure;

[0029] FIG. 18 is a graph of the performance of the isolated grain boundary of the sensor of FIG. 9, as extracted from real-time sensing experiments, in which the inset magnifies the curves of the grain boundary region, the right grain and the left grain, and in which the order of the responses is isolated grain boundary, grain boundary region, right grain, left grain;

[0030] FIG. 19 is a false-color SEM image of a device with seven grain boundaries formed between eight linearly-disposed graphene grains;

[0031] FIG. 20 is a false-color SEM image of a polycrystalline graphene-based device;

[0032] FIG. 21 is a graph of the variation of the sensitivity of devices as a function of the number of grain boundaries traversed;

[0033] FIG. 22 is a schematic view of model device used as the basis for simulation experiments;

[0034] FIG. 23 is a plot of the calculated sensitivity of a multiple grain boundary device as a function of the number of grain boundaries traversed;

[0035] FIG. 24 is a schematic plan view of a model of a grain boundary between graphene grains;

[0036] FIG. 25 is a schematic cross-sectional view of a model of the grain boundary of FIG. 24;

[0037] FIG. 26 is a two-dimensional electrostatic potential energy profile across the grain boundary of FIG. 24;

[0038] FIG. 27 is a graph of one-dimensional potential profiles (with and without DMMP molecules) obtained by averaging of the 2D potential along the direction normal to the grain boundary, in which the top-to-bottom order of the legend is the same as the top-to-bottom order of the traces; and

[0039] FIG. 28 is a graph of performance of a graphene GB sensor for exposure to multiple pulses of DMMP (2 femtogram), showing full reversibility within 3-5 seconds.

DETAILED DESCRIPTION OF THE INVENTION

[0040] Grain boundaries are known to dominate the electronic, thermal, mechanical and optical properties of polycrystalline graphene. Previous experiments have suggested that the electrical conductance through grain boundaries is suppressed by a strong carrier scattering from atomic-scale quantum barriers. While the presence of grain boundaries is conventionally regarded as highly undesirable, the present inventors have unexpectedly determined that the graphene grain boundary itself is a highly advantaged structure for detection of gaseous analytes. As described in more detail herein, the inventors have determined that an isolated graphene grain boundary can have, for example, up to about 300 times greater sensitivity to a gaseous analyte as compared to a single crystalline graphene grain itself. While not intending to be bound by theory, the inventors believe, based on hybrid electronic and transport modeling, that the increased sensitivity of the grain boundary is a result of a synergetic combination of gas molecule accumulation at the grain boundary, together with the existence of a sharp onset energy in the transmission spectrum of the low-gap grain boundary conduction channels.

[0041] Topological defects have been shown to improve the sensitivity of carbon-based chemical sensors toward gas molecules due to an efficient physisorption and enhanced charge transfer process. Since such defects are formed within a single-crystalline graphene lattice, they have a modest effect on electronic properties of the device. Grain boundaries in graphene are different from mere defects in that they can form between crystalline grains that are not substantially oriented with respect to one another. Without intending to be

bound by theory, the inventors believe that this can potentially give rise to electronic transport gaps. The emergence of transmission gaps in graphene grain boundaries can be employed to acquire an on/off like behavior for the passage of charge carriers upon exposure to gas molecules. In certain aspects of the invention as described herein, an individual grain boundary is isolated, and is demonstrated to have an ultra-high sensitivity to adsorbed molecules. Grain boundary-based sensors are demonstrated to have significantly higher sensitivity as compared to polycrystalline graphene sensors.

[0042] The devices described herein can be used to detect a wide variety of chemical species. For example, in certain embodiments, the devices are used to detect gaseous species. A wide variety of gaseous species can be detected, for example, organophosphorus compounds (e.g., dimethyl methyl phosphonate), organosulfur compounds (e.g., phosgene), halogens (e.g., chlorine, bromine, iodine), ketones (e.g., acetone, methyl ethyl ketone), alcohols (e.g., methanol, ethanol, isopropanol), aldehydes (e.g., formaldehyde), aromatic volatile organic compounds (e.g., benzene, toluene), alkanes (e.g., methane, hexane, decane), alkenes (e.g., isoprene), amides (e.g., dimethylformamide), heterocyclic compounds (e.g., tetrahydrofuran), and inorganic gases (e.g., ammonia, nitrous oxide). Thus, the devices can be useful in detecting a wide variety of agents, such as solvents, incapacitating agents, greenhouse gases, pulmonary agents, diagnostically important gases and pollutants.

[0043] One embodiment of the invention is shown in schematic plan view in FIG. 1. A sensing device 100 includes a first graphene grain 110, and a second graphene grain 112. Notably, the second graphene grain is disposed in substantial contact with the first graphene grain, such that a grain boundary 120 is formed between them. The device 100 includes a first electrode 130 operatively coupled to the first graphene grain 110, and a second electrode 132 operatively coupled to the second graphene grain. The device 100 also includes an electrical measurement system 150 coupled to the first electrode and the second electrode. The electrical measurement system 150 is configured to measure one or more electrical properties of the grain boundary. For example, the electrical measurement system can be configured to measure the resistance or impedance of the grain boundary (either directly or indirectly), for example, as a chemiresistor or chemFET.

[0044] As the person of ordinary skill in the art will appreciate, graphene is a substantially carbonaceous material (*e.g.*, more than 95%, more than 98%, or even more than 99%

carbon by weight) that includes one or more one-atom-thick substantially planar layers of sp^2-bonded carbon atoms, densely packed in a honeycomb-type array. The material may include only a single layer of carbon atoms, or may include a plurality of layers of carbon atoms. For example, in certain embodiments, the graphene is provided as a substantial monolayer of carbon atoms. In other embodiments, the graphene is provided as about 2 to about 10 layers of carbon atoms (e.g., about 2 to about 7 layers, or about 2 to about 5 layers). The graphene may, for example, be doped, for example to form n-type graphene (in which the majority of the carriers are electrons) or p-type graphene (in which the majority of the carriers are holes). The graphene grains themselves can be formed in a variety of matters (e.g., chemical vapor deposition) and are desirably grown together such that the grain boundary is formed between them. As the person of ordinary skill in the art will appreciate, the graphene can be grown via deposition on a first substrate (e.g., a copper foil) and transferred to a second substrate (e.g., an insulating substrate such as silicon dioxide-on-silicon). One particular method for making graphene grains with well-defined grain boundaries is described in the Examples, below.

[0045] Each graphene grain is desirably substantially single-crystalline. That is, each grain may include minor defects that do not substantially detract from the overall order of the grain.

[0046] As the person of ordinary skill in the art will appreciate, the grain boundary between the two grains is defined by a substantial disruption in the honeycomb pattern of the atomic structures as one grain abuts the other. For example, the two grains may be offset from one another positionally, angularly, or both, such that the honeycomb pattern of the first grain does not exactly match the honeycomb pattern of the second grain. For example, in certain embodiments, there is a substantial angular disruption from one grain to the other.

[0047] As the first grain is in substantial contact with the second grain, the grain boundary itself is typically very narrow, for example, less than about 100 nm, less than about 30 nm, less than about 10 nm, less than about 5 nm, or even less than about 1 nm in width. In various embodiments of the devices and methods as described herein, the grain boundary is desirably greater than about 1 μm, greater than about 3 μm, greater than about 5 μm, greater than about 7 μm, or even greater than about 10 μm in length. For example, in certain embodiments, the grain boundary has a length in the range of about 1 μm to about 50 μm, about 1 μm to about 30 μm, about 1 μm to about 20 μm, about 1 μm to about 15 μm, about

3 μm to about 50 μm, about 3 μm to about 30 μm, about 3 μm to about 20 μm, about 3 μm to about 15 μm, about 5 μm to about 50 μm, about 5 μm to about 30 μm, about 5 μm to about 20 μm, about 5 μm to about 15 μm, about 7 μm to about 50 μm, about 7 μm to about 30 μm, about 7 μm to about 20 μm, about 7 μm to about 15 μm, about 10 μm to about 50 μm, about 10 μm to about 30 μm, or about 10 μm to about 20 μm. The person of ordinary skill in the art will appreciate that the grains are desirably entirely distinct from one another, i.e., the grain boundary is not merely a defect in an otherwise single grain.

[0048] The electrodes can be configured in a variety of fashions and formed from a variety of materials, depending on the particular measurement method to be used. For example, in certain embodiments of the devices and methods as described herein, the first electrode can be disposed in substantial electrical contact with the first grain. Similarly, the second electrode can be disposed in substantial electrical contact with the second grain. Such a configuration can be useful, for example, in measuring the resistance or impedance of the grain boundary. One way to provide substantial electrical contact is to form the electrodes on the grains themselves (e.g., by deposition). Accordingly, in certain embodiments of the devices and methods as described herein, the first electrode is disposed on the first graphene grain; and/or the second electrode is disposed on the second graphene grain.

[0049] As noted above and described in further detail below, the inventors have determined sensitivity can be greatly increased by isolating the grain boundary, i.e., configuring the device to minimize the amount of the graphene grains themselves that are interrogated by the measurement. Accordingly, the first and second electrodes are desirably disposed close to the grain boundary. For example, in certain embodiments of the devices and methods as described herein, the first electrode is disposed within about 50 μm of the grain boundary, within about 20 μm of the grain boundary, within about 5 μm of the grain boundary, within about 2 μm of the grain boundary, within about 1 μm of the grain boundary, or even within about 500 nm of the grain boundary. In certain such embodiments, the first electrode is disposed at least about 50 nm, at least about 100 nm, or at least about 200 nm from the grain boundary. Similarly, in certain embodiments of the devices and methods as described herein, the second electrode is disposed within about 50 μm of the grain boundary, within about 20 μm of the grain boundary, within about 5 μm of the grain boundary, within about 2 μm of the grain boundary, within about 1 μm of the grain boundary, or even within about 500 nm of the grain boundary. In certain embodiments of the devices and methods as

described herein, the second electrode is disposed within about 50 μm of the first electrode, within about 20 μm of the first electrode, within about 5 μm of the first electrode, within about 2 μm of the first electrode, or even within about 1 μm of the first electrode. In certain such embodiments, the first electrode is disposed at least about 50 nm, at least about 150 nm, or at least about 300 nm from the second electrode. Desirably, there is no additional grain boundary between the first electrode and the second electrode (i.e., there is only a single grain boundary between the first electrode and the second electrode). Desirably, there are no substantial crystalline defects between the first electrode and the second electrode (i.e., other than the grain boundary).

[0050] The electrodes can be formed from a variety of materials, as is conventional in the art. For example, the electrodes can be formed as a thin layer of chromium (to improve adhesion to the grains and to other materials of the device topped with a layer of gold (for good electrical contact to wires, probes, and other electrical components of the device). Electrodes may be patterned and formed using photolithography, deposition, and other conventional techniques.

[0051] As the person of ordinary skill in the art will appreciate, the device may be constructed on a substrate. The substrate can, for example, be an insulating substrate, to electrically isolate the graphene grains and the grain boundary. The substrate can have multiple layers; in certain embodiments, while the topmost layer is insulating, the others need not be. Examples of substrates include silicon dioxide, silicon nitride and silicon oxynitride (e.g., each of which can be disposed on silicon or glass), a glass material, or a polymeric material; the person of ordinary skill in the art will appreciate that a variety of alternative substrates can be used. A schematic cross-sectional view of the device of FIG. 1 is shown in FIG. 2. Here, the graphene grains are disposed on a substrate 140. Of course, the person of ordinary skill in the art will appreciate that other configurations may also be used.

[0052] As the person of ordinary skill in the art will appreciate, the electrical measurement system may take a number of forms. For example, the electrical measurement system can be provided as a specially-configured circuit or device, or can be assembled from general purpose components. The electrical measurement system can, for example, include a computer for the collection and/or analysis of data. The person of ordinary skill in the art

will configure the electrical measurement system depending on the measurement to be performed, in view of the present disclosure.

[0053] In certain embodiments, the electrical measurement system is configured to measure the resistance or impedance of the grain boundary. For example, the resistance or impedance can be measured directly, with the device configured as a chemiresistor. For example, in the device shown in FIG. 1, the electrical measurement system can run a known current through the electrodes, and determine the resistance by measuring the voltage drop. Of course, other methods of determining resistance can be used.

[0054] In other embodiments, the device is configured as a chemical field-effect transistor (chemFET). One example of such an embodiment is shown in cross-sectional view in FIG. 3. Here, the substrate 340 includes a top insulating layer 342 (e.g., SiO_2), and a layer 344 (e.g., n-doped silicon) that can act as a gate in the field-effect transistor. The person of ordinary skill in the art will recognize that the gate can be formed only in a portion of the substrate. The device also includes first and second graphene grains 310 and 312 disposed on the insulating layer 342, such that the insulating layer is disposed between the graphene grains and the gate, and configured together to form a grain boundary 322, and the first and second electrodes 330 and 332, as described above with reference to FIGS. 1 and 2. Here, the first and second electrodes can act as source and drain for the chemFET; together with the gate they are coupled to the electrical measurement system. The electrical measurement system can be configured to measure the current flow between the first electrode and the second electrode, for example, at a variety of voltages applied at the gate, thereby providing an indirect measure of resistance or impedance of the grain boundary. Of course, the person of ordinary skill in the art will determine other sensing architectures in which the grain boundary-based devices described herein can be configured.

[0055] Multiple grain boundaries can be used in the construction of a grain-boundary device, for example, by linking them together electrically. For example, in certain embodiments, grain-boundary devices are linked together in series. In the chemiresistor embodiment shown in schematic plan view in FIG. 4, the device includes contiguous graphene grains 410, 412, 413 and 414, as well as contiguous graphene grains 415 and 416. The grain boundary between grain 410 and grain 412 is identified reference numeral 422; the person of ordinary skill in the art will appreciate that grain boundaries are formed between other pairs of contiguous grains. Electrodes 430 and 432 are disposed on grains

410 and 412, close to the grain boundary 422 as described above. Electrodes 433 and 434; 435 and 436 and 437 and 438 are disposed on various grains close to the other grain boundaries. Electrode 432 is connected to electrode 433, electrode 435 is connected to electrode 435, and electrode 436 is connected to electrode 437, such that the four grain boundaries in the device are connected in series. The electrical measurement system 450 is coupled to electrode 430 and electrode 438, and thus can be used to measure the overall resistance of the four series-connected grain boundaries. Of course, the person of ordinary skill in the art will appreciate that multiple grain boundaries can be electrically interconnected in a different fashion, e.g., in parallel, in parallel-series, or in series-parallel.

[0056] The devices described herein can be used in a wide variety of chemical sensing systems. Such systems can include not only the grain boundary devices as described herein, but also other additional components. For example, in certain embodiments, in order to cancel out environmental effects, a system can include two devices as described herein, with one device exposed to analyte and another device not exposed to analyte. The response of the unexposed device can be used to cancel out environmental effects (e.g., temperature, humidity) from the measurement. Alternatively, temperature, humidity or other interferents can be measured differently (e.g., by conventional measurement devices included in the system) and used to cancel their effect on the output of the graphene grain boundary-based device.

[0057] In certain embodiments of the systems, devices and methods as described herein, the device is positioned at the output end of a chromatography column, e.g., a gas chromatograph. Accordingly, in certain embodiments, chromatography can be used to separate various analytes from one another; and the devices described herein can be used to quantify the amount of each analyte. Of course, the person of ordinary skill in the art will appreciate that other preprocessing (e.g., filtration, exposure to molecular sieves) can be used before contacting an analyte with the device.

[0058] The signal obtained from the graphene grain boundary-based sensors described herein will depend strongly on the initial doping level and configuration of the grain boundary-based device as well as on the analyte itself. For example, as demonstrated below, for substantially identical devices dimethyl methylphosphonate and 1,2-dichlorobenzene can provide responses that are opposite in sign. Accordingly, a sensing system can be provided with a plurality of grain boundary-based sensors, which are each

tuned to a different initial doping condition. Each sensor can thus provide different response characteristics for different analytes. The different responses can be used to distinguish among analytes, for example, using a library of signal responses for different analytes. Accordingly, as the person of ordinary skill in the art will appreciate, use of a plurality of devices in such manner can allow for the selective determination of the identity and amounts of a plurality of analytes in the same sensing environment. In certain embodiments, a sensing system includes in the range of 2-40, in the range of 5-40, in the range of 10-40, in the range of 20-40, in the range of 2-20, in the range of 5-20, in the range of 10-20, in the range of 2-10, or in the range of 5-10 grain boundary-based sensing devices. The initial doping condition of each device can be selected in a number of different ways. for example, by the application of different gate voltages (when configured as a chemFET), the deposition of the sensors on different substrates, by doping with different amounts and types of dopants, or by the use of layers of different materials in the device, for example, on the substrate, or under or above the graphene layer.

[0059] Accordingly, in one embodiment a system can include multiple grain boundary devices as described herein, each having different response characteristics. The system can include, for example, a microprocessor or other computer system configured to receive the different responses from the grain boundary devices and determine the presence and/or concentration of one or more analytes. The individual grain boundary devices can differ from one another by one or more of different gate voltages (when configured as chemFETs), the use of different substrates, different kinds and amounts of dopants in the graphene grains, or by the use of layers of different materials in the devices.

[0060] For example, in certain embodiments, the sensing devices are fabricated on different underlying substrates. The identity of the substrate can have a significant effect on the performance of the device with respect to particular analytes. For example, different sensing devices can be built on different siliconoxynitride substrates having different amounts of oxygen and nitrogen therein (including optionally pure silicon dioxide and pure silicon nitride). The different substrates can be integrated together into a single chip (e.g., different silicon oxynitride substrate layers can be disposed side-by-side on the same silicon chip to provide an integrated multi-sensor system).

[0061] In certain embodiments, the sensing devices can have different coatings disposed thereon, for example, as a layer on top of the graphene. The coatings can be, for example,

layers of polymers or other chemical species that will react differently with different analytes, thereby providing differentiable signals for different analytes. In certain embodiments, the layers can tune the response of the graphene itself, independent of any analyte-specific effects.

[0062] The multiple devices can be fabricated, for example, on a single chip (or other discrete physical entity) by the person of ordinary skill in the art, in order to provide integrated devices. Of course, in other embodiments, the multiple devices are fabricated on a plurality of chips (or other discrete physical entities).

[0063] The devices described herein can be configured, for example, as a so-called "electronic nose," or otherwise configured for use in gas discrimination applications.

[0064] The devices and systems described herein can be used in sensing a variety of analytes. The analyte may be, for example, a gaseous analyte. In certain embodiments, the analyte is a gaseous organic analyte.

[0065] In one embodiment, the invention provides a method for sensing an analyte, including contacting a device as described herein with the analyte, and measuring one or more electrical properties of the grain boundary.

[0066] In another embodiment, a method for sensing an analyte includes contacting the analyte with a sensing device; and measuring one or more electrical properties of the grain boundary (for example, as described herein, for example, resistance or impedance). The sensing device includes a first graphene grain; a second graphene grain disposed in substantial contact with the first graphene grain, the first graphene grain and the second graphene grain having a grain boundary formed therebetween. The graphene grains and the grain boundaries can be as described herein.

[0067] As the person of ordinary skill in the art will appreciate, the methods can be performed as otherwise described herein.

[0068] Certain aspects of the invention will be further described by the following non-limiting examples.

EXAMPLES

Methods

[0069] Graphene growth: Graphene grains were synthesized on copper foils (from Alfa Aesar, product no. 46365) by chemical vapor deposition process at ambient pressure (see, e.g., Yu, Q. *et al.*, "Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition," Nat Mater.,10, 443–449 (2011), which is hereby incorporated herein by reference in its entirety). First, copper foils were treated for 10-20 minutes in hydrochloric acid (10% in deionized water) and rinsed thoroughly in acetone and isopropanol followed by drying in argon gas flow to clean the surface. The cleaned samples were immediately loaded into the chemical vapor deposition chamber, then the chamber was evacuated (down to 1 mtorr) and then purged with forming gas (5% hydrogen diluted in argon) up to atmospheric pressure. The samples were heated up to 1050 °C in the forming gas atmosphere and annealed for 60 minutes. Annealing in hydrogen helps to improve the copper substrate quality by reducing nucleating points. Finally, graphene growth was carried out by introducing 20 ppm diluted methane (in argon) for a precisely controlled time to obtain the desired grain size and surface coverage, such that, for at least some of the grown graphene grains, adjacent grains grew together to provide a grain boundary therebetween. The samples were then rapidly cooled down to room temperature in forming gas atmosphere, and carefully removed from the chamber for further processing.

[0070] Raman Spectroscopy: Raman spatially resolved maps were obtained using a Horiba JobinYvonXplora confocal Raman microscope equipped with a motorized sample stage from Marzhauser Wetzlar. The laser excitation wavelength was 532 nm and the maps were obtained for graphene grain boundary samples transferred to a SiO_2 substrate. The spectral resolution of the laser was 2.5 cm^{-1}, and pixel size of the map was 500 nm. D (~1350 cm^{-1}), G (~1580 cm^{-1}) and 2D-band (~2690 cm^{-1}) spatial maps were extracted.

[0071] Transmission Electron Microscopy: Transmission electron microscopy (TEM) images and diffraction patterns were acquired on an aberration-corrected JEOL JEM-ARM200CF, operated at 80 kV to minimize beam damage effects. Graphene samples were first transferred to a 30 nm thick silicon nitride membrane using a polymer assisted transfer technique. Samples were then annealed at 350 °C for 3-4 hours in the presence of forming

gas (5% hydrogen in argon) to remove any residual contamination before being loaded into the microscope for characterization.

[0072] Scanning Electron Microscopy: Scanning Electron Microscopy (SEM) was performed in order to visualize the morphology of the sensing devices. The instrument used for characterization is integrated in a Raith e-LiNE plus ultra-high resolution electron beam lithography system. During imaging the samples were maintained at a distance of 10 mm from the electron source and the voltage was maintained at 10 kV. The devices were imaged without additional sample preparation.

[0073] Device Fabrication: The grown graphene films (on Cu) with distinguishable grain boundaries were transferred to a highly-doped Si/SiO_2 wafer, using a polymer (poly(methyl methacrylate) (PMMA))-assisted technique. After transfer, samples were annealed in a furnace at 350 °C for 90 minutes under forming gas (5% hydrogen in argon, 70 sccm flow rate) to remove the polymer residue. Based on the geometrical shape of the flakes in the partially covered graphene film, it was possible to detect the GBs and locate them relative to the predefined alignment marks on the substrate. The images obtained from bright-field optical microscopy (or SEM at low acceleration voltage) were used to design and place the electron beam lithography patterns. In a first lithography step, excess graphene flakes were etched away to remove any potential electrical pathways between the desired locations of the electrodes. In a second lithography step, electrode patterns were transferred onto the sample and chromium/gold (7/50 nm) electrodes were deposited using electron beam evaporation. The geometry of the sensors was defined to reduce the edge defects and eliminate their corresponding gas sensing response. Bilayer PMMA coating was used in both lithography steps to facilitate metal lift-off process and obtain higher etch resistance. Before being used as sensors, the samples were again annealed at 400 °C for 2 hours to remove any residues from the fabrication process.

[0074] Sensing Experiments: The sensing experiments were performed using a customized sensing platform. As shown in the perspective view of FIG. 5, a probe station equipped with 7 micro positioners was used to make electrical connections to the sensors and position the capillary column of a HP 6890 gas chromatography system directly on top of the sensor. The measurement electronics included a dual channel source-meter from Keithley (model 2612A) and a combo delta-mode system (model 6221/2182A). Data acquisition was automated through MATLAB. FIG. 6 is a close-up view of the needles and

the capillary column on top of a fabricated sensor. The GC was used to inject a known volume (0.2 μL) of dimethyl methylphosphonate (DMMP) or 1,2-dichlorobenzene (DCB). DMMP and DCB were purchased from Sigma-Aldrich and used without further purification. Electrical resistances of the devices were monitored using the Keithley 2612A source-meter. A constant current (50 μA) was applied across the electrodes during the sensing experiments.

[0075] Density Functional Theory: Classical molecular dynamics simulations were performed using NAMD and the CHARMM32 force field. For the purposes of the calculations, the temperature was fixed at 300 K by Langevin dynamics with a damping constant of γ_{Lang}=10 ps^{-1}. The non-bonded interaction switching distance was set to 7 Å, and the cutoff was set to 10 Å. The systems were simulated as NVT ensembles, where the particle mesh Ewald summation is considered for Coulombic coupling. First-principles calculations were carried out using the density functional theory approach implemented in the TeraChem code. In all of these simulations the energies and forces were evaluated using the Becke, Lee, Yang, and Parr (BLYP) exchange-correlation functional with a DFT-D dispersion correction with 3-21g basis set. The charges were calculated within the Mulliken scheme.

Results

[0076] As described above, graphene was synthesized using atmospheric pressure chemical vapor deposition, with precise control over the growth time and environmental conditions. In this approach, single crystalline hexagonal graphene grains grow discretely and subsequently coalesce together forming an individual grain boundary between adjacent grains. FIG. 7 is an optical microscopy image of graphene (after transfer to a Si/SiO_2 substrate) demonstrating the array of merged grains (scale bar – 100 μm). FIG. 8 is a high-magnification image of the selected square region of FIG. 8. This image clearly illustrates the formation of hexagonal coalesced grains (scale bar – 20 μm).

[0077] FIG. 9 is an annotated top view of a fabricated sensor according to one embodiment of the invention. As is evident, two hexagonal substantially single-crystalline grains have grown together to form a grain boundary (i.e., the interface between the two hexagonal grains). Chrome/gold electrodes are disposed at various positions on the grains. FIG. 10 is a spatially resolved Raman spectroscopy map of the grains of FIG. 9, obtained for the disorder-induced D band (wavenumber ~1350 cm^{-1}). The intense I_D signal obtained in the

merging region (and the generally low I_D signal in the remainder of the plot) of the grains provides strong evidence for the defective nature of GB region. The occasional I_D signals in the grains themselves are evidence of structural defects within the perfect lattice, which can be attributed to the nucleation points. The presence of such occasional defects does not prevent the grains from being considered substantially single crystalline. FIG. 11 is a map of the ratio of 2D-to G-band intensity (I_{2D}/I_G) where the high intensity ratio (> 2.5) over the entire scanned area confirms the uniform existence of monolayer graphene. FIG. 12 provides selected area electron diffraction (SAED) patterns obtained from transmission electron microscopy (TEM) for the grains (GL and GR) and the grain boundary region (GB). Identical and sharp hexagonal diffraction patterns recorded for the grains in different regions confirm their substantially single crystalline nature. However, a twofold diffraction pattern was observed when the aperture was located exactly at the merging region, demonstrating a crystallographic mismatch between the grains, thus providing further evidence for the existence of the grain boundary.

[0078] The molecular sensing characteristics of an individual grain boundary was determined by monitoring the resistance change of the grain boundary region during the exposure to gas molecules and comparing it with that observed in the gas-exposed grains. All sensing experiments were performed in ambient conditions using pulse injection method (see methods). Sensing platforms as set forth herein permit the simultaneous sensing response for the left grain (G_L, between electrodes 2 and 3), the right grain (G_R, between electrodes 4 and 5) and the grain boundary (i.e., between electrodes 3 and 4) to be recorded. A known concentration (50 ppb) of gas molecules (dimethyl methylphosphonate (DMMP) and 1,2-dichlorobenzene (DCB) were injected over the sensing devices. DMMP and DCB analytes represent analytes having electron donating and electron accepting features, respectively. FIG. 13 is a graph of the typical sensing response towards DMMP and DCB gas molecules for the grains and the GB region. Here, sensitivity (S) is defined as $S = (R - R_0)/R_0$, where R_0 and R are the initial resistance (i.e., in the absence of gas exposure) and final resistance (after gas exposure), respectively. Upon injection of gas molecules, the two grains and the grain boundary responded immediately and reach maximum sensitivity within ~10 s. For all fifteen devices tested, positive signals (i.e., an increase in resistance) were exhibited for DMMP, and negative signals (i.e., a decrease in resistance) were exhibited for DCB. This is consistent with the electron-donating or electron-accepting nature of the molecules, as described in Schedin et al., "Detection of individual gas

molecules adsorbed on graphene," Nat Mater., 6, 652–655 (2007), which is hereby incorporated herein by reference in its entirety.

[0079] Notably, the sensitivity in the grain boundary region (between electrodes 3 and 4) of each of the devices was significantly higher than the sensitivities of the grains themselves (i.e., between electrons 2 and 3 or between electrons 4 and 5), regardless of the type of gas molecules. For DMMP, the sensitivity in the grain boundary region (39.5%) is more than one order of magnitude (14 times) that of the grains themselves (2.8%). Similarly, for DCB, the sensitivity of the grain boundary region (11%) is almost 5 times that of the grains themselves (2.3%). These data suggests that the grain boundary itself is substantially responsible for the enhanced sensitivity in the grain boundary region.

[0080] Moreover, the present inventors have determined that the sensitivity of a grain boundary is significantly improved as the grain boundary is isolated from its adjacent grains (i.e., when the electrodes are closer to the grain boundary). An experimental sensor, shown in the photomicrograph of FIG. 14, was fabricated with several electrodes located at different distances from the grain boundary. As shown in FIG. 15, the sensitivity of the grain boundary region increased from 17% to 70% (50 ppb DMMP) as the distance between the active electrodes was reduced from 43.6 m to 2.8 m. The extension of a fitted exponential curve reveals that a much higher sensitivity may be achieved by further minimizing the distance between the patterned electrodes.

[0081] To entirely exclude the contribution of adjacent graphene regions, a simultaneous sensing experiment was carried out on the left grain, right grain and grain boundary regions of the device of FIG. 9, shown in annotated view in FIG. 16. At each time step, the measured sheet resistances of the left and right grains was used to solve for the additional resistance in the grain boundary region, which is directly attributed to the grain boundary. The sheet resistances of the left and right grains were calculated using the *I-V* characteristics of device ($R_{2\text{-}3}$ for left grain and $R_{4\text{-}5}$ for right grain) and considering the geometry of the flakes using the equation ($R_{\square}=R.W_{Avg.}/L$). For each grain, L is the distance between corresponding electrodes and $W_{Avg.}$ is the geometric mean of the sample width, calculated from $\frac{1}{W_{Avg.}} = \frac{1}{L}\int_0^L \frac{dx}{W(x)}$. Using an inverse approach, the resistance of the portions of the grains between electrodes 3 and 4 and the grain boundary were calculated ($R_{3\text{-}G}$ and $R_{4\text{-}G}$), and the resistance of the isolated grain boundary was extracted as ($R_{GB}=R_{3\text{-}4}-R_{3\text{-}G}-R_{4\text{-}G}$). In the measurement setup, resistances of left, right and grain boundary region were monitored

simultaneously, and the time-dependent resistance of the isolated grain boundary was plotted. The sensitivity for the isolated grain boundary was calculated as a percentage of the initial resistance of the device (i.e., in the absence of analyte).

[0082] While not intending to be bound by theory, the inventors believe that the suppressed electrical conductivity at the grain boundary is due to enhanced scattering at grain boundary defect sites. In absence of any gas molecules, the sheet resistance of ~740Ω/sq was observed for the grain boundary region of the device shown in FIG. 9 (i.e., as measured between electrodes 3 and 4) while slightly lower values of 680Ω/sq and 695Ω/sq were recorded for the left and right grains, respectively. I-V curves for the three regions are provided as FIG. 17. Using an equivalent resistance model (shown as three resistors in series in the annotations of FIG. 9), the isolated resistance of the grain boundary itself can be determined as $R_{GB}=R_{3\text{-}4}-(R_L+R_R)$, where R_L and R_R are calculated using the sheet resistances of the left and right grains, in each snapshot. In the devices prepared as described above with reference to FIG. 9, the calculated R_{GB} values before exposure to gas molecules are found to be in the range of 5-35 ohms. For the device shown in FIG. 9, R_{GB} changed from 15.3 to 142 ohms upon exposure to 50 ppb of DMMP gas molecules. FIG. 18 shows the time-dependent sensitivity of the isolated grain boundary, demonstrating a maximum senstivity of 828% -- about 300 times higher compared to the adjacent single crystalline grains under identical experimental conditions.

[0083] Grain boundaries are also present in large area polycrystalline graphene sensors; in a typical polycrystalline graphene sensor, many grain boundaries are disposed between electrodes. To compare the performance of a polycrystalline graphene sensor to the sensors according to various aspects of the invention, the sensing response of a polycrystalline graphene sample was investigated. FIG. 19 is a false-color SEM image of a device with seven grain boundaries formed between eight linearly-disposed graphene grains. Electrodes were disposed along the grains to allow current to be measured across multiple grains and grain boundaries. A polycrystalline sensor was also fabricated and tested; a false-color SEM is provided as FIG. 20. The results (at 50 ppb DMMP) are provided in FIG. 21. As the number of grain boundaries increased from two to seven, the sensitivity dropped from 38.9% to 19.8% as the number of grain boundaries traversed. As discussed above with respect to FIG. 15, for the case of a single grain boundary, there is a strong length dependency; this dependency was less significant when multiple grain boundaries were

traversed. Thus, as the number of grain boundaries increased, the sensitivity approached that of a polycrystalline device. This behavior can be explained using an equivalent resistance model for the multiple GBs sensor where the sensitivity of the polycrystalline sensor is anticipated to be around 17%, fairly close to the experimental result (15%). The model is based on a repeating unit cell of the resistances in series having similar configuration to the fabricated single grain boundary device, as shown in FIG. 22. In this model, the sensitivity can be represented as:

$$S = \frac{N \cdot \Delta R_{GB} + 2N \cdot \Delta R_{G1} + (N-1) \cdot \Delta R_{G2}}{N \cdot R_{GB} + 2N \cdot R_{G1} + (N-1) \cdot R_{G2}}, \qquad (S1)$$

where N is the number of grain boundaries, R_{GB} is the resistance of an isolated grain boundary, R_{G1} is the resistance of a grain region adjacent the grain boundary, and R_{G2} is the resistance of the single crystalline region, with the deltas being calculated as the difference before and after gas exposure. The sensitivity of the model as a function of N is calculated using the typical experimental values of the single grain boundary device previously described. For the case of one grain boundary, R_{G2} is eliminated, thus the sensitivity is greatly increased. The inventors believe that the minor differences between the experimental data (FIG. 21) and the calculated values (FIG. 23) are due, for example, to the asymmetric nature of the fabricated devices in terms of variation in the position of the electrodes with respect to grain boundaries, and non-equal resistances of the grain boundaries and the grain regions. However, the calculations agree with the experimental results in consistently suggesting that the sensitivity is greatly suppressed in polycrystalline devices, and that a single isolated grain boundary can provide the highest sensitivity

[0084] Accordingly, a sensor based on an isolated grain boundary can be greatly advantaged in sensitivity as compared to polycrystalline graphene-based sensors. The response of the device can be improved by interrogating only the area immediately surrounding a grain boundary; as less of the graphene grains themselves are interrogated, the response is increased as the grain boundary becomes more isolated, approaching the very large sensitivity shown in FIG. 13. This effect is generally not achievable in a conventional polycrystalline device, since the resistances of the graphene grains themselves are not avoided.

[0085] While not intending to be bound by theory, in order to explain the increased sensitivity of the grain boundary, the electronic structure and transport in a typical graphene

grain boundary with an 18° mismatch angle can be modeled. The model grain boundary, shown in schematic view in FIGS. 24 and 25, consists of a quasi-periodic meandered line of defects formed between two graphene grains which are deposited on an amorphous SiO_2 substrate to obtain their realistic doping conditions. The stress-relaxed structure forms a corrugation along the GB, giving rise to an effective $p - p' - p$ doping distribution due to different equilibrium heights from the substrate. This has been demonstrated by calculating a two-dimensional (2D) electrostatic potential profile (FIG. 26) in the grain boundary region, showing significant electric field gradients. DMMP molecules with permanent dipole were attracted to the regions of high electric field gradient, thus residing mostly on the $p - p' - p$ interface (locally accumulated on the grain boundary). FIG. 27 shows a one-dimensional potential obtained by averaging the 2D potential along the direction normal to the grain boundary (with and without DMMP molecules). In the grain boundary region the resulting 1D potential has a significant modulation compared to the pristine grain regions. The accumulation of molecules on grain boundary results in a more intense charge donation, and consequently greater shift in the local doping level.

[0086] Moreover, since a typical grain boundary is significantly meandered, its local regions with different orientations with respect to the graphene grains can be seen as individual channels for an electron passage through the grain boundary. The electron transport properties of these channels are determined by the crystallographic orientation of the grains, local angles of these grain boundary regions, and local topologies of grain boundary defects. In general, such channels can have transmission spectra with different transport gaps. Depending on the sizes of these gaps and the level of substrate doping, initial state of the transport channels can be opened or closed. Upon adsorption of polar analytes, with an electron donating or accepting nature, close to the grain boundary, the transmission spectra of the channels can be further shifted with respect to the Fermi level. The local doping by analytes can open more or close back some of the electron transport channels, with a dramatic effect on the grain boundary resistance resulting in the high sensitivity of the grain boundary to the gas molecules.

We Claim

1. A sensing device comprising

a first graphene grain;

a second graphene grain disposed in substantial contact with the first graphene grain, the first graphene grain and the second graphene grain having a grain boundary formed therebetween;

a first electrode operatively coupled to the first graphene grain, the first electrode being disposed within about 20 μm of the grain boundary;

a second electrode operatively coupled to the second graphene grain, the second electrode being disposed within about 20 μm of the grain boundary; and

an electrical measurement system coupled to the first electrode and the second electrode, the electrical measurement system being configured to measure one or more electrical properties of the grain boundary.

2. The sensing device according to claim 1, wherein the first electrode is disposed on the first graphene grain and the second electrode is disposed on the second graphene grain.

3. The sensing device according to claim 1, wherein the first electrode is disposed in substantial electrical contact with the first graphene grain and the second electrode is disposed in substantial electrical contact with the second graphene gain.

4. The sensing device according to any of claims 1-3, wherein the electrical measurement system is configured to measure the resistance or impedance of the grain boundary.

5. The sensing device according to any of claims 1-3, wherein the sensing device further comprises a gate and an insulating layer disposed on the gate, wherein the first graphene grain and the second graphene grain are disposed on the insulating layer, such that the insulating layer is disposed between the graphene grains and the gate, and wherein the electrical measurement system is further coupled to the gate.

6. The sensing device according to claim 5, wherein the electrical measurement system is configured to measure the current flow between the first electrode and the second electrode.

7. The sensing device according to any of claims 1-6, wherein the first electrode is disposed within about 5 μm of the grain boundary.

8. The sensing device according to any of claims 1-6, wherein the first electrode is disposed within about 1 μm of the grain boundary.

9. The sensing device according to any of claims 1-8, wherein the second electrode is disposed within about 5 μm of the grain boundary.

10. The sensing device according to any of claims 1-8, wherein the second electrode is disposed within about 1 μm of the grain boundary.

11. The sensing device according to any of claims 1-10, wherein the first electrode is within about 20 μm of the second electrode.

12. The sensing device according to any of claims 1-10, wherein the second electrode is disposed within about 5 μm of the first electrode.

13. A method for sensing an analyte, comprising contacting a device according to any of claims 1-12 with the analyte, and measuring one or more electrical properties of the grain boundary.

14. A method for sensing an analyte, the method comprising

contacting with the analyte a sensing device including

a first graphene grain; and

a second graphene grain disposed in substantial contact with the first graphene grain, the first graphene grain and the second graphene grain having a grain boundary formed therebetween;

measuring one or more electrical properties of the grain boundary.

15. The method according to claim 13 or claim 14, wherein the measured electrical property is resistance or impedance.

16. A chemical sensing system comprising a plurality of sensing devices according to any of claims 1-12.

17. A chemical sensing system according to claim 16 wherein the sensing devices are configured as chemFETs, each having a different gate voltage.

18. A chemical sensing system according to claim 16, wherein the sensing devices have differently-doped graphene grains.

19. A chemical sensing system according to claim 16, wherein the sensing devices have different underlying substrates.

20. A chemical sensing system according to any of claims 16-19, further comprising a chromatography column having an input end and an output end, wherein the one or more sensing devices are disposed at the output end of the chromatography column.

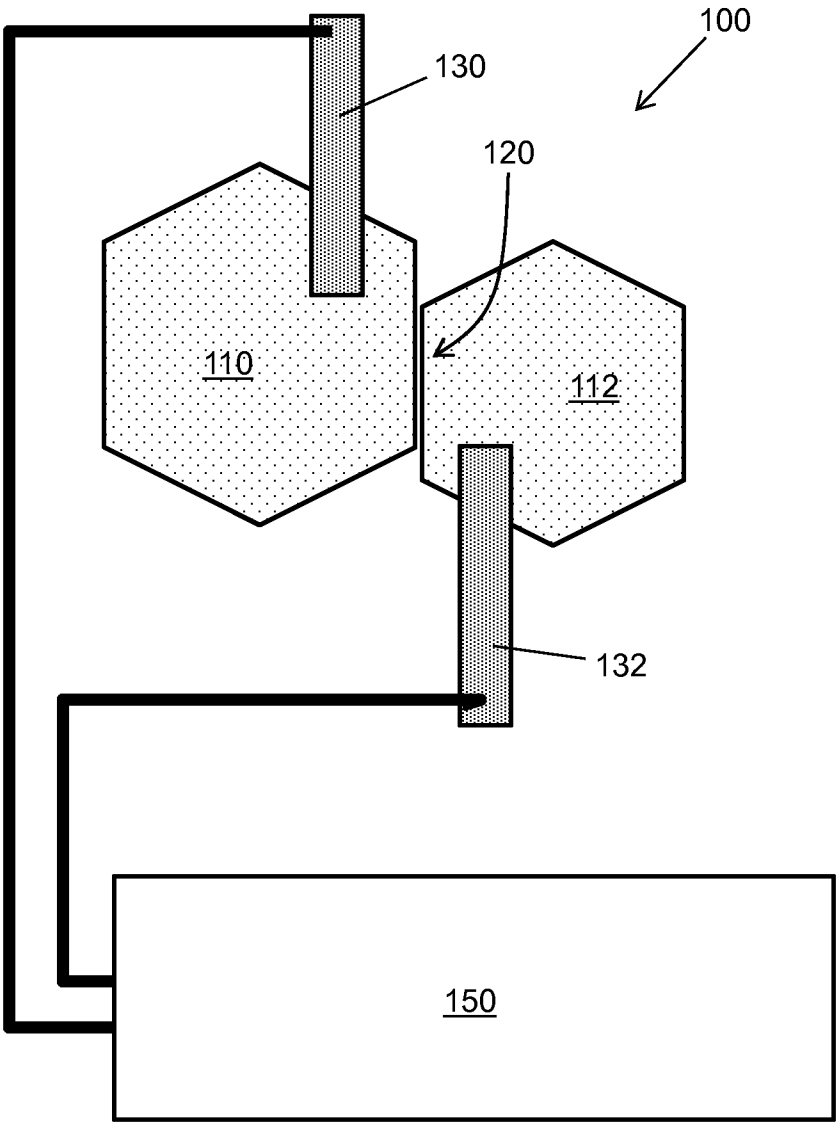


FIG. 1

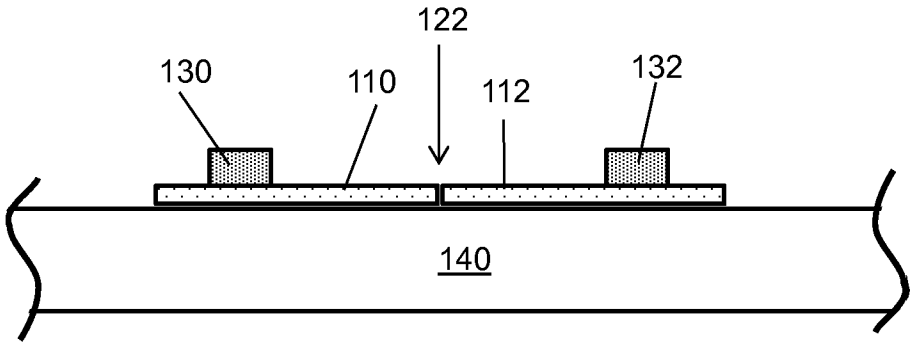


FIG. 2

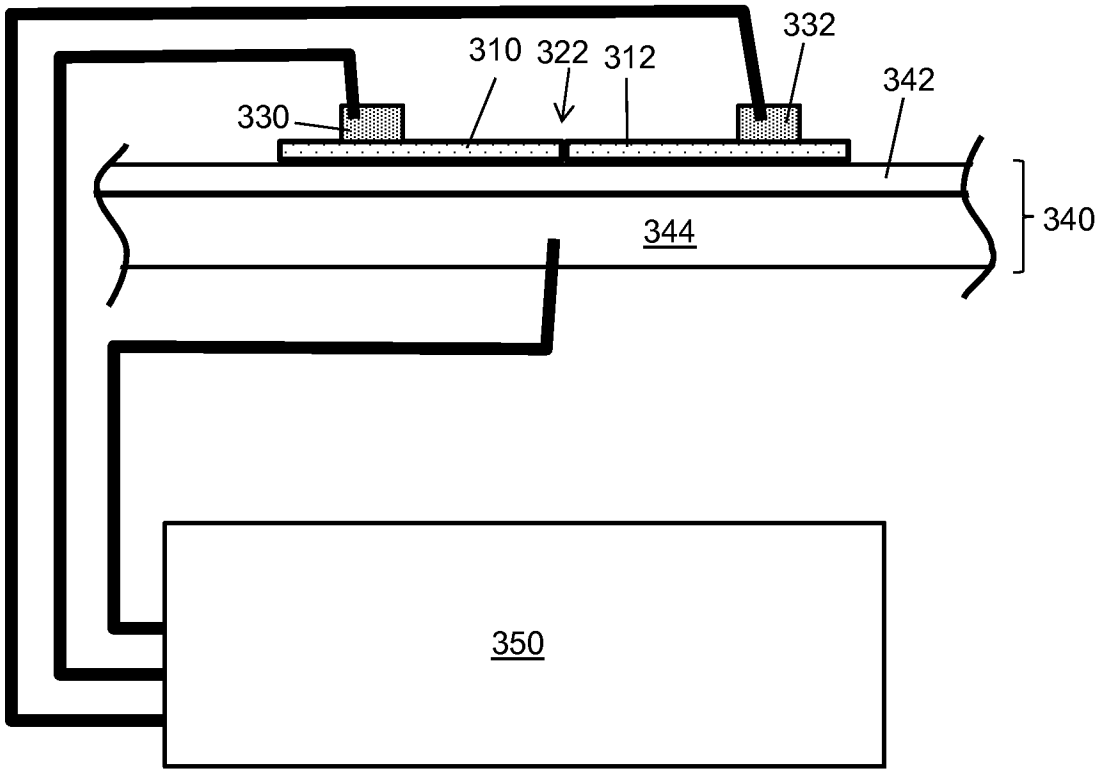


FIG. 3

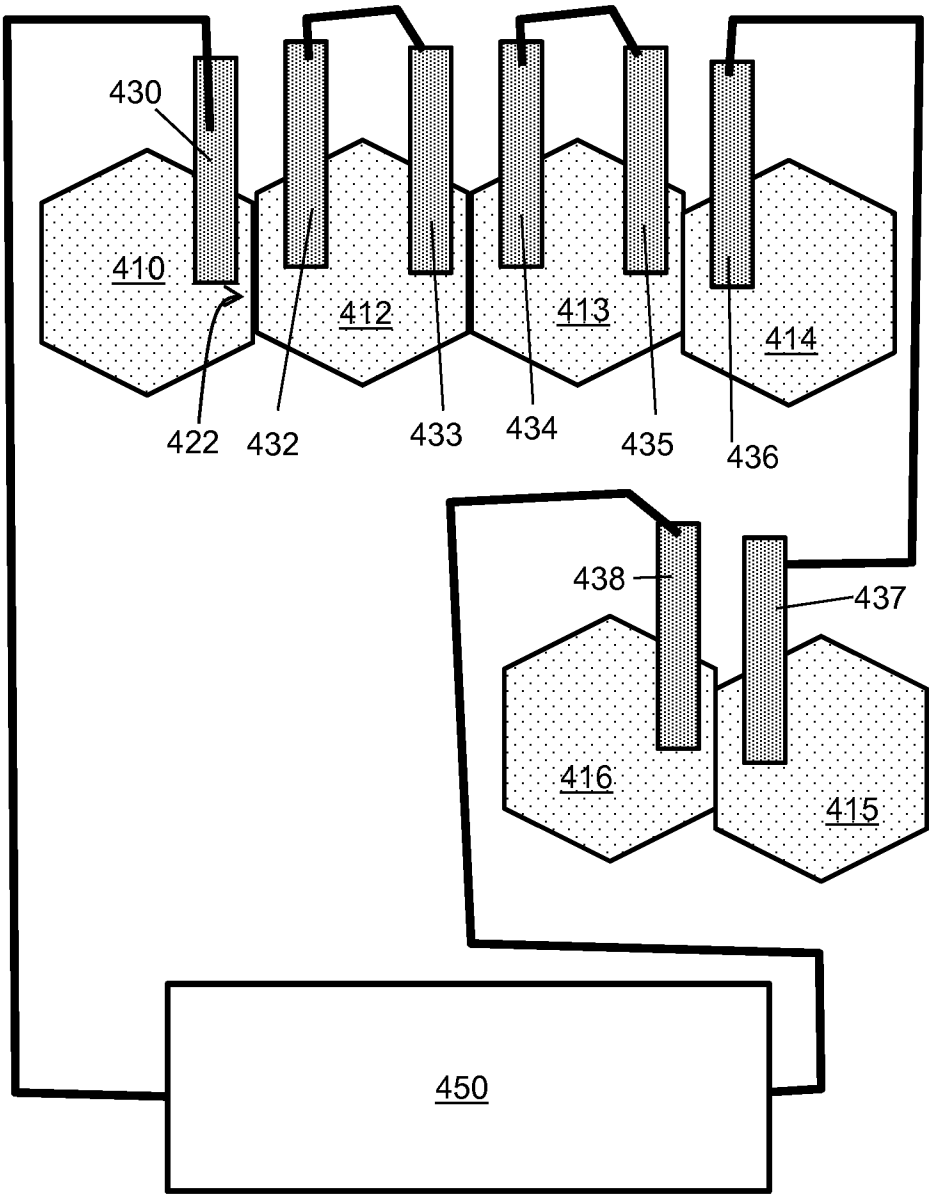


FIG. 4

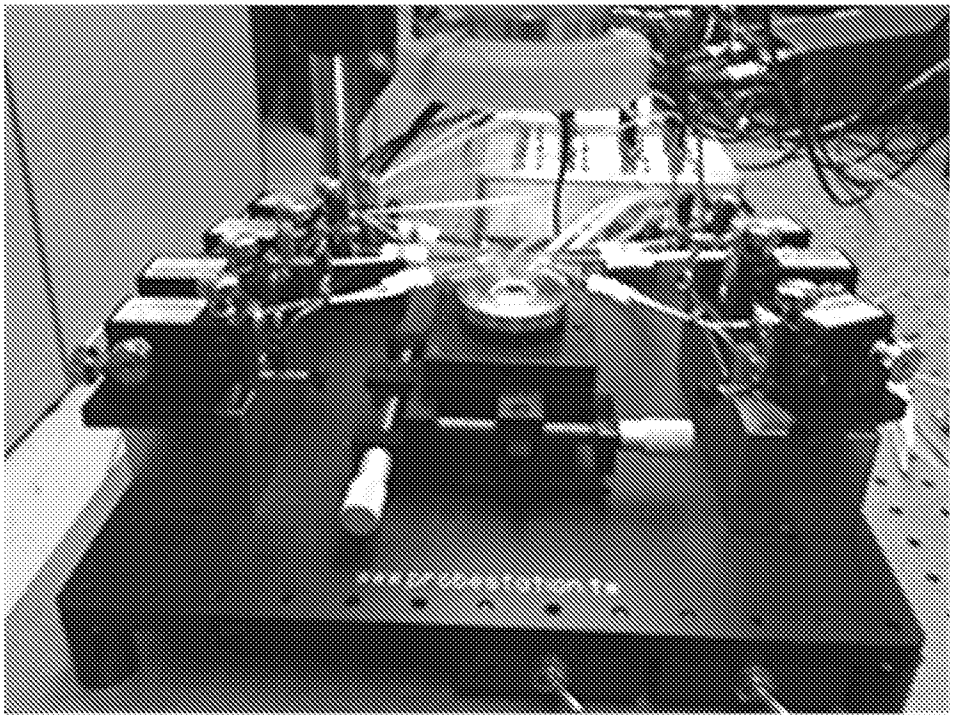


FIG. 5

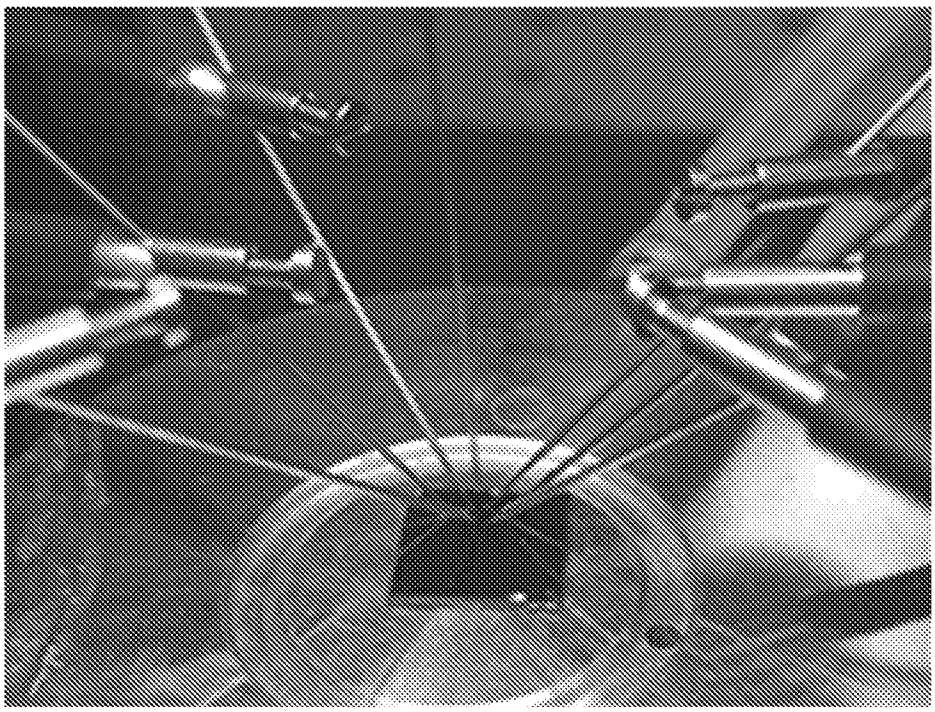


FIG. 6

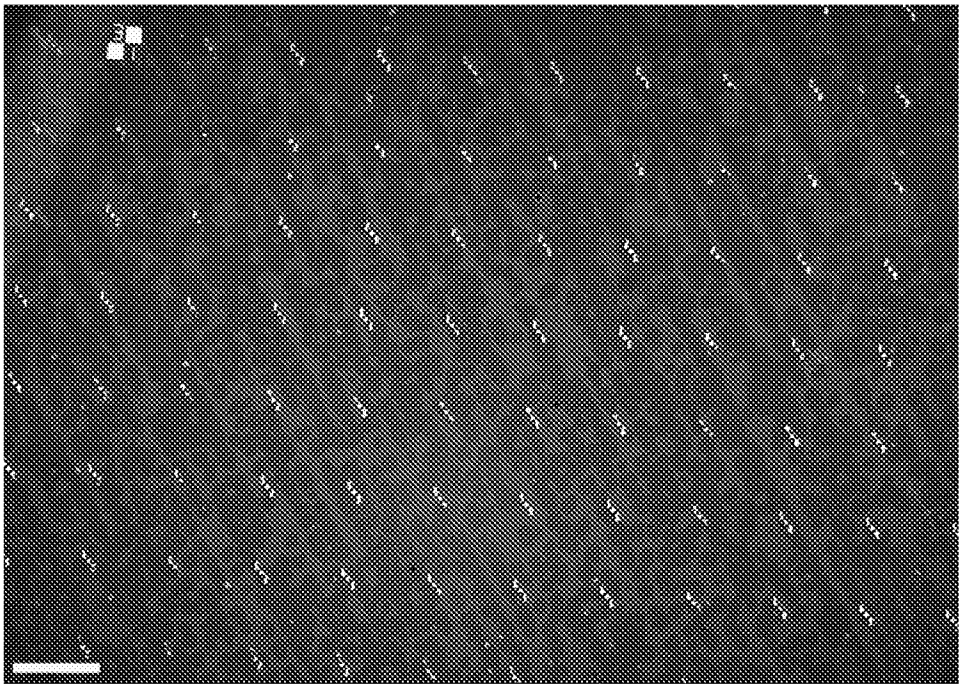


FIG. 7

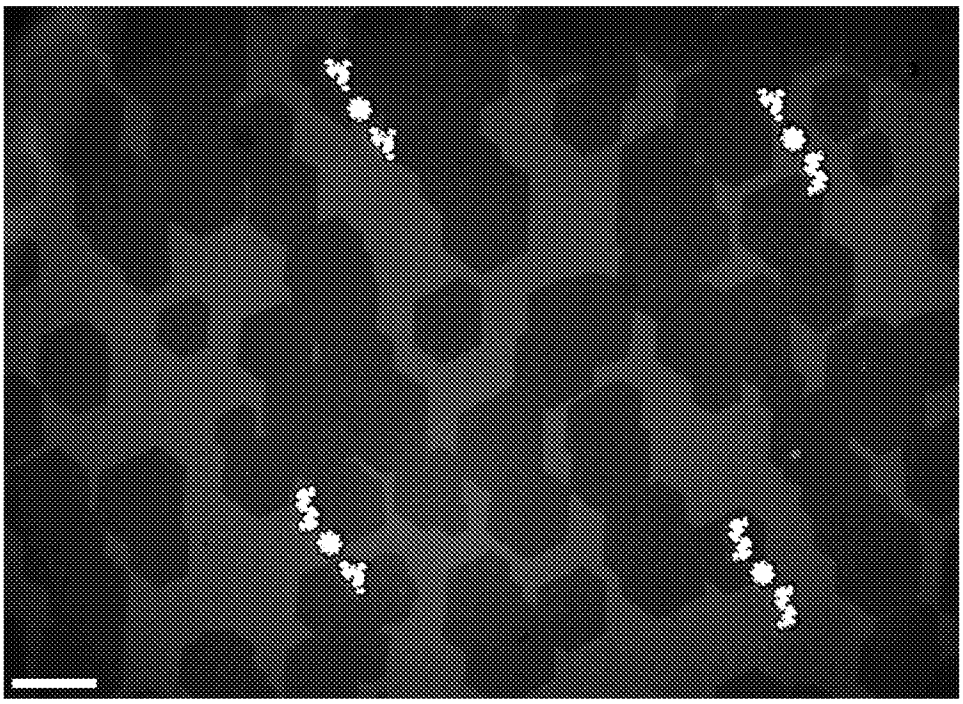


FIG. 8

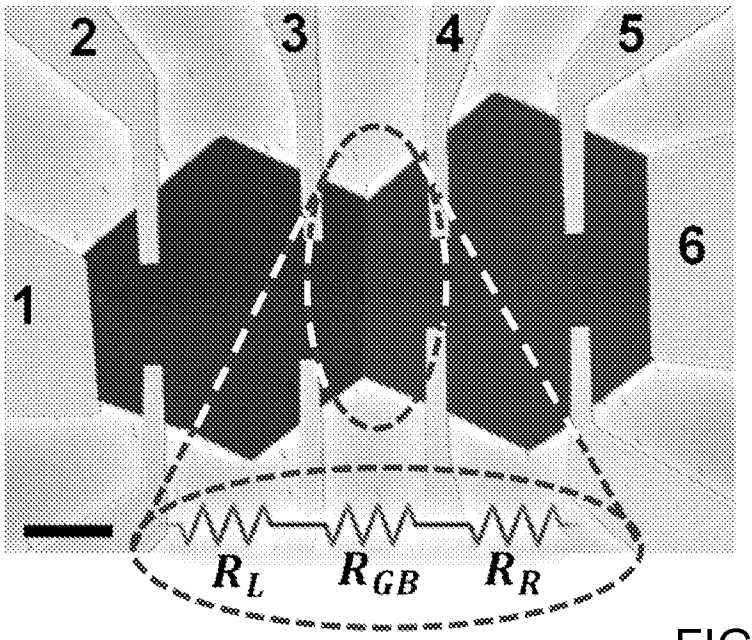


FIG. 9

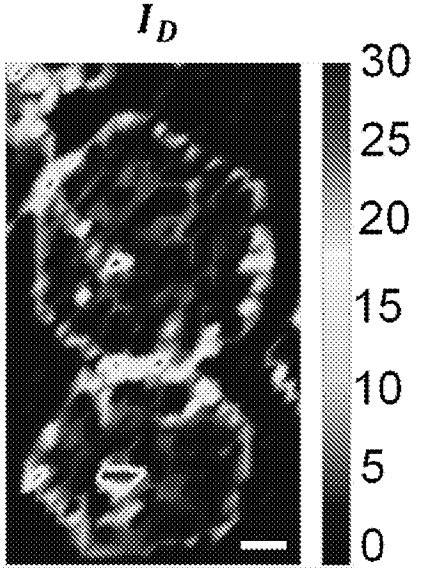


FIG. 10

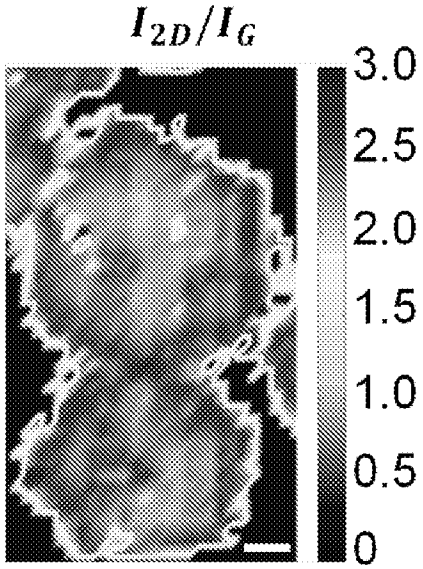


FIG. 11

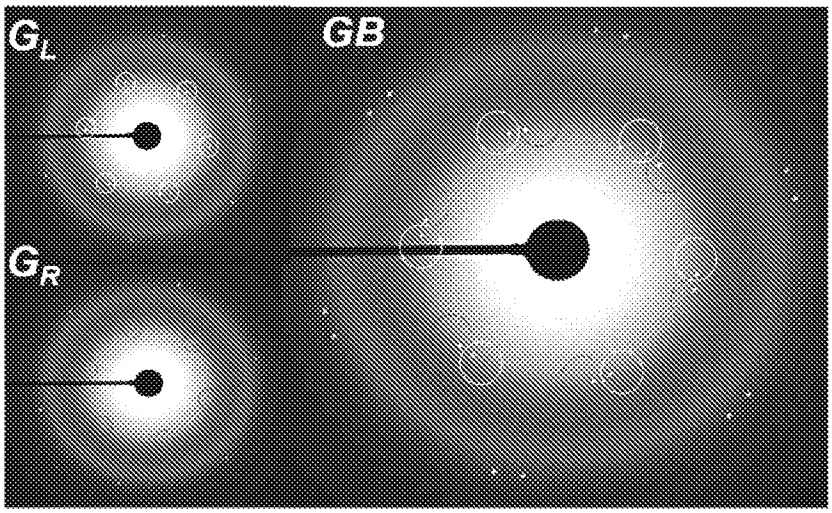

G_L
GB
G_R

FIG. 12

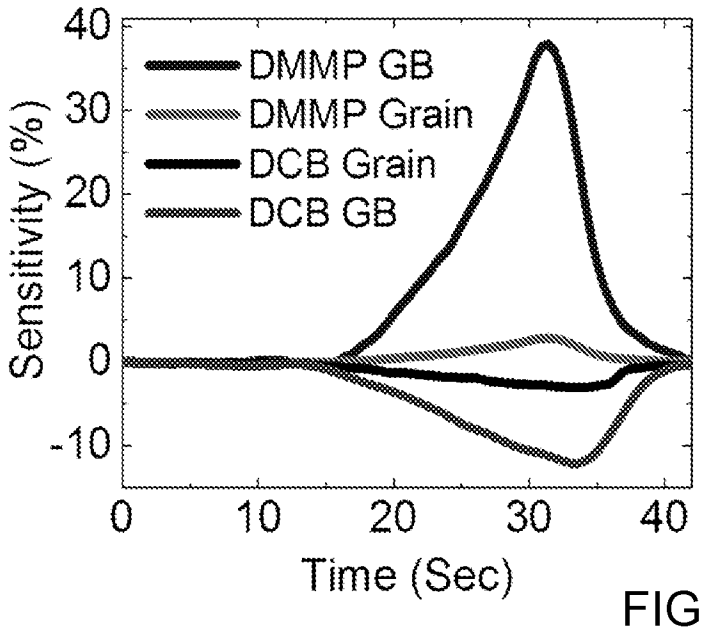

40
30
20
10
0
-10
Sensitivity (%)
DMMP GB
DMMP Grain
DCB Grain
DCB GB
0
10
20
30
40
Time (Sec)

FIG. 13

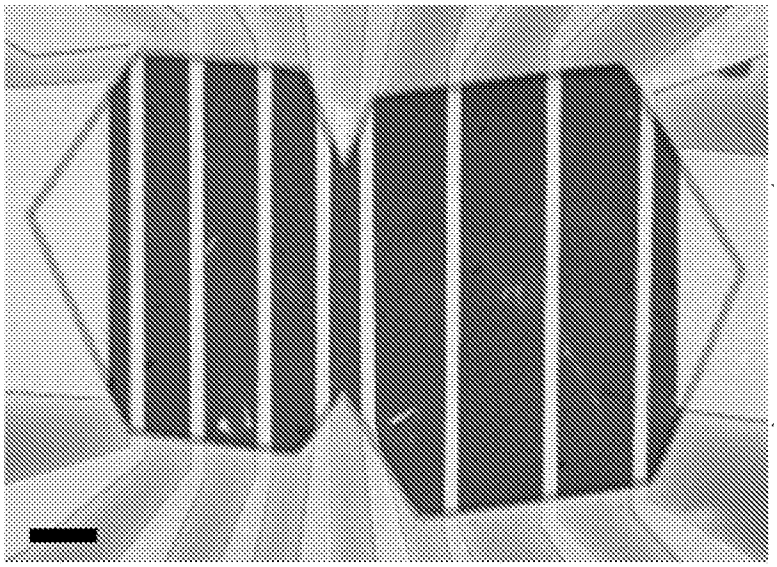


FIG. 14

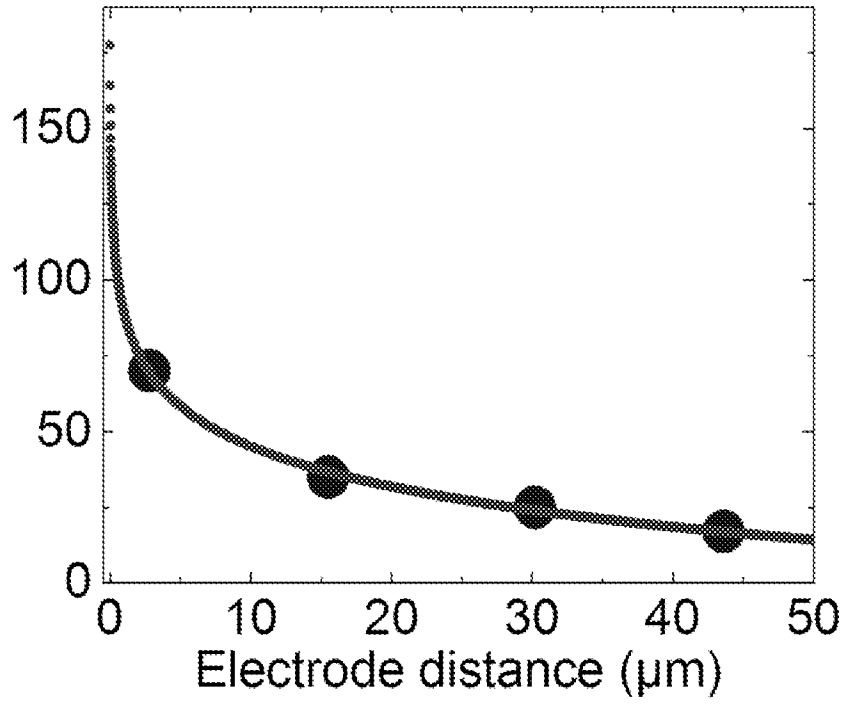
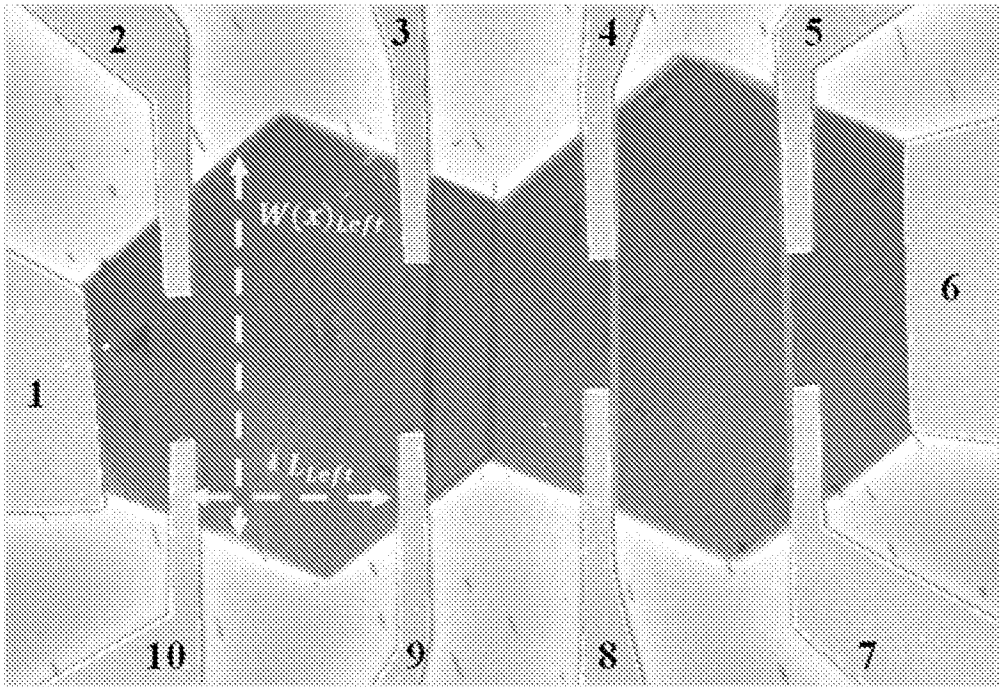


FIG. 15


2
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4
5
6
1
10
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8
7

FIG. 16

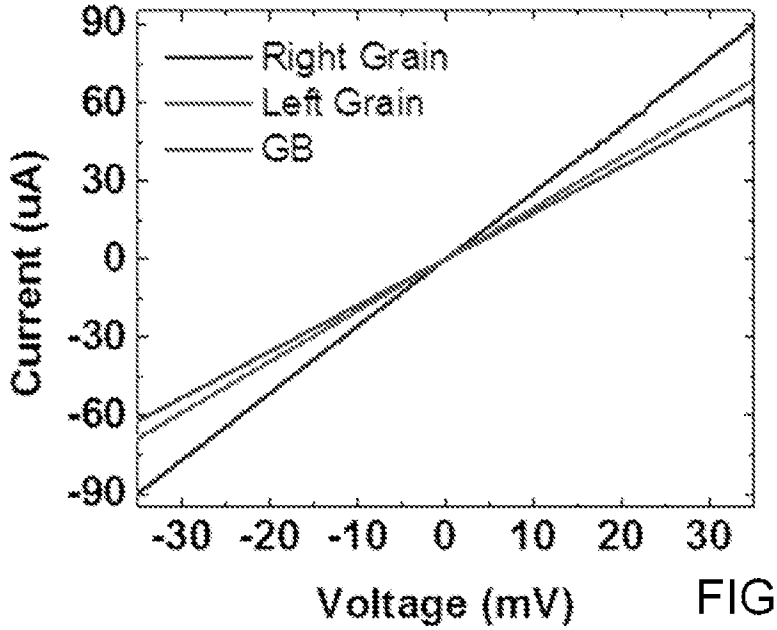
90
60
30
0
-30
-60
-90
Current (uA)
Right Grain
Left Grain
GB
-30 -20 -10 0 10 20 30
Voltage (mV)

FIG. 17

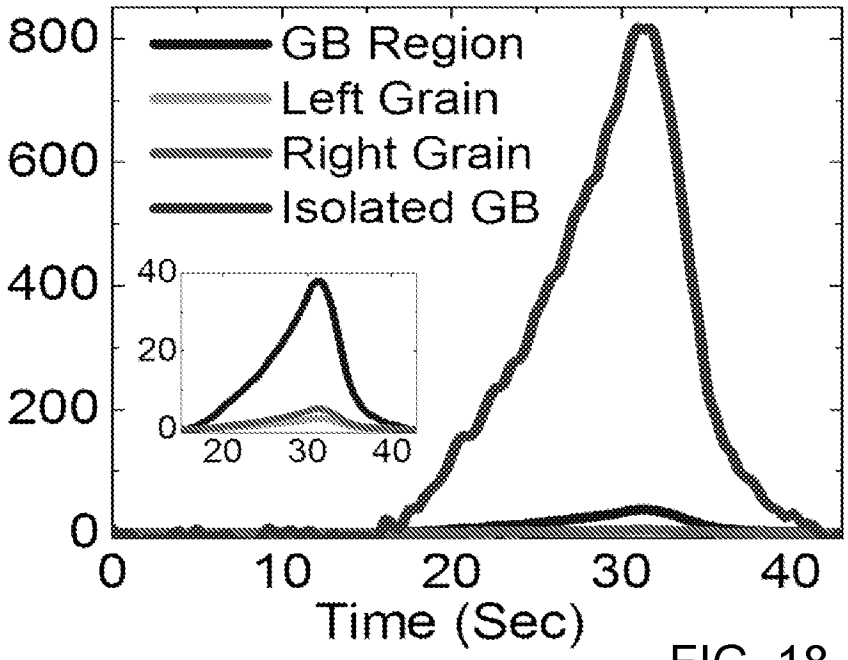
800
600
400
200
0
GB Region
Left Grain
Right Grain
Isolated GB
40
20
0
20
30
40
0
10
20
30
40
Time (Sec)

FIG. 18

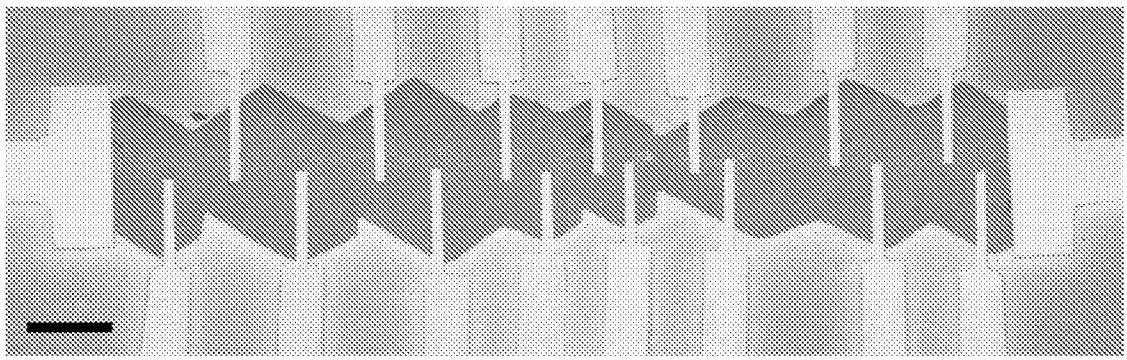

FIG. 19

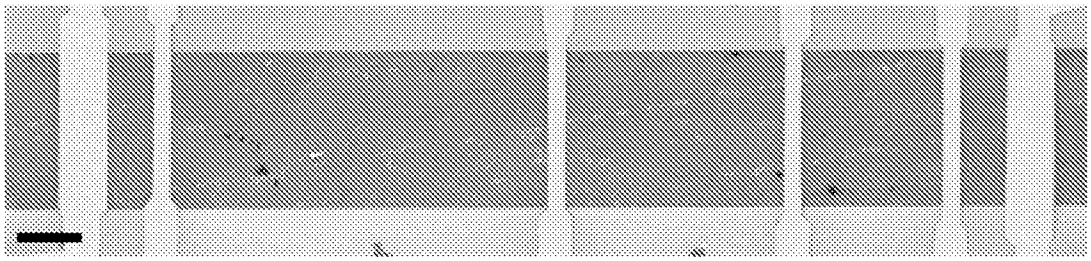

FIG. 20

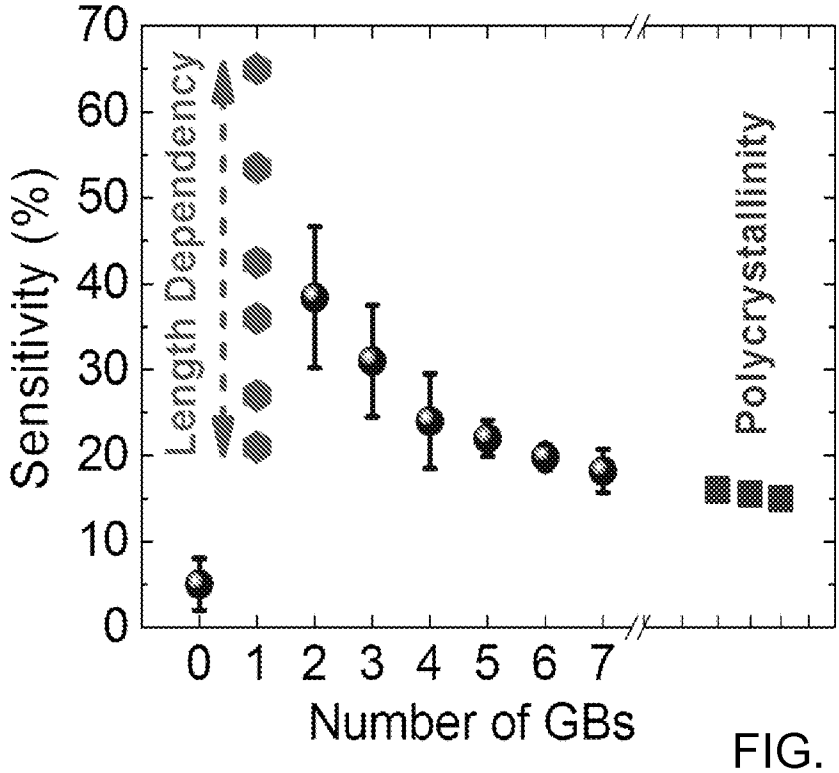
Sensitivity (%)
70
60
50
40
30
20
10
0
Length Dependency
Polycrystallinity
0 1 2 3 4 5 6 7
Number of GBs

FIG. 21

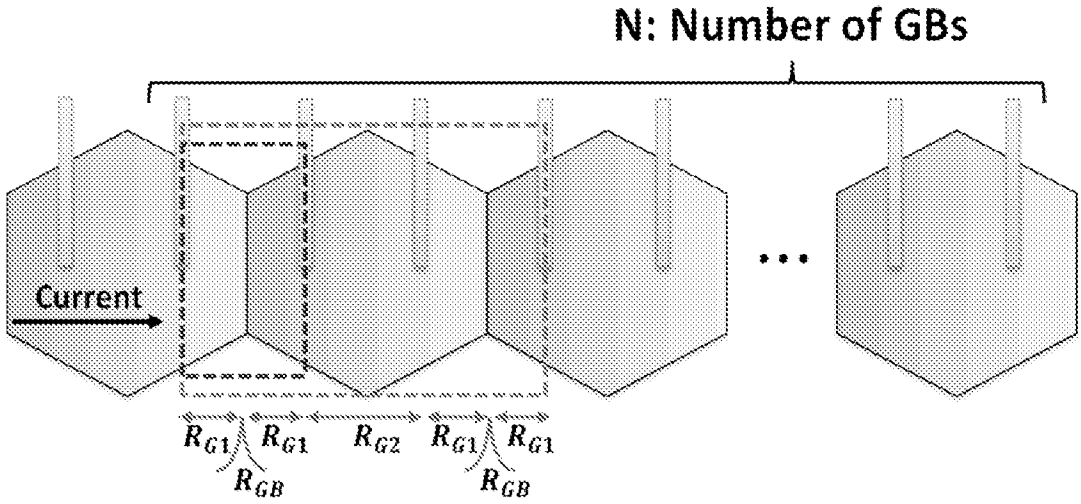
N: Number of GBs
Current
R_{G1}
R_{GB}
R_{G1}
R_{G2}
R_{G1}
R_{GB}
R_{G1}

FIG. 22

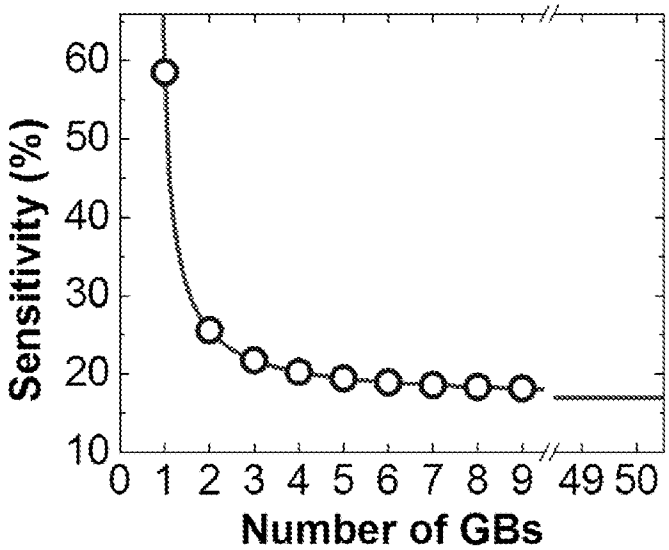
Sensitivity (%)
60
50
40
30
20
10
0 1 2 3 4 5 6 7 8 9 49 50
Number of GBs

FIG. 23

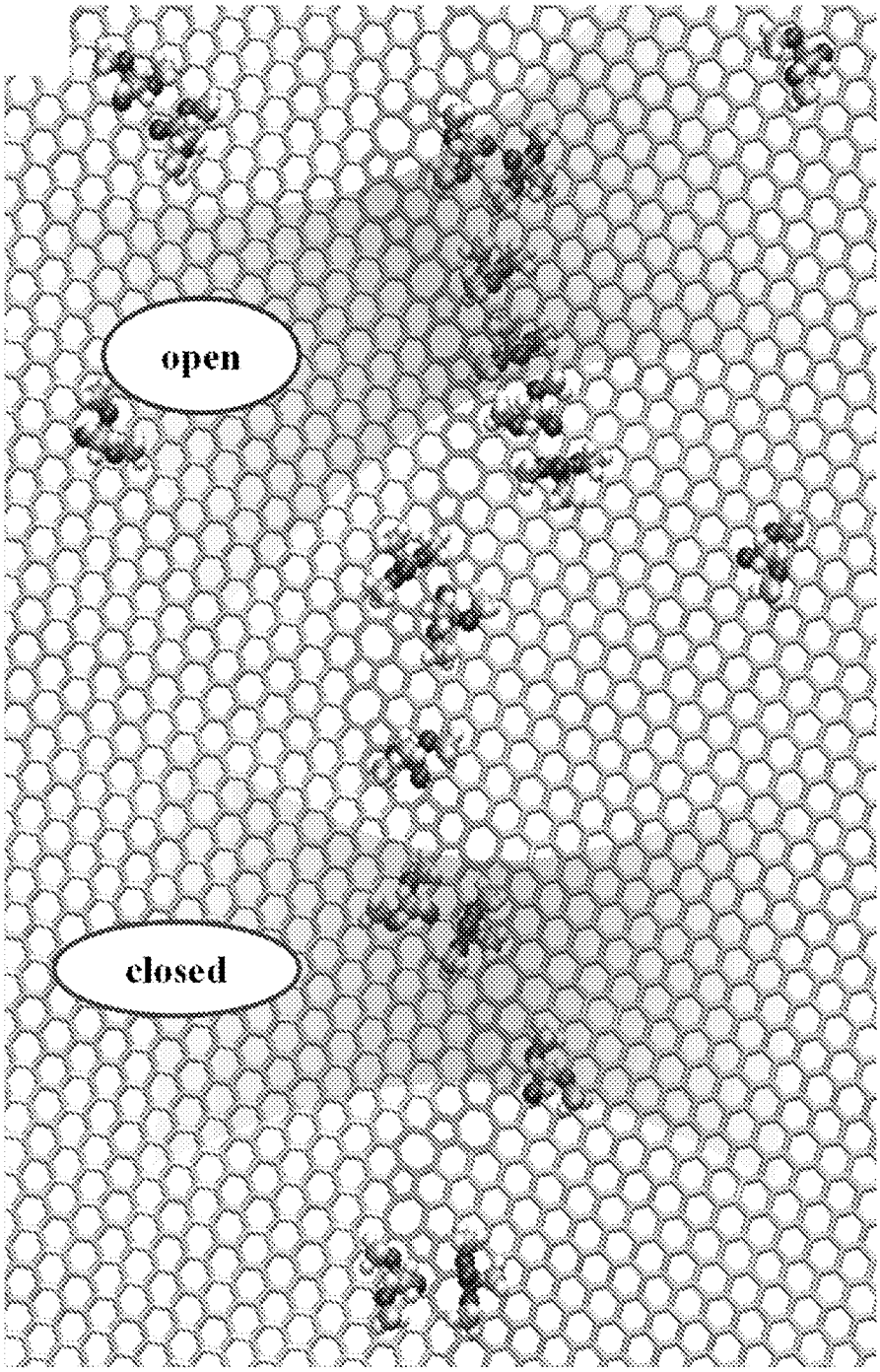

FIG. 24

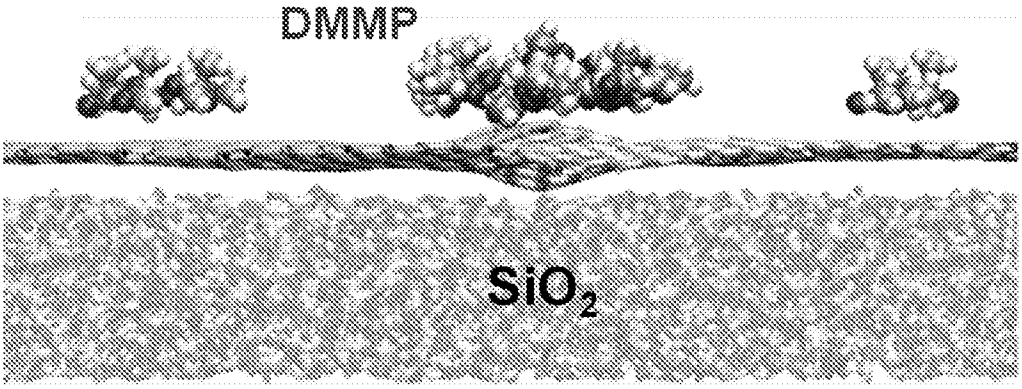

FIG. 25

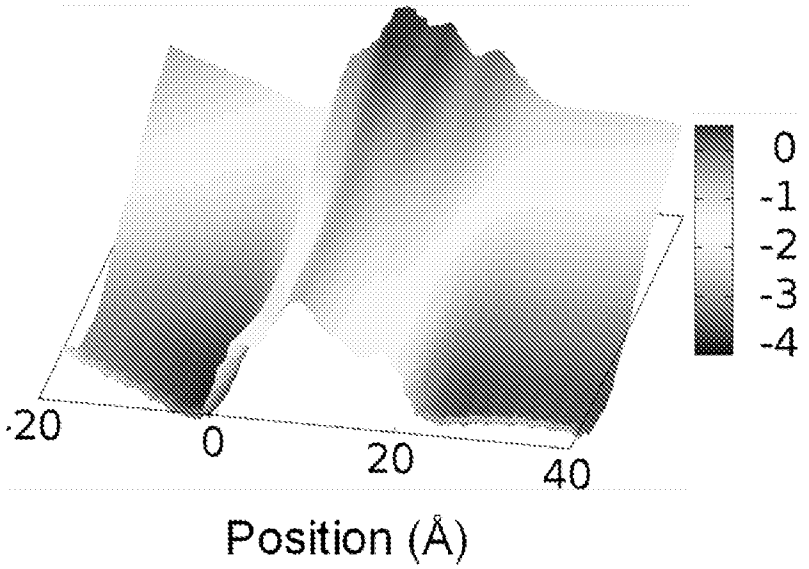

FIG. 26

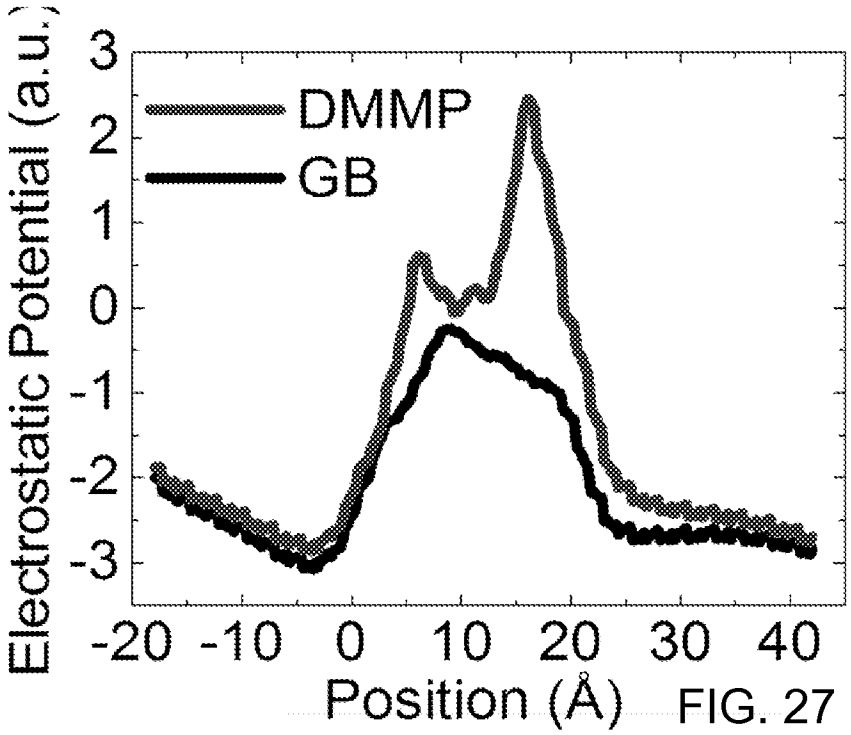
Electrostatic Potential (a.u.)
3
2
1
0
-1
-2
-3
DMMP
GB
-20 -10 0 10 20 30 40
Position (Å)

FIG. 27

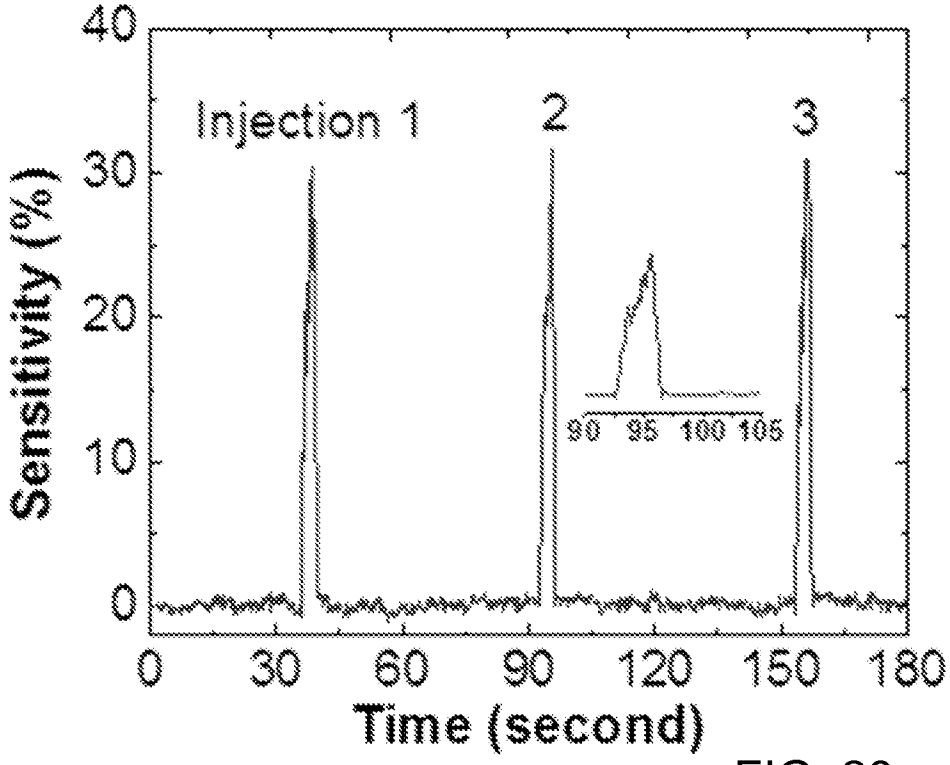
Sensitivity (%)
40
30
20
10
0
Injection 1
2
3
90 95 100 105
0 30 60 90 120 150 180
Time (second)

FIG. 28

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/38111

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B82Y 15/00; H01L 27/28, 29/04 (2015.01)
CPC - G01N 27/414; Y10S 977/734
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)
IPC(8): B82Y15/00; G01R 27/08; H01L 21/8232; H01L 27/28; H01L 29/04 (2015.01);
CPC: G01N 27/414; G01N 27/12, 27/127; H01L 45/149; Y10S 977/734

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)
PatSteer (EP, WO, US, JP, CN, KR, CA, DE, FR, GB, ES, AU, IN, CH, AT, BR, TH , RU, PH, SE, NO, INPADOC Data); ProQuest; IEEE; Google/GoggleScholar; KEYWORDS: grain boundar*, defect*, crack*, irregular lattice, graphene, gas*, impedance, *resist*, conduct*, FET, analyz*, chemiresist*

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0309776 A1 (DRNDIC M. et al.) November 21, 2013; figures 26, 44, 56-57, 62; paragraphs [0032-0037], [0067], [0080], [0091-0097], [0108-0109], [0144-0156]	1-6, 14
A	US 2012/0212242 A1 (MASEL, RI et al.) August 23, 2012; entire document	1-6, 14
A	US 8,294,132 B2 (MIAO, F et al.) October 23, 2012; entire document	1-6, 14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 August 2015 (26.08.2015)	07 OCT 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/38111

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

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

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

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

3. ☒ Claims Nos.: 7-13, 15-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.