



- (51) **International Patent Classification:**
H01L 29/66 (2006.01) H01L 31/0312 (2006.01)
H01L 21/302 (2006.01)
- (21) **International Application Number:**
PCT/US2016/040456
- (22) **International Filing Date:**
30 June 2016 (30.06.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
14/790,995 2 July 2015 (02.07.2015) US
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- (81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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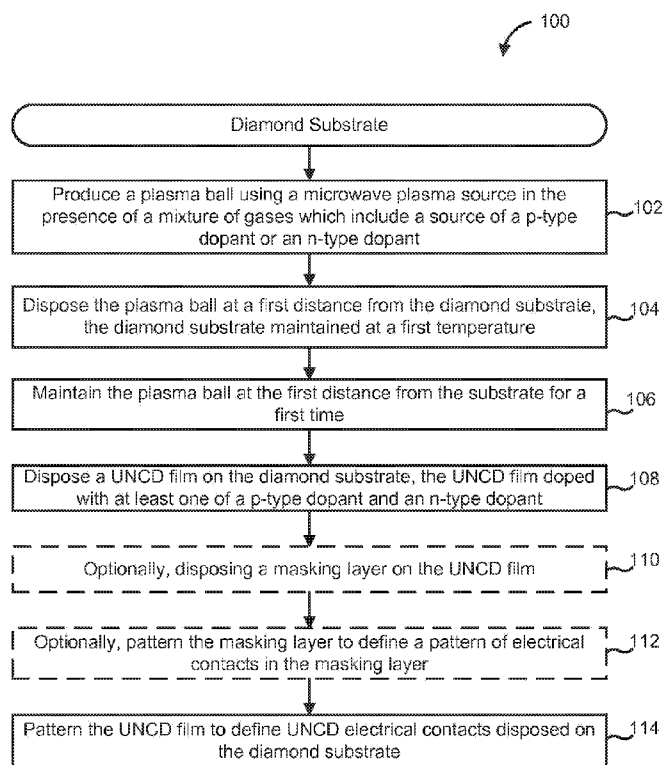
(54) **Title:** ULTRANANOCRYSTALLINE DIAMOND CONTACTS FOR ELECTRONIC DEVICES

FIG. 1

(57) **Abstract:** A method of forming electrical contacts on a diamond substrate comprises producing a plasma ball using a microwave plasma source in the presence of a mixture of gases. The mixture of gases include a source of a p-type or an n-type dopant. The plasma ball is disposed at a first distance from the diamond substrate. The diamond substrate is maintained at a first temperature. The plasma ball is maintained at the first distance from the diamond substrate for a first time, and a UNCD film, which is doped with at least one of a p-type dopant and an n-type dopant, is disposed on the diamond substrate. The doped UNCD film is patterned to define UNCD electrical contacts on the diamond substrate.



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

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

ULTRANANOCRYSTALLINE DIAMOND CONTACTS FOR ELECTRONIC DEVICES

Cross Reference to Related Patent Application

[0001] This application claims priority from U.S. Patent Application No. 14/790,995, filed July 2, 2015, incorporated herein by reference in its entirety.

[0002] The United States Government claims certain rights in this invention pursuant to Contract Nos. DE-AC02-98CH10886 and DE-SC0012704 awarded by the U.S. Department of Energy to Brookhaven Science Associates, LLC, Contract No. W-31-109-ENG-38 between the United States Government and the University of Chicago and/or pursuant to DE-AC02-06CH11357 between the United States Government and UChicago Argonne, LLC representing Argonne National Laboratory.

Technical Field

[0003] The present disclosure relates generally to the field of electronic devices and X-ray monitoring devices.

Background

[0004] The progress of solid state devices has allowed fabrication of micro and nano-scale electronic devices for a wide range of applications. Most conventional electronic devices are fabricated in silicon, germanium or some other semi-conductor material. Metallic electrical contacts are generally used to interface such micro and nano-scale electronic devices with macro electronics. The metallic contact pads are susceptible to corrosion so noble metals such as platinum and gold are often used to form the electrical contacts which increase the cost of such electronic devices.

[0005] X-ray monitors are a class of electronic devices that are used to monitor position of X-ray beams, flux and timing of X-ray beams. Such X-ray beams can be included in synchrotron radiation which is defined as an electromagnetic wave radiated in a direction tangent to an orbit of an electron having been accelerated by an electron accelerator. Synchrotron radiation can include light wavelengths ranging from visible light to hard X-

rays and can be used to perform spectroscopy and diffraction experiments. To perform such experiments, the X-ray beam monitors are necessary to monitor and stabilize X-ray beams.

[0006] Conventional X-ray monitors are formed from semi-conductor materials such as silicon and germanium. Such devices generally include a p-n junction formed in the semiconductor material. When X-ray beams are injected into the p-n junction, electron-hole pairs are generated which produce current. However, such semi-conductor devices have a smaller response speed due to small saturated velocity of carriers because of the electric properties of silicon or germanium. For example, silicon has a resistivity of 10^5 Ohm-cm and germanium has low resistivity. Furthermore, such detectors produce excessive dark current.

[0007] In contrast, diamond is particularly attractive for fabricating X-ray monitors to measure flux, position and timing of monochromatic and white X-ray beam. Diamond, because of its low Z (atomic number), has lower absorption for X-rays, extreme resistance to corrosion and radiation damage, high thermal conductivity and the ability to operate at high temperatures with low leakage. A voltage is applied to an intrinsic region of such diamond based X-ray monitors which acts as an active element obviating the need for a p-n junction. This is because diamond has sufficiently high resistivity in its intrinsic region. Therefore, electron-hole pairs are generated in the entire region of the diamond through which X-ray beams pass.

[0008] Conventional diamond based X-ray monitors, however include metal electrical contacts. Since metals have high atomic number (Z), the metal electrical contacts absorb a significantly higher amount of X-rays relative to the diamond thereby, drastically reducing the efficiency of such diamond detectors.

Summary

[0009] Embodiments described herein relate generally to electronic devices that include p-doped or n-doped ultrananocrystalline diamond (UNCD) electrical contacts and in particular to diamond X-ray monitors that include the p-doped or n-doped UNCD electrical contacts.

[0010] In some embodiments, a method of forming electrical contacts on a diamond substrate comprises producing a plasma ball using a microwave plasma source in the

presence of a mixture of gases. The mixture of gases includes a source of a p-type or an n-type dopant. The plasma ball is disposed at a first distance from the diamond substrate. The diamond substrate is maintained at a first temperature. The plasma ball is maintained at the first distance from the diamond substrate for a first time, and a UNCD film, which is doped with at least one of a p-type dopant and an n-type dopant, is disposed on the diamond substrate. The doped UNCD film is patterned to define UNCD electrical contacts on the diamond substrate.

[0011] In other embodiments, a device comprises a diamond substrate which includes electronic circuitry disposed within the diamond substrate. At least one electrical contact is disposed on the diamond substrate. The at least one electrical contact includes a p-doped or an n-doped UNCD which is in electrical communication with the electronic circuitry.

[0012] In still another embodiment, an X-ray monitor comprises a diamond substrate having a surface. A plurality of electrical contacts are disposed on the surface. The plurality of electrical contacts include a p-doped or an n-doped UNCD and have an X-ray absorption of less than about 1%.

[0013] It should be appreciated that all combinations of the foregoing concepts and additional concepts discussed in greater detail below (provided such concepts are not mutually inconsistent) are contemplated as being part of the inventive subject matter disclosed herein. In particular, all combinations of claimed subject matter appearing at the end of this disclosure are contemplated as being part of the inventive subject matter disclosed herein.

Brief Description of Drawings

[0014] The foregoing and other features of the present disclosure will become more fully apparent from the following description and appended claims, taken in conjunction with the accompanying drawings. Understanding that these drawings depict only several implementations in accordance with the disclosure and are therefore, not to be considered limiting of its scope, the disclosure will be described with additional specificity and detail through use of the accompanying drawings.

[0015] FIG. 1 is a schematic flow diagram of an exemplary method of forming p-doped or n-doped UNCD contacts on a diamond substrate according to an embodiment.

[0016] FIG. 2 is a schematic illustration of one embodiment of an electronic device that includes p-doped or n-doped UNCD electrical contacts.

[0017] FIG. 3 is a schematic illustration of another embodiment of an X-ray monitor that includes p-doped or n-doped UNCD electrical contacts which have an X-ray absorption of less than about 1%.

[0018] FIG. 4 is a schematic illustrations of an experimental setup for X-ray beam induced current mapping using a diamond detector that includes UNCD electrical contacts.

[0019] FIG. 5 panel (A) is an X-ray topography image, panel (B) is an image of a n-doped UNCD (N-UNCD) contact grown on diamond, and panel (C) is a birefringence image of the N-UNCD contact of panel (B).

[0020] FIG. 6 is a plot of responsivity of 0.3 mm thick diamond H1D10 coated with N-UNCD on both sides as contacts.

[0021] FIG. 7 panels (A-D) are 2D responsivity maps for diamond with N-UNCD grown as contacts taken at: 350 eV and + 50 V (panel (A)); 1,000 eV and – 50 V (panel (B)); 19 keV and + 50 V (panel (C)); and 19 keV and -50 V (panel (D)).

[0022] FIG. 8 is a plot of near edge X-ray absorption fine structure (NEXAFS) data taken at a beam line comparing the partial electron yield (PEY) between clean diamond and UNCD contacts.

[0023] Reference is made to the accompanying drawings throughout the following detailed description. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative implementations described in the detailed description, drawings, and claims are not meant to be limiting. Other implementations may be utilized, and other changes may be made, without departing from the spirit or scope of the subject matter presented here. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the figures, can be arranged, substituted, combined, and designed in a wide variety of different configurations, all of which are explicitly contemplated and made part of this disclosure.

Detailed Description of Various Embodiments

[0024] Embodiments described herein relate generally to electronic devices that include p-doped or n-doped UNCD electrical contacts and in particular to diamond X-ray monitors that include the p-doped or n-doped UNCD electrical contacts.

[0025] Embodiments of the electronic devices that include the p-doped or n-doped UNCD electrical contacts described herein provide several benefits including, for example: (1) replacing metal contacts with p-doped (e.g., boron doped) or n-doped (e.g., nitrogen doped) UNCD electrical contacts; (2) having high chemical resistance, high electrical conductivity, high thermal conductivity and resistance to oxidation or otherwise corrosion even at high temperatures of up to about 800 degrees Celsius; (4) providing superior adhesion to diamond substrates used in X-ray monitors; (3) having a low atomic number which enables the doped UNCD electrical contacts to have an X-ray absorption of less than 1% thereby having minimal or no impact on the efficiency of the diamond X-ray monitor; and (5) having superior resistance to damage which can be caused by high flux X-rays relative to metal electrical contacts.

[0026] As used herein, the term “ultrananocrystalline diamond (UNCD)” refers to crystalline diamond that has a grain size in the range of 2 nm to 10 nm.

[0027] As used herein, the term “p-type dopant” refers to elements that can be incorporated into a semi-conductor such as silicon, germanium or UNCD to create a deficiency of valence electrons called “holes” in the semi-conductor, thereby greatly increasing the conductivity of the semi-conductor. Such p-type dopants can include, for example boron, aluminum or gallium or any other element that can create holes in the semi-conductor.

[0028] As used herein, the term “n-type dopant” refers to elements that can be incorporated into a semi-conductor such as silicon, germanium or UNCD to provide free electrons, thereby greatly increasing the conductivity of the semi-conductor. Such n-type dopants include phosphorous, antimony, arsenic, nitrogen or any other element that can contribute free electrons to the semi-conductor.

[0029] FIG. 1 is schematic flow diagram of an exemplary method 100 for fabricating a p-doped or an n-doped UNCD electrical contact on a diamond substrate. The diamond

substrate can be included in an electronic device, for example an X-ray monitor for measuring flux, position and/or timing of monochromatic and white X-ray beam due to its low absorption, extreme resistance to corrosion and radiation damage, high thermal and electrical conductivity, and the ability to operate at high temperatures with low leakage.

[0030] The method 100 includes producing a plasma ball using a microwave plasma source in the presence of a mixture of gases which include a source of a p-type or an n-type dopant, at 102. The substrate can have any shape or size, for example a sheet, a block, a wafer, etc.

[0031] In one embodiment, the substrate can be disposed or positioned in an internal volume defined by a chamber (e.g., a microwave plasma chemical vapor deposition (MPCVD) chamber). The chamber can be sealed and any air or otherwise gases contained within the chamber can be evacuated by applying a vacuum to the chamber. The mixture of gases can be introduced into the internal volume of the chamber. In some embodiments, the mixture of gases can include argon, methane (e.g., about 0.1% to 1% by volume) and hydrogen (e.g., about 5% to about 10% by volume). In other embodiments, the mixture of gases can include methane and argon only. In still other embodiments, the mixture of gases can include other hydrocarbon sources such as acetylene in combination with other inert gases such as Neon, Helium, Xenon, etc.

[0032] As described herein, the mixture of gases also include a source of a p-type dopant or an n-type dopant. In one embodiment, the mixture of gases can include a source of boron such as a boron gas (e.g., B_2H_6 or trimethyl borate, or solid boron source such as boron powder) as the p-type dopant. In other embodiments, the mixture of gases can include a source of nitrogen as the n-type dopant. Nitrogen gas can be used as the source of nitrogen in the range of about 5% by volume to about 20% by volume. Furthermore, the p-type doping and n-type doping can also be achieved using other means such as ion-implantation.

[0033] The chamber can be maintained at a first pressure. In some embodiments, the first pressure can be in the range of about 40 Torr to about 70 Torr (e.g., about 40 Torr, 45 Torr, 50 Torr, 55 Torr, 60 Torr, 65 Torr or about 70 Torr inclusive of all ranges and values therebetween).

[0034] In some embodiments, a 915 MHz microwave plasma source can be used to produce the plasma ball. In other embodiments, any other microwave plasma source can be

used, for example a 2.45 MHz microwave plasma source. In such embodiments, the plasma ball can have a diameter in the range of about 15 cms to about 30 cms, for example, about 16 cms, 18 cms, 20 cms, 22 cms, 24 cms, 26 cms, 28 cms or about 29 cms inclusive of all ranges and values therebetween. In some embodiments, the diameter of the plasma ball can be about 25 cms. Furthermore, any suitable power can be used to produce the plasma source, for example a power in the range of about 2 kW to about 3 kW (e.g., 2 kW, 2.2 kW, 2.4 kW, 2.6 kW, 2.8 kW or about 3 kW inclusive of all ranges and values therebetween).

[0035] The plasma ball is maintained at a first distance from the diamond substrate and maintained at a first temperature, at 104. For example, the diamond substrate can be disposed or positioned on a first microwave electrode maintained at the first temperature. In some embodiments, the first temperature can be in the range of about 200 degrees Celsius to about 450 degrees Celsius (e.g., about 220 degrees Celsius, 240 degrees Celsius, 260 degrees Celsius, 280 degrees Celsius, 300 degrees Celsius, 320 degrees Celsius, 340 degrees Celsius, 360 degrees Celsius, 380 degrees Celsius, 400 degrees Celsius, 420 degrees Celsius, or about 440 degrees Celsius, inclusive of all ranges and values therebetween). In other embodiments, the first temperature can be in the range of about 350 to about 900 degrees Celsius (e.g., 350 degrees Celsius, 400 degrees Celsius, 450 degrees Celsius, 500 degrees Celsius, 550 degrees Celsius, 600 degrees Celsius, 650 degrees Celsius, 700 degrees Celsius, 750 degrees Celsius, 800 degrees Celsius, 850 degrees Celsius or 900 degrees Celsius inclusive of all ranges and values therebetween). In particular embodiments, the first distance can be about 0.5 mm to about 5 mm (e.g., about 1 mm, 2 mm, 3 mm, or about 4 mm) inclusive of all ranges and values therebetween.

[0036] The plasma ball is maintained at the first distance from the diamond for a first time, at 106. In some embodiments, the first time can be about 20 minutes to about 60 minutes (e.g., about 25 minutes, 30 minutes, 35 minutes, 40 minutes, 45 minutes, 50 minutes, or about 55 minutes inclusive of all ranges and values therebetween).

[0037] A UNCD film is disposed (e.g., deposited, coated or grown) over the diamond substrate and is doped with at least one of a p-type or an n-type dopant, at 108. For example, the UNCD film can be a boron doped UNCD (B-UNCD) film having a concentration of the boron in the B-UNCD film can be in the range of about 1×10^{21} atoms per cm^3 to about 9×10^{21} atoms per cm^3 (e.g., about 2×10^{21} , 3×10^{21} , 4×10^{21} , 5×10^{21} , 6×10^{21} , 7×10^{21} , or about 8×10^{21} atoms per cm^3 inclusive of all ranges and values therebetween). In one

embodiment, the boron concentration in the B-UNCD films can be about 4.8×10^{21} atoms per cm^3 .

[0038] In other embodiments, the UNCD film can be a nitrogen doped UNCD (N-UNCD) film having a percentage of nitrogen in the N-UNCD film of about 0.05 atom% to about 0.5 atom% (e.g., about 0.05 atom%, 0.06 atom%, 0.07 atom%, 0.08 atom%, 0.09 atom%, 0.1 atom%, 0.2 atom%, 0.3 atom%, 0.4 atom% or about 0.5 atom% inclusive of all ranges and values therebetween).

[0039] While described as being disposed or deposited using a microwave plasma source, any other method can be used to dispose or deposit the doped UNCD film over the diamond substrate. In one embodiment, the UNCD film is disposed or deposited over the sacrificial layer using hot filament chemical vapor deposition (HFCVD).

[0040] In particular embodiments, the thickness of the doped UNCD film can be in the range of about 20 nm to about 200 nm (e.g., 20 nm, 40 nm, 60 nm, 80 nm, 100 nm, 120 nm, 140 nm, 160 nm, 180 nm or about 200 nm inclusive of all ranges and values therebetween).

[0041] In some embodiments, a masking layer is optionally disposed (e.g., deposited, coated or formed) on the doped UNCD film, at 110. In such embodiments, the masking layer is patterned to define a pattern of electrical contacts in the masking layer, at 112. In some embodiments, masking layer can include an optical photolithography photoresist or an electron beam photoresist (e.g., hydrogen silsesquioxane (HSQ)). In other embodiments, the masking layer can include a metallic layer, for example, a titanium and platinum layer.

[0042] In still other embodiments, multiple masking layers can be used. For example, a first masking layer which includes a metal can be disposed (e.g., deposited, coated or formed) on the diamond substrate. A second masking layer, for example the optical or electron beam photoresist can be disposed (e.g., deposited, coated or formed) on the first masking layer. The second masking layer can be patterned using optical lithography or electron beam lithography to define a pattern of the electrical contacts in the second masking layer. The second masking layer is then used as a masking layer for the first masking layer. The first masking layer can, for example be etched using etchants (e.g., acids) to transfer the pattern in the first masking layer. The second masking layer is removed such that the first masking layer can serve as an etch mask for the doped UNCD film. In one embodiment, the

first and second masking layer can together be used as an etch mask for the doped UNCD film.

[0043] The doped UNCD film is patterned to define UNCD electrical contacts on the diamond substrate, at 114. In some embodiments, the masking layer (e.g., the first and/or second masking layer) can be used as an etch mask for patterning the doped UNCD film to define electrical contacts in the doped UNCD film. The doped UNCD film can be etched using any suitable process such as, for example, oxygen plasma etching, using reactive ion etch process or any other suitable etching process.

[0044] The masking layer is removed to leave the diamond substrate with UNCD electrical contacts disposed thereon. In some embodiments, the UNCD film can be patterned to define the electrical contacts without using a masking layer, for example via laser etching.

[0045] In this manner B-UNCD or N-UNCD electrical contacts can be formed on a diamond substrate. The doped UNCD electrical contacts have low X-ray absorption, high thermal and electrical conductivity, good adhesion to diamond and excellent thermal properties. In some embodiments, the doped UNCD electrical contacts can have an X-ray absorption of less than about 1%. Thus the doped UNCD electrical contacts are particularly beneficial as electrical contacts for X-ray monitors.

[0046] The doped UNCD electrical contacts can have high thermal stability. In some embodiments, the UNCD electrical contacts do not oxidize or otherwise corrode up to a temperature of about 800 degrees Celsius in vacuum. Furthermore, the doped UNCD electrical contacts are resistant to ozone exposure and are resistant to acids. The doped UNCD electrical contacts have sufficient electrical conductivity to allow ampere level currents to pass through while limiting charge injection and persistent current. The UNCD electrical contacts provide devices with linear flux response over a broad range of X-ray wavelengths, for example in the range of 100 eV to 30 keV inclusive of all ranges and values therebetween.

[0047] FIG. 2 shows a schematic illustration of a device 200 that includes a diamond substrate 210 and at least one p-doped or n-doped UNCD electrical contact 220. The device 200 can include any electronic device such as, for example p-n junction devices (e.g., solar cells, photocells, diodes, tunnel diodes, zener diodes, LEDs), PIN diodes, transistors, metal

oxide semi-conductor field effect transistors (MOSFET), sensors (e.g., Hall effect sensors), integrated circuits, charge coupled devices (CCDs), ROMs, RAMs, etc.

[0048] The diamond substrate 210 includes electronic circuitry 212 disposed within the diamond substrate 210. For example, the diamond substrate 210 can be implanted with a p-type dopant (e.g., boron) and/or an n-type dopant (e.g., phosphorous) to form electronic circuits (e.g., a p-n junction) within the diamond substrate 210. The diamond substrate 210 based electronic device can have similar or superior electronic properties to conventional semi-conductor materials (e.g., silicon or germanium) but has higher durability, is resistant to high temperature and chemicals, and provides excellent thermal conductivity.

[0049] The device 200 includes at least one p-doped or n-doped UNCD electrical contact 220 disposed or deposited on the diamond substrate 210. The doped UNCD electrical contact 220 is in electrical communication with the electronic circuitry 212 and is configured to provide electrical interface of the electronic circuitry 212 with electronic instrumentation.

[0050] In some embodiments, the UNCD electrical contacts 220 can be doped with a p-type dopant. For example, the UNCD electrical contacts 220 can be doped with boron (i.e., B-UNCD) and have a concentration of the boron in the B-UNCD electrical contacts 220 can be in the range of about 1×10^{21} atoms per cm^3 to about 9×10^{21} atoms per cm^3 (e.g., about 2×10^{21} , 3×10^{21} , 4×10^{21} , 5×10^{21} , 6×10^{21} , 7×10^{21} , or about 8×10^{21} atoms per cm^3 inclusive of all ranges and values therebetween). In one embodiment, the boron concentration in the B-UNCD electrical contacts 220 can be about 4.8×10^{21} atoms per cm^3 .

[0051] In other embodiments, the UNCD electrical contacts 220 can be doped with an n-type dopant. For example, the UNCD electrical contacts 220 can be doped with nitrogen such that the electrical contacts 220 include N-UNCD. In such embodiments, N-UNCD electrical contacts 220 can have a concentration of nitrogen in the electrical contacts in the range of about 0.05 atom% to about 0.5 atom% (e.g., about 0.05 atom%, 0.06 atom%, 0.07 atom%, 0.08 atom%, 0.09 atom%, 0.1 atom%, 0.2 atom%, 0.3 atom%, 0.4 atom% or about 0.5 atom% inclusive of all ranges and values therebetween).

[0052] The doped UNCD electrical contacts 220 can be formed using any suitable method, for example the method 200 or any other method described herein. The doped UNCD electrical contacts 220 can have high thermal stability. In some embodiments, the

doped UNCD electrical contacts 220 do not oxidize or otherwise corrode up to a temperature of about 800 degrees Celsius in vacuum. Furthermore, the doped UNCD electrical contacts 220 are resistant to ozone exposure and are resistant to acids. The doped UNCD electrical contacts 220 have sufficient electrical conductivity to allow ampere level currents to pass through while limiting charge injection and persistent current.

[0053] FIG. 3 is a schematic illustration of an X-ray monitor 300 that includes a diamond substrate 310 and p-doped or n-doped UNCD electrical contacts 320, according to an embodiment. The X-ray monitor 300 can be used as a flux, position and/or timing monitor for monochromatic and white X-ray beam due to its low absorption, extreme resistance to corrosion and radiation damage, high thermal conductivity and the ability to operate at high temperatures with low leakage.

[0054] The diamond substrate 310 can be in the form of a sheet or a plate. The diamond substrate 310 is disposed or positioned in line with and perpendicular to a X-ray beam which can be produced, for example by a synchrotron. The diamond substrate 310 includes a first surface 311 and a second surface 313 opposing the first surface 311. The diamond substrate 310 is disposed or positioned such that the X-rays impinge perpendicularly on the second surface 313. The X-rays generate electron-hole pairs in the entire region of the diamond substrate 310 through which they pass generating photoelectrons.

[0055] The plurality of p-doped or n-doped UNCD electrical contacts 320 are disposed or deposited on the first surface 311 of the X-ray monitor 300. The doped UNCD electrical contacts 320 are in electrical communication with the diamond substrate 310 and are configured to provide electrical interface of the diamond substrate 310 with electronic instrumentation 330. The plurality of doped UNCD electrical contacts 320 can have a thickness in the range of about 50 nm to about 200 nm.

[0056] In some embodiments, the UNCD electrical contacts 220 can be doped with a p-type dopant. For example, the UNCD electrical contacts 220 can be doped with boron (i.e., B-UNCD). A concentration of the boron in the B-UNCD electrical contacts 320 can be in the range of about 1×10^{21} atoms per cm^3 to about 9×10^{21} atoms per cm^3 (e.g., about 2×10^{21} , 3×10^{21} , 4×10^{21} , 5×10^{21} , 6×10^{21} , 7×10^{21} , or about 8×10^{21} atoms per cm^3 inclusive of all ranges and values therebetween). In one embodiment, the boron concentration in the B-UNCD electrical contacts 320 can be about 4.8×10^{21} atoms per cm^3 .

[0057] In other embodiments, the UNCD electrical contacts 320 can be doped with an n-type dopant. For example, the UNCD electrical contacts 320 can be doped with nitrogen such that the electrical contacts 320 include N-UNCD. In such embodiments, N-UNCD electrical contacts 320 can have a concentration of nitrogen in the electrical contacts in the range of about 0.05 atom% to about 0.5 atom% (e.g., about 0.05 atom%, 0.06 atom%, 0.07 atom%, 0.08 atom%, 0.09 atom%, 0.1 atom%, 0.2 atom%, 0.3 atom%, 0.4 atom% or about 0.5 atom% inclusive of all ranges and values therebetween).

[0058] The doped UNCD electrical contacts 320 have an X-ray absorption of less than about 1%. The doped UNCD electrical contacts 320 have high thermal and electrical conductivity, good adhesion to diamond and excellent thermal properties. While FIG. 13 shows the doped UNCD electrical contacts 320 as being disposed only the first surface 311, in some embodiments a plurality of doped UNCD electrical contacts 320 can also be disposed on the second surface 313 of the diamond substrate 320.

[0059] The doped UNCD electrical contacts 320 can be formed using any suitable method, for example the method 200 or any other method described herein. The doped UNCD electrical contacts 320 can have high thermal stability. In some embodiments, the doped UNCD electrical contacts 320 do not oxidize or otherwise corrode up to a temperature of about 800 degrees Celsius in vacuum. Furthermore, the doped UNCD electrical contacts 320 are resistant to ozone exposure and are resistant to acids. The doped UNCD electrical contacts 320 have sufficient electrical conductivity to allow ampere level currents to pass through while limiting charge injection and persistent current. The doped UNCD electrical contacts 320 provide devices with linear flux response over a broad range of X-ray wavelengths, for example in the range of 100 eV to 30 keV inclusive of all ranges and values therebetween.

[0060] As described herein, when the X-ray beam irradiates the diamond substrate 310, electron-hole pairs are generated in the diamond substrate 310. The electronic instrument 330 can be used to exert a positive potential on the doped UNCD electrical contacts 340. The electrons generated in the diamond substrate 310 are communicated via the doped UNCD electrical contacts 320 to the electronic instrumentation 330. The amount of current communicated or any other electronic parameter can be used by the electronic instrumentation to determine a flux and/or position of the X-ray beam by the X-ray monitor.

[0061] The following section describes examples of X-ray detectors that includes UNCD contacts. These examples are only for illustrative purposes and are not meant to limit the scope of the concepts described herein.

Experimental Examples

[0062] FIG. 4 shows a schematic illustration of an experimental setup for X-ray beam induced current mapping using a diamond detector that includes N-UNCD electrical contacts. Copper (Cu) mount electrodes are electrically coupled to the N-UNCD contacts to allow interface with detector electronics. The Cu mount electrodes are however disposed on an area of the N-UNCD electrical contacts which is sufficiently distal to a portion of the N-UNCD electrical contacts which is in line with the X-ray beam. The Cu mount electrodes therefore, do not interfere with the X-ray beam detection. The detector is raster scanned through the X-ray microbeam. Pulse bias is provided at low photon energy to reduce trapping effects. The setup is used to measure both the X-ray responsivity and uniformity mapping.

[0063] FIG. 5 panel (A) is an X-ray topography image of N-UNCD electrical contact deposited on the diamond substrate which shows an excellent crystalline quality of the N-UNCD electrical contacts. FIG. 5 panel (B) is an optical image of an N-UNCD electrical contact grown on a diamond substrate. FIG. 5 panel (C) is a birefringence image of the N-UNCD coated diamond of FIG. 5 panel (B). The birefringence is clean in the active area of the device which typically results in a device free of hotspots. This is advantageous in a UNCD coated device, as the contacts will not prevent photoconductive gain in the diamond substrate.

[0064] FIG. 6 is a plot of responsivity of a 0.3 mm thick diamond (HID10) coated with N-UNCD diamond on both sides as electrical contacts. The plot shows measured responsivity of electrons and holes as carriers. These responsivity curves are compared to the calculated curves of a model Pt coated X-ray detector (labelled "Theory"). The responsivity of the diamond with N-UNCD contacts matches well with the "Reference" plot demonstrating that the diamond detector with N-UNCD contacts is suitable as a calibrated X-ray detector.

[0065] FIG. 7 panels (A-D) are 2D responsivity maps for diamond with N-UNCD grown as contacts taken at: 350 eV and + 50 V (panel (A)); 1,000 eV and – 50 V (panel

(B)); 19 keV and + 50 V (panel (C)); and 19 keV and -50 V (panel (D)). The low energy response (panel (A)) shows the effects of the thickness of the UNCD contact with a lower response in the center where the coating is the thickest. Once the photon energy increases such that most of the x-rays are transmitted through the UNCD contact, the active area shows good response uniformity (panels (B-D)).

[0066] FIG. 8 is a plot of NEXAFS data taken at an X-ray beamline (Beamline U7A at the national synchrotron light source, Brookhaven National Laboratory) comparing the PEY between clean diamond and the UNCD contacts. The detector current from a diamond X-ray detector with UNCD contacts, converted to a NEXAFS spectrum, is also shown for comparison. These data confirm that the contact is predominately diamond (as opposed to non-diamond carbon) and that the detector has the expected response across the carbon edge.

[0067] As used herein, the terms “about” generally means plus or minus 10% of the stated value. For example, about 0.5 would include 0.45 and 0.55, about 10 would include 9 to 11, about 1000 would include 900 to 1100.

[0068] It should be noted that the term “exemplary” as used herein to describe various embodiments is intended to indicate that such embodiments are possible examples, representations, and/or illustrations of possible embodiments (and such term is not intended to connote that such embodiments are necessarily extraordinary or superlative examples).

[0069] The terms “coupled,” and the like as used herein mean the joining of two members directly or indirectly to one another. Such joining may be stationary (e.g., permanent) or moveable (e.g., removable or releasable). Such joining may be achieved with the two members or the two members and any additional intermediate members being integrally formed as a single unitary body with one another or with the two members or the two members and any additional intermediate members being attached to one another.

[0070] It is important to note that the construction and arrangement of the various exemplary embodiments are illustrative only. Although only a few embodiments have been described in detail in this disclosure, those skilled in the art who review this disclosure will readily appreciate that many modifications are possible (e.g., variations in sizes, dimensions, structures, shapes and proportions of the various elements, values of parameters, mounting arrangements, use of materials, colors, orientations, etc.) without materially departing from the novel teachings and advantages of the subject matter described herein. Other

substitutions, modifications, changes and omissions may also be made in the design, operating conditions and arrangement of the various exemplary embodiments without departing from the scope of the present invention.

WHAT IS CLAIMED IS:

1. A method of forming electrical contacts on a diamond substrate, comprising:
producing a plasma ball using a microwave plasma source in the presence of a mixture of gases which include a source of a first p-type dopant or a first n-type dopant;
disposing the plasma ball at a first distance from the diamond substrate, the diamond substrate maintained at a first temperature;
maintaining the plasma ball at the first distance from the substrate for a first time;
disposing an ultrananocrystalline diamond film on the diamond substrate, the ultrananocrystalline diamond film doped with at least one of a second p-type dopant and a second n-type dopant; and
patterning the ultrananocrystalline film to define ultrananocrystalline diamond electrical contacts on the diamond substrate.
2. The method of claim 1, further comprising:
disposing a masking layer on the ultrananocrystalline diamond film; and
patterning the masking layer to define a pattern of the electrical contacts in the masking layer.
3. The method of claim 1, wherein the ultrananocrystalline diamond electrical contacts have an X-ray absorption of less than about 1%.
4. The method of claim 1, wherein the first p-type dopant and the second p-type dopant include boron.
5. The method of claim 1, wherein the first n-type dopant and the second n-type dopant include nitrogen.
6. The method of claim 5, wherein the ultrananocrystalline diamond film has a percentage of nitrogen in the range of about 0.05 atom% to about 0.5 atom%.
7. The method of claim 1, wherein the first temperature is in the range of about 350 degrees Celsius to about 950 degrees Celsius.

8. The method of claim 1, wherein the ultrananocrystalline diamond film is patterned using oxygen plasma etching.
9. The method of claim 1, wherein the ultrananocrystalline diamond does not oxidize up to a temperature of about 800 degrees Celsius.
10. A device, comprising:
a diamond substrate including electronic circuitry disposed within the diamond substrate;
at least one electrical contact disposed on the diamond substrate, the at least one electrical contact including a p-doped or an n-doped ultrananocrystalline diamond, the electrical contacts in electrical communication with the electronic circuitry.
11. The device of claim 10, wherein the p-type dopant includes boron.
12. The device of claim 10, wherein the n-type dopant includes nitrogen.
13. The device of claim 12, wherein the ultrananocrystalline diamond film has a percentage of nitrogen in the range of about 0.05 atom% to about 0.5 atom%.
14. The device of claim 10, wherein the device includes at least one of a solar cell, photocell, diode, light emitting diode, a sensor, a detector, a transistor, a field effect transistor, an integrated circuit, a read only memory and a random access memory.
15. An X-ray monitor, comprising:
a diamond substrate having a surface; and
a plurality of electrical contacts disposed on the surface, the plurality of electrical contacts including at least one of a p-doped and a n-doped ultrananocrystalline diamond,
wherein the electrical contacts have an X-ray absorption of less than about 1%.
16. The X-ray monitor of claim 15, wherein the p-type dopant includes boron and the n-type dopant includes nitrogen.
17. The X-ray monitor of claim 16, wherein the ultrananocrystalline diamond film has a percentage of nitrogen in the range of about 0.05 atom% to about 0.5 atom%.

18. The X-ray monitor of claim 15; wherein the surface is a first surface, the diamond substrate further comprising:

a second surface disposed opposite the first surface; and

a plurality of at least one of a of a p-doped and n-doped ultrananocrystalline diamond electrical contacts disposed on the second surface.

19. The X-ray monitor of claim 15, wherein electrical contacts do not oxidize up to a temperature of about 800 degrees Celsius in vacuum.

20. The X-ray monitor of claim 15, wherein the X-ray monitor has a linear flux response to X-rays having energy in the range of 100 eV to 30 keV.

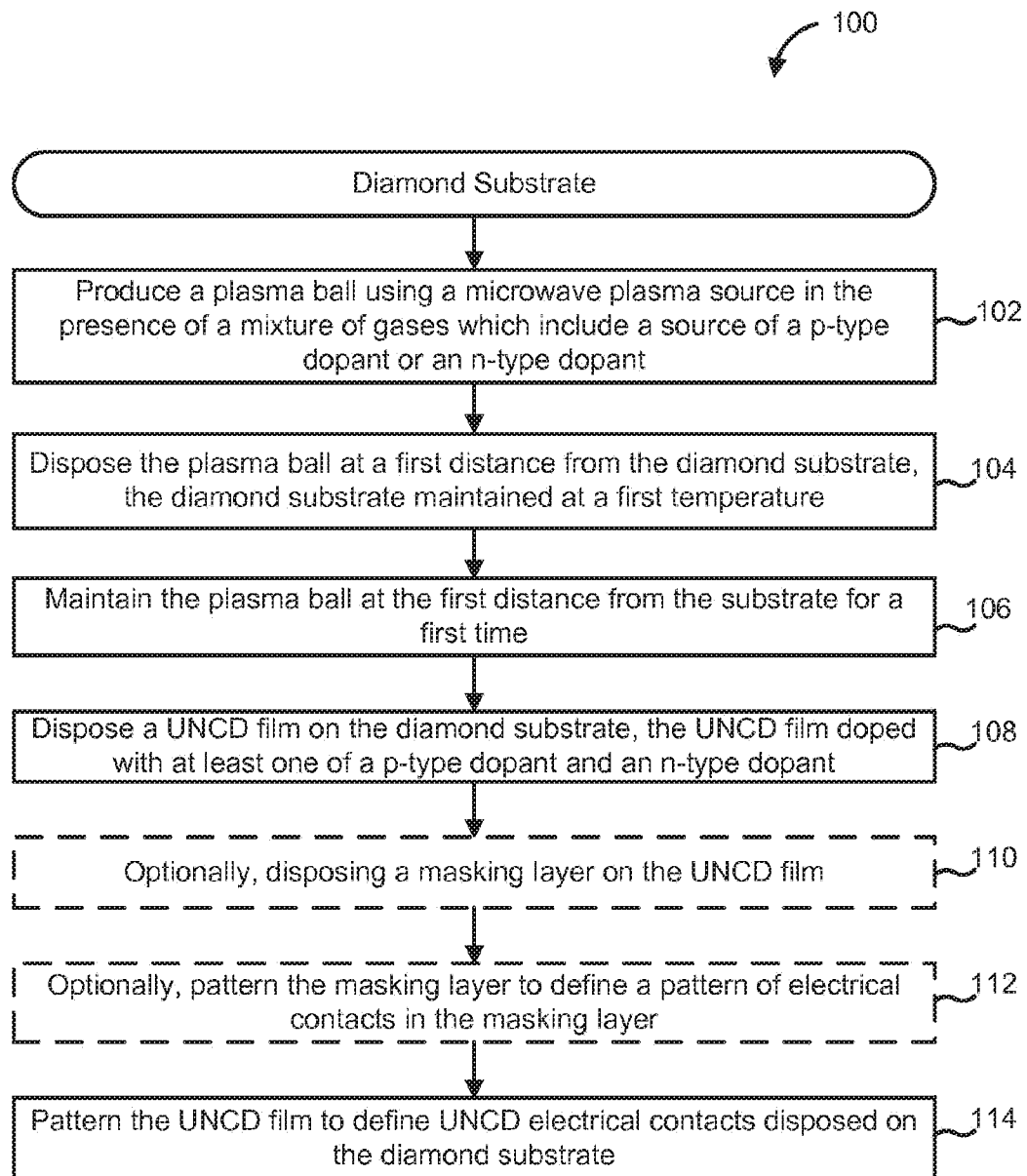


FIG. 1

FIG. 2

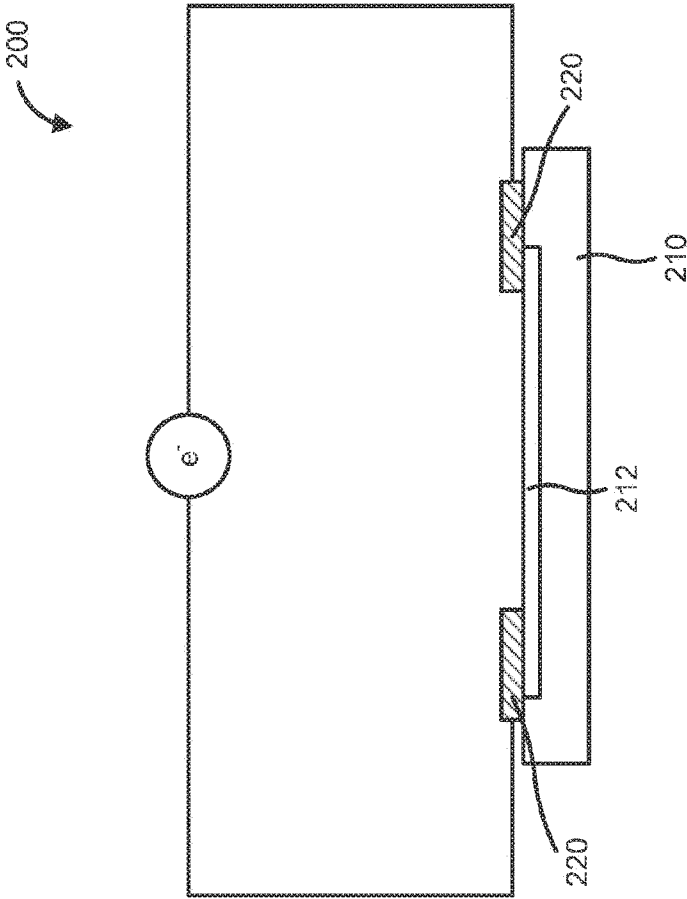


FIG. 3

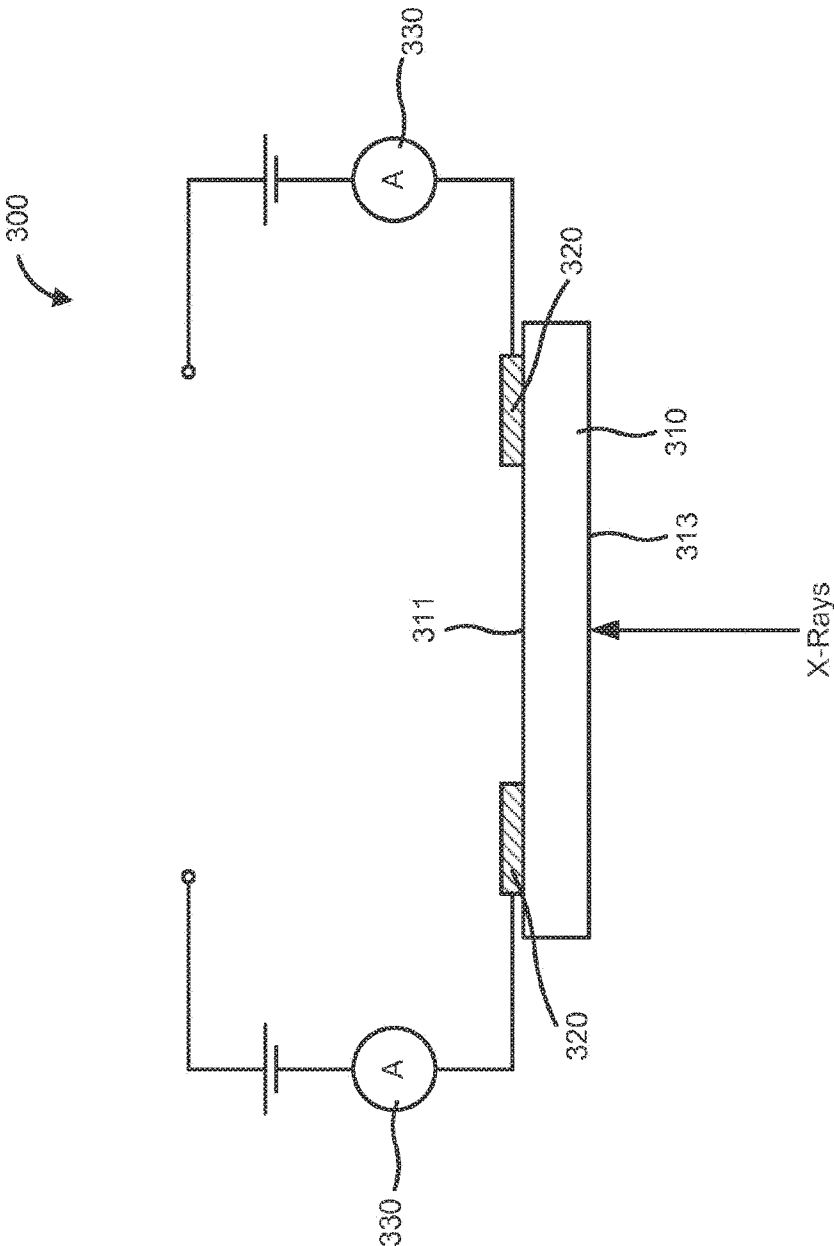


FIG. 4

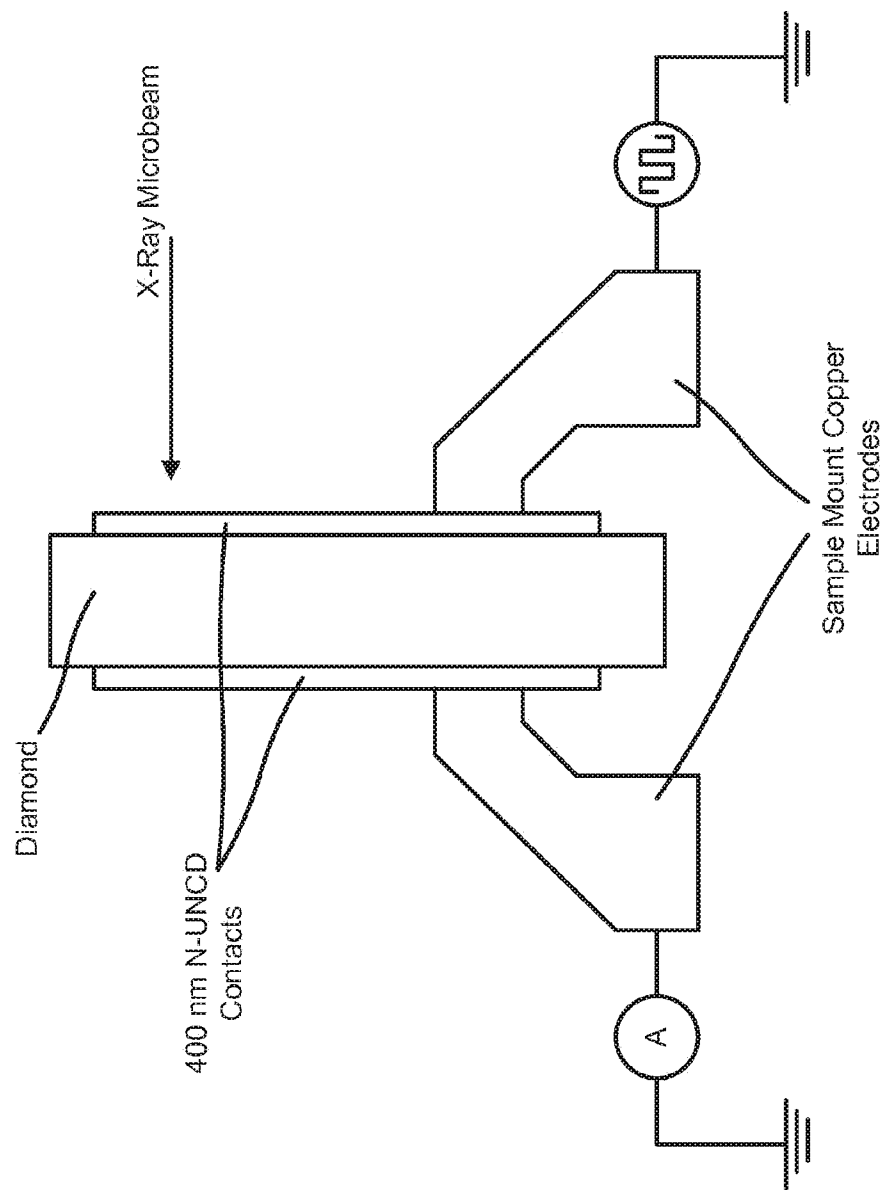
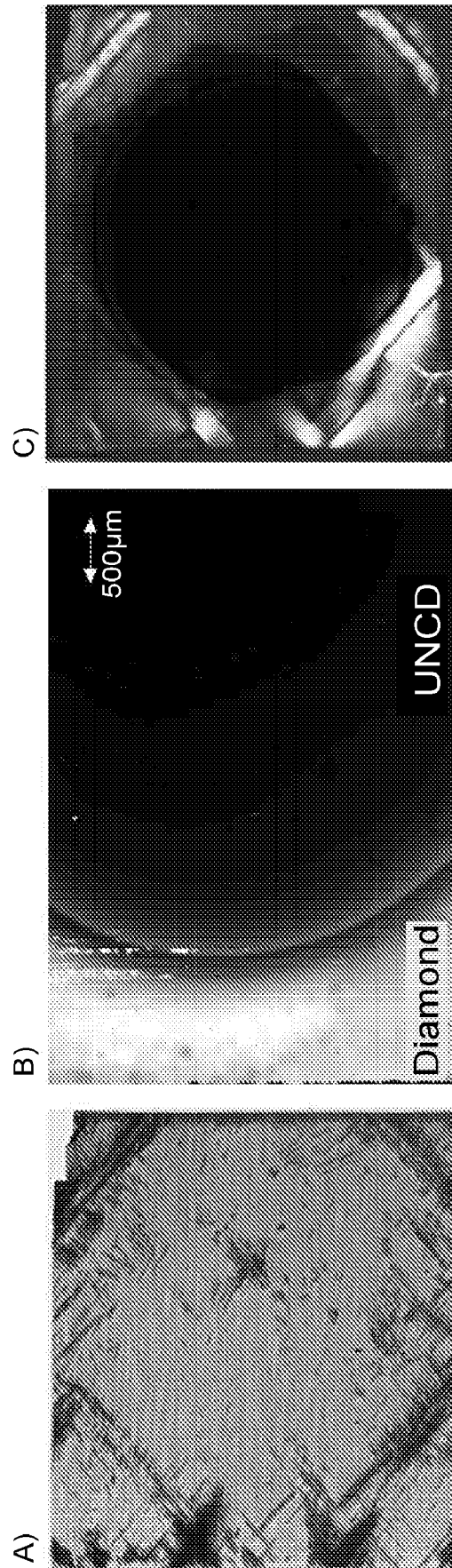


FIG. 5



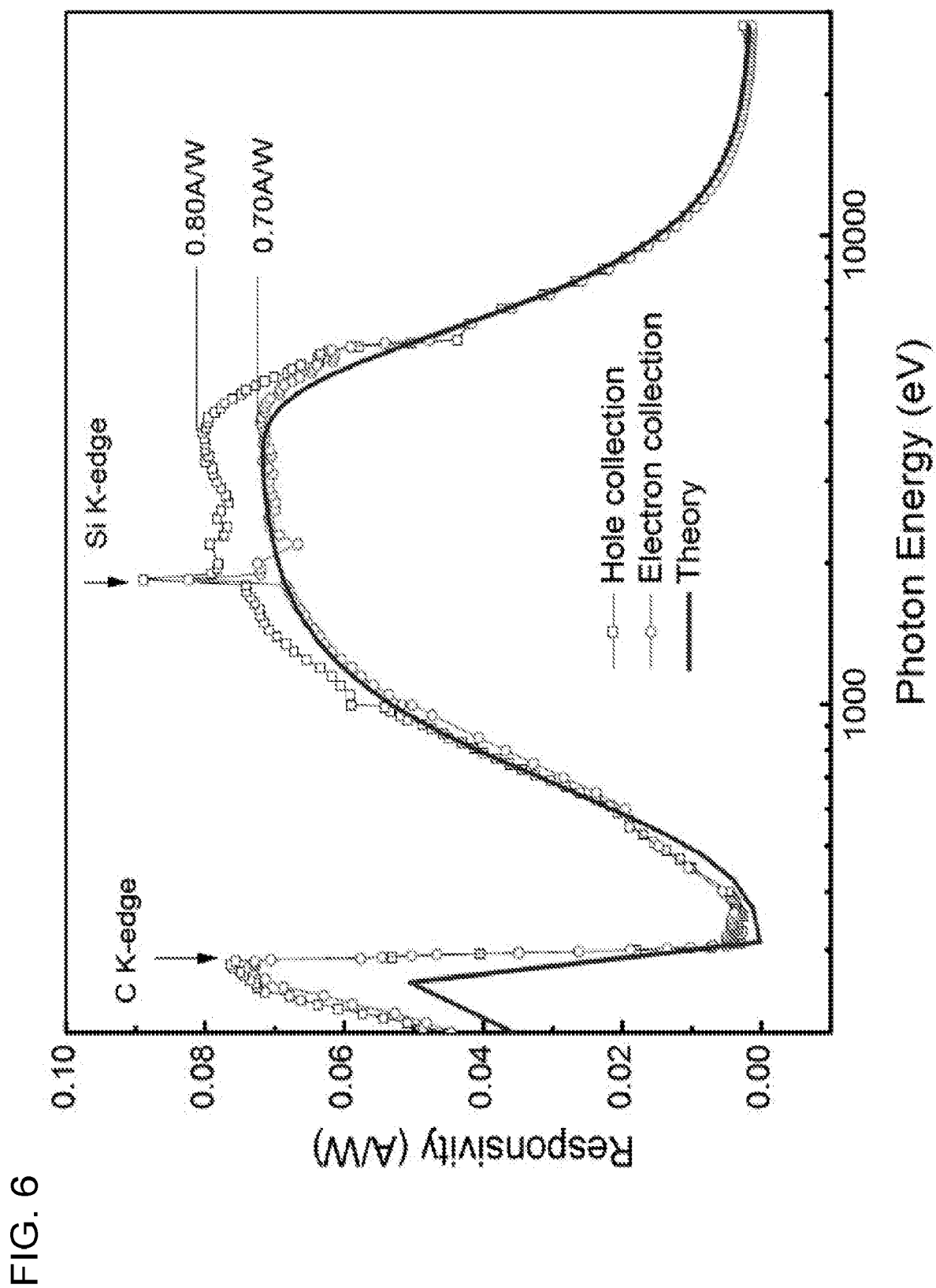


FIG. 7

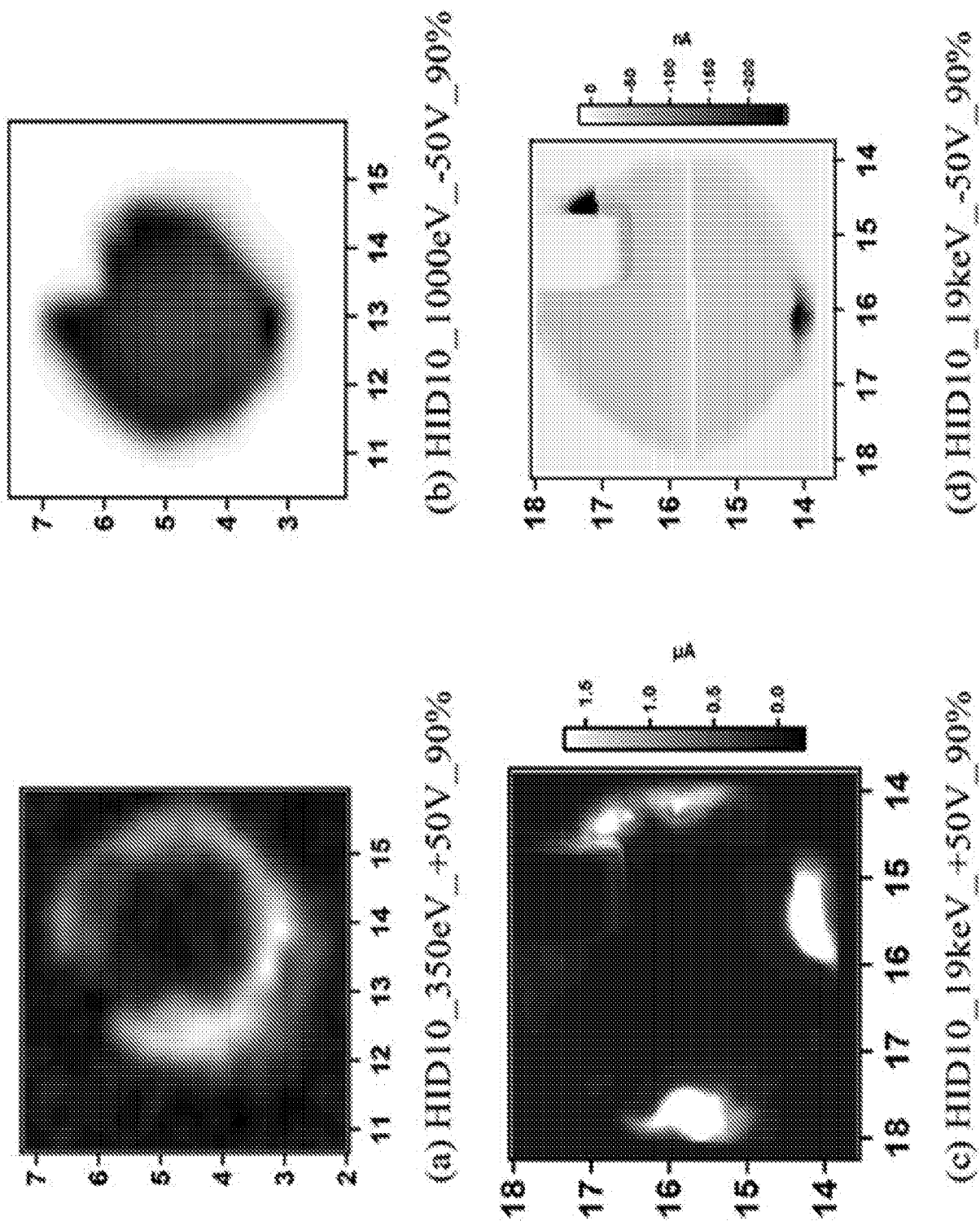
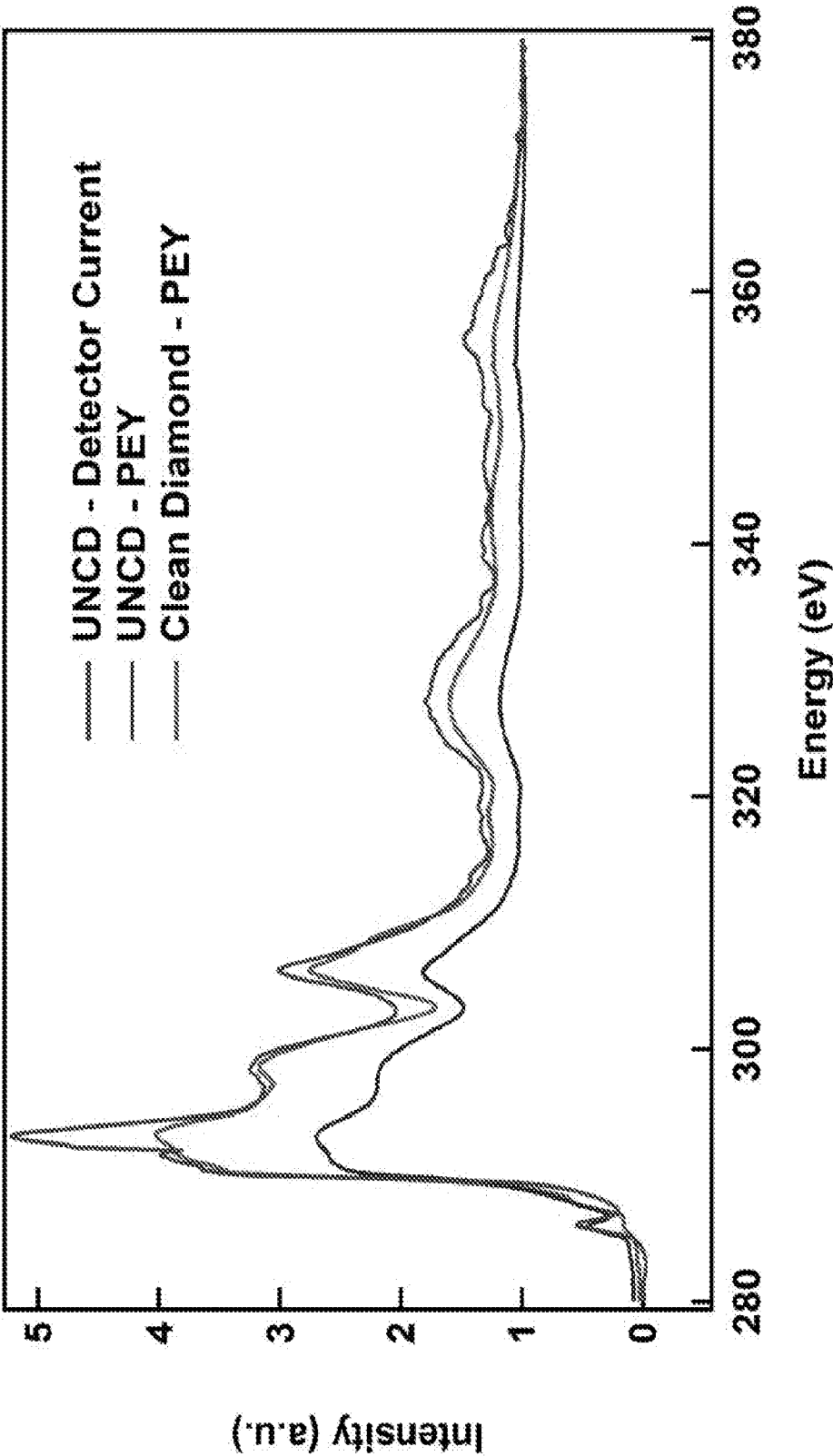


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/040456

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 29/66; H01L 21/302; H01L 31/0312 (2016.01)

CPC - H01L 29/66015; H01L 21/02376; H01L 29/66045 (2016.08)

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 - H01L 29/66; H01L 21/302; H01L 31/0312

CPC - H01L 29/66015; H01L 21/02376; H01L 29/66045

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

USPC- 257/77, 288; 427/575; 428/408; 438/931 (keyword delimited)

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

Orbit, Google Patents, Google Scholar

Search terms used: diamond substrate, plasma, contacts, doping, microwave, x ray monitor, doped, absorption

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,183,530 A (YAMAZAKI) 02 February 1993 (02.02.1993) entire document	1-9
Y	US 2009/0239078 A1 (ASMUSSEN et al) 24 September 2009 (24.09.2009) entire document	1-9
Y	US 2015/0092925 A1 (UCHICAGO ARGONNE, LLC) 02 April 2015 (02.04.2015) entire document	3
Y	US 2005/0217561 A1 (NAMBA et al) 06 October 2005 (06.10.2005) entire document	5, 6
Y	US 5,622,902 A (KURTZ et al) 22 April 1997 (22.04.1997) entire document	9
A	US 2006/0060864 A1 (GERBI) 23 March 2006 (23.03.2006) entire document	1-9
A	US 2008/0134960 A1 (KASU et al) 12 June 2008 (12.06.2008) entire document	1-9
A	US 7,781,257 B2 (TAYLOR) 24 August 2010 (24.08.2010) entire document	1-9



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

24 October 2016

Date of mailing of the international search report

04 NOV 2016

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

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Facsimile No. 571-273-8300

Authorized officer

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/040456

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

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

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

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

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

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

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

See supplemental page

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-9

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.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/040456

Continued from Box No. III Observations where unity of invention is lacking

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

Group I, claims 1-9, drawn to a method of forming electrical contacts on a diamond substrate.

Group II, claims 10-14, drawn to a device, comprising: a diamond substrate including electronic circuitry.

Group III, claims 15-20, drawn to an X-ray monitor.

The inventions listed as Groups I, II and III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature of the Group I invention: producing a plasma ball using a microwave plasma source in the presence of a mixture of gases which include a source of a first p-type dopant or a first n-type dopant; disposing the plasma ball at a first distance from the diamond substrate as claimed therein is not present in the invention of Groups II and III. The special technical feature of the Group II invention: electronic circuitry disposed within the diamond substrate; the electrical contacts in electrical communication with the electronic circuitry as claimed therein is not present in the invention of Groups I or III. The special technical feature of the Group III invention: wherein the electrical contacts have an X-ray absorption of less than about 1% as claimed therein is not present in the invention of Groups I or II.

Groups I, II and III lack unity of invention because even though the inventions of these groups require the technical feature of at least one electrical contact disposed on the diamond substrate, the at least one electrical contact including a p-doped or an n-doped ultrananocrystalline diamond, this technical feature is not a special technical feature as it does not make a contribution over the prior art.

Specifically, US 2006/0060864 A1 (GERBI) 23 March 2006 (23.03.2006) teaches at least one electrical contact disposed on the diamond substrate (Paras. 7-8), the at least one electrical contact including a p-doped or an n-doped ultrananocrystalline diamond (Abstract and Para. 16).

Since none of the special technical features of the Group I, II or III inventions are found in more than one of the inventions, unity of invention is lacking.