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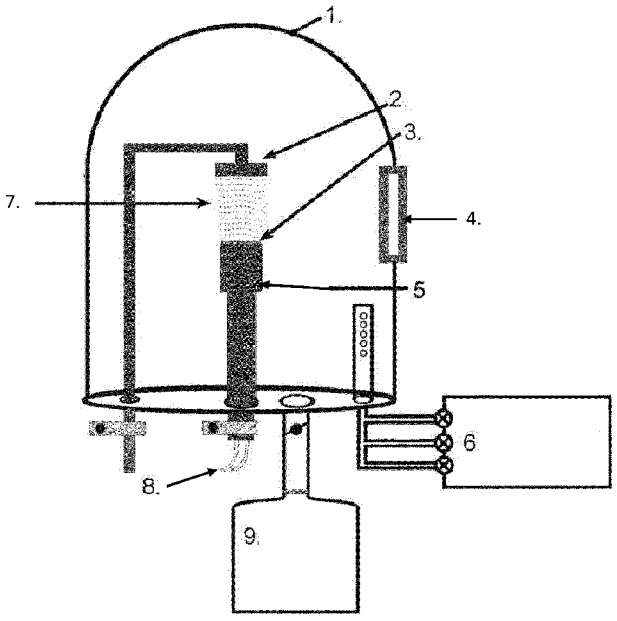

Fig. 1

(57) **Abstract:** Described herein is a process for integrating tritium into diamond, the process comprising infusing or implanting tritium into the diamond substrate to provide diamond containing tritium, wherein tritium is substitutionally and/or interstitially integrated into the diamond substrate.

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PROCESS FOR INTEGRATING TRITIUM INTO DIAMOND

Field of the Invention

The present invention is directed towards processes for integrating/embedding tritium into diamond, for example processes for infusing or implanting tritium into diamond (e.g. synthetic diamond) to provide diamond containing tritium, where tritium is substitutionally and/or interstitially integrated into the diamond. The present invention also relates to beta-voltaic power sources including diamond containing tritium and radiation powered devices.

Background of the Invention

One of the alternatives to current battery technology is the use of radiation powered batteries, also known as atomic batteries, nuclear batteries, radioisotope batteries, or radioisotope generators. These devices directly convert nuclear decay products (e.g. alpha or beta particles or gamma radiation) into electricity.

Various device structures and materials have been developed to extract electrical energy from nuclear sources. Methods can generally be grouped into two main types: thermal and non-thermal. In thermal devices the radioactive source heats up a cathode electrode causing emission of electrons which flow to a cooler anode electrode generating electricity, e.g. thermoelectric or thermionic generators. In non-thermal devices radioactive decay products from a radioactive source generate electron-hole pairs in a semiconductor disposed adjacent the radioactive source in order to generate electricity, e.g. alpha-voltaic or beta-voltaic devices. Thermal and non-thermal processes can also be combined in device structures using both a thermal gradient and radiation induced electron-hole pair generation to produce electricity.

Compared to chemical battery technologies, radioisotope batteries tend to have low power output. However, they have the advantage of long lifetimes, reduced size, and high energy density. As such, they are useful as power sources for equipment that must operate for long periods of time, particularly in environments which are difficult to access such as spacecraft, medical implants (e.g. pacemakers), underwater systems, automated scientific stations in remote parts of the world, high radiation environments, harsh chemical or physical environments, etc. They are also useful as power sources in miniaturized systems where the size of the power source is of importance.

WO2018/206958 A1 describes radiation devices comprising diamond material where a radioactive source is embedded in the diamond material. This document describes integration of the radioactive source during formation of the synthetic diamond material, for example by Chemical Vapour Deposition (CVD).

WO2021/044140 A2 describes chemical deposition processes for producing diamond, including producing radioisotope containing diamond where the radioisotope is embedded into the diamond structure during diamond crystal growth.

Beta-voltaic batteries are essentially a semiconductor device with a beta radioisotope in close proximity, the radioisotope provides a source of high energy electrons which can generate power or electrical current, and this is very similar to photovoltaic (PV) cells/panels which make use of light to generate power (see, for example, Alam et al. 2016; and Spencer et al. 2019).

Beta-voltaic batteries typically make use of a semiconductor junction, an example is a simple Schottky Diode with the appropriate material doping and electric connections designed to produce an internal device voltage or built-in potential, this allows for the collection of mobile secondary electrons created by beta radiation to generate electrical power.

For beta-voltaic devices, the efficiency or conversion of beta electrons to useful electrical power is very dependent on the coupling of the radioisotope to the semiconductor. High collection efficiencies, of the order of 0.95 can be achieved if beta electrons are injected directly into the depletion area of the semiconductor. This semiconductor depletion area is where electrical charge exists, this in-built device voltage or potential gradient provides a drift zone for the movement and efficient collection of electrons. If the radioisotope is external to the semiconductor or in a separate layer then self-absorption losses or suboptimal beta paths or trajectories result in much reduced battery efficiencies, this increases manufacture costs and reduces the power output of devices.

Diamond is in many ways the ideal material for use in radiation powered devices such as radioisotope batteries and related devices. First, diamond is extremely radiation hard and therefore has a higher tolerance to ionising radiation than other semiconductor materials improving stability and lifetime. Secondly, the large band-gap of diamond enables a significant improvement in the internal efficiency of the device. Thirdly, diamond is chemically inert, non-toxic, has high thermal conductivity, and is stable up to very high temperatures. Non-toxicity for example is highly important for human handling and sub-dermal implantation of devices for applications including pacemakers and/or hearing aids.

Embedding of radioactive sources within diamond reduces/prevents radiation leakage.

There is a need to provide alternative processes for producing diamond containing radioisotopes to provide radiation powered devices, in particular efficient processes that avoid the need for radioisotopes to be embedded into diamond during growth of synthetic diamond such as during chemical vapour deposition of diamond.

Summary of the Invention

The present inventors have found that tritium can be integrated into diamond, i.e. a diamond semiconductor, after the diamond (e.g. synthetic diamond) has been formed. The present inventors have found that tritium can be infused or implanted into diamond to provide diamond containing tritium, wherein tritium is substitutionally and/or interstitially integrated into the diamond.

Tritium (hydrogen-3) is a radioactive isotope of hydrogen which is a pure beta emitter. The present inventors have found that tritium is suitable for embedding into diamond, particularly due to tritium's low mass, a compatible energy spectrum of the emitted beta particles on decay with an average energy of 5.6keV, and due to tritium being readily available as a waste product from the nuclear industry.

The present inventors have found that for beta-voltaic devices, the efficiency or conversion of beta electrons to useful electrical power is very dependent on the coupling of the radioisotope to the semiconductor. High collection efficiencies, of the order of 0.95 can be achieved if beta electrons are injected directly into the depletion area of the semiconductor. This semiconductor depletion area is where electrical charge exists, this in-built device voltage or potential gradient provides a drift zone for the movement and efficient collection of electrons. If the radioisotope is external to the semiconductor or in a separate layer then self-absorption losses or suboptimal beta paths or trajectories result in much reduced battery efficiencies, this increases manufacture costs and reduces the power output of devices. Each beta decay releases an electron of high energy, in the case of Tritium an average energy of 5690eV, this immediately interacts with the electrons of the material, in the case of a semiconductor, electron energy states are engineered to receive this energy by moving electrons up in energy to the conduction band, higher energies in which they are free to move or drift in the presence of the internal potential within the device. This is the same mechanism utilised in a photovoltaic cell, the difference being that light is the energy source, a single photon to elevate an electron into the conduction band and charge collection provides power generation. The other difference is that each beta particle or high energy electron in a beta-voltaic device can elevate many electrons to the conduction band for energy generation as per equation (I) and (II) below which are provided by theoretical and proven experimentally (see Butler et al. 2009 and CVD Diamond Handbook 2015).

$$\mathbf{e} = 2.8\mathbf{Eg} + 0.5\text{eV} \quad \text{(I)}$$

where **e** is the average energy dissipated to generate one electron hole pair, or elevate an electron to the conduction band, **Eg** is the band gap of the material or semiconductor, for diamond this is 5.47eV.

$$e_n = 5690eV / (2.8Eg + 0.5eV) \quad (II)$$

So, for a Diamond Schottky Diode, with Tritium as the active energy source, each beta decay provides an e_n of approximately 360 electrons (measured slightly higher using the method outlined by Canali et al. 1979), this invention provides for maximal device efficiency in that these electrons elevated to the conduction band are in the drift region of the semiconductor for maximum collection and providing increased power generation and efficiency. The radioisotope (tritium) can be described as intrinsic to the diamond crystal (i.e. substitutionally or interstitially integrated into the diamond/diamond substrate) providing the highest theoretical device efficiency by employing the processes described herein.

The present inventors have found that the processes described herein allow for the provision of improved beta-voltaic devices, e.g. devices having improved efficiency, due to providing for an atomic-level integration of the beta radioisotope directly into the diamond (substitutional or interstitial integration of tritium into the diamond/diamond substrate/diamond crystal).

With conventional beta-voltaic device-layered geometries the efficiency is affected by the backscattering coefficient, primary electrons being deflected back by collisions within the semiconductor crystal as secondary electrons are propagated. Backscatter is low for diamond and helps with confinement of the primary beta particles, however the process described herein produces a product in which the radioisotope is intrinsic to the semiconductor reducing backscatter and self-absorption losses to the theoretical minimum.

Diamond is an excellent material for beta-voltaics, one important material parameter is the minimum energy for atomic displacement and is directly related to the high bond strength. Diamond has the highest bond strength of any semiconductor used in beta-voltaics, measured at 35eV and thereby providing the highest radiation resistance. The threshold for lattice damage is 200keV which is an order of magnitude above the maximum Tritium beta energies and energy spectrum (up to 20keV).

The cost of production of diamond beta batteries is dominated by the CVD growth of diamond with expensive plant, running costs and the handling of radioisotopes in their fabrication to maximise the efficiency of the final battery. The present invention provides great advantages by providing for intrinsic incorporation of tritium within the diamond device, inside the depletion layer of the semiconductor where primary beta electronics can generate the maximum secondary electrons and at the greatest collection efficiency.

The processes described herein comprise infusion or implantation of tritium into diamond/a diamond substrate/a diamond crystal, i.e. tritium is directly infused/implanted in to diamond/a diamond

substrate/a diamond crystal to provide diamond containing tritium, wherein tritium is substitutionally and/or interstitially integrated into the diamond/diamond crystal/diamond substrate.

The processes described herein provide major cost savings in a fabrication process of a diamond beta battery and aids the safe handling of radioisotopes.

At it's most general, the present invention provides a process for integrating tritium into diamond (for example, a diamond crystal), the process comprising infusing or implanting tritium into diamond to provide diamond containing tritium, wherein tritium is substitutionally and/or interstitially integrated into the diamond substrate.

In place of tritium, deuterium can be employed in the processes described herein to produce diamond containing deuterium. In some examples described herein deuterium is employed instead of tritium due to it's ease of handling relative to tritium.

In a first aspect, the present invention provides a process for integrating tritium into diamond, the process comprising:

providing a diamond substrate; and

infusing or implanting tritium into the diamond substrate to provide diamond containing tritium, wherein tritium is substitutionally and/or interstitially integrated into the diamond substrate,

wherein infusing or implanting tritium into the diamond substrate comprises exposing the diamond substrate to tritium and an energy source.

In a second aspect, the present invention provides an electrical power source comprising a semiconductor, the semiconductor comprising diamond containing tritium obtainable or obtained by a process described herein, wherein the diamond containing tritium contains tritium substitutionally or interstitially integrated into diamond.

In a third aspect, the present invention provides a beta-voltaic battery comprising a semiconductor disposed between a first electrode and a second electrode, the semiconductor comprising diamond containing tritium obtainable or obtained by a process described herein, wherein the diamond containing tritium contains tritium substitutionally or interstitially integrated into diamond.

The process for integrating tritium into diamond may comprise:

providing a diamond substrate; and

infusing or implanting tritium into the diamond substrate to provide diamond containing tritium, wherein tritium is substitutionally and/or interstitially integrated into the diamond substrate,

wherein infusing or implanting tritium into the diamond substrate comprises exposing the diamond substrate to tritium and an energy source.

In embodiments, the energy source is elevated temperature (for example at least about 800 K), a plasma or an ion beam (e.g. having an energy of at least about 25 eV).

The present inventors have found that tritium can be infused/implanted into diamond by exposing the diamond to tritium and an energy source, for example exposing the diamond to:

a tritium plasma;

elevated temperature (for example a temperature of at least about 800 K, at least about 850K, at least about 900K, at least about 950K, at least about 1000 °K, at least about 1050 °K, at least about 1100 °K, at least about 1150 °K, at least about 1200 °K, or at least about 1250 °K) and a tritium atmosphere (for example a tritium atmosphere having a pressure of at least about 1 bar, for example a pressure in the range of about 1-6 bar, or about 1-4 bar); or

a tritium ion beam (for example a tritium ion beam having an energy of at least about 25 eV, for example at least about 25 eV to about 5000 eV, or about 250 eV to about 5000 eV; in some examples the tritium ion beam has a current of at least about 20mA, for example at least about 30 mA, or at least about 40 mA).

In embodiments, the process comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber; and

exposing the diamond substrate to tritium and an energy source.

In embodiments, infusing tritium into the diamond substrate comprises exposing the diamond to:

a tritium plasma; or

elevated temperature (for example a temperature of at least about 800 K, at least about 850 K at least about 900 K, at least about 950 K, at least about 1000K, at least about 1050 °K, at least about 1100 °K, at least about 1150 °K, at least about 1200 °K, or at least about 1250 °K) and a tritium atmosphere (for example a tritium atmosphere having a pressure of at least about 1 bar, for example a pressure in the range of about 1-6 bar, or about 1-4 bar).

In embodiments, implanting tritium into the diamond substrate comprises irradiating the diamond substrate with a tritium ion beam, for example a tritium ion beam having an energy of at least about 25 eV, for example at least about 250 eV, about 25 eV to about 5000 eV, or about 250 eV to about 5000 eV.

Definitions

The terms "diamond" and "diamond material" are used herein to refer to a material composed of diamond. The skilled person understands that diamond can be described as a crystalline material (a polycrystalline material or a single crystal material). The skilled person also understands that diamond can be described as the diamond allotrope of carbon in which carbon atoms are arranged in a cubic Bravais lattice over which is laid a four-atom tetrahedral motif.

Diamond (or diamond material) may contain at least about 90% sp^3 bonds, for example at least about 95 % sp^3 bonds, at least about 97% sp^3 bonds, at least about 98% sp^3 bonds, at least about 99% sp^3 bonds, at least about 99.5% sp^3 bonds, at least about 99.9% sp^3 bonds, or about 100% sp^3 bonds. The sp^3 bond content in the diamond material may be determined by methods known to the skilled person, for example using X-ray photoelectron spectroscopy (XPS) (for example, as described by Yan 2018 and Taki 1998.

The skilled person understands that diamond may have a single active Raman mode at 1332 cm^{-1}.

The diamond material may have a band gap at room temperature (about 25 ˚C) of greater than about 5.3eV, or about 5.4eV or greater, or about 5.5eV.

The diamond (or diamond material) may have a thermal conductivity measured at room temperature (about 25 ˚C) of greater than about 100 W/mK, for example, greater than about 500 W/mK, greater than about 1000 W/mK, greater than about 1500 W/mK, or greater than about 2000 W/mK, or about 2200 W/mK or greater. Thermal conductivity of diamond may be determined according to the 3ω method (Frank 1993).

The diamond (or diamond material) may have a density of greater than about 3300 kg/m^3, for example greater than about 3400 kg/m^3, or greater than about 3500kg/m^3.

The term "diamond substrate" is used herein to refer to a material composed of diamond (i.e. crystalline diamond).

The processes described herein integrate tritium into diamond such that tritium is substitutionally or interstitially integrated into diamond. Tritium "substitutionally" integrated into diamond refers to tritium occupying defect/vacant sites in the diamond (i.e. missing carbon atom sites). Tritium "interstitially" integrated into diamond refers to tritium occupying hydrogen positions in diamond. The present inventors have surprisingly found that the processes described herein allow hydrogenic species within the diamond lattice, which may be incorporated into diamond during formation of diamond (for example formation of synthetic diamond by CVD), to be displaced and replaced by tritium.

Brief description of the Drawings

Embodiments of the present invention are described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram of a pressurisable chamber which may be employed in embodiments of the processes described herein; and

Figure 2 is a graph showing the result of thermal desorption spectroscopy of deuterium infused diamond produced according to an illustrative Example.

Detailed Description

Processes for integrating tritium into diamond

Using a tritium plasma to Infuse tritium into diamond

Described herein is a process for integrating tritium into diamond, the process comprising exposing the diamond substrate to a tritium plasma.

In embodiments, infusing tritium into the diamond substrate comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber;

charging the pressurisable chamber with tritium; and

activating the tritium to provide a tritium plasma.

In embodiments, the pressurisable chamber employed may be a CVD (Chemical Vapour Deposition) chamber. Figure 1 is a schematic diagram of a pressurisable chamber 1 which is a CVD chamber which is a DC plasma system containing an anode 5 and a cathode 2 to allow a voltage to be applied to activate a tritium to provide a tritium plasma. The pressurisable chamber 1 may comprise a vacuum pump 9 which can be used to apply a vacuum to the pressurisable chamber.

The pressurisable chamber 1 shown in figure 1 includes water-cooled electrical feedthroughs 8 to provide temperature control if required and a view port 4. A diamond substrate 3 is shown in figure 1 as being positions on the anode 5.

The pressurisable chamber 1 shown in figure 1 includes a gas supply 6 for supplying tritium to the pressurisable chamber. Once the pressurisable chamber 1 has been charged with tritium, the gas can be activated by applying a DC current across the anode 5 and cathode 2 to provide a tritium plasma 7 between the anode 5 and the cathode 2.

In embodiments, prior to charging the pressurisable chamber with tritium, a vacuum is applied to the pressurisable chamber to reduce the pressure of the chamber to a pressure of less than about 1 mTorr, for example less than about 0.1 mTorr, or about 1 μTorr or less. Suitably the chamber is evacuated to a pressure of about 5 μTorr or less. In embodiments, after the vacuum has been applied, the pressurisable chamber is flushed with high purity inert gas, for example Argon gas. Flushing the pressurisable chamber with a high purity inert gas such as Argon may be carried out in order to purge residual oxygen on the internal surfaces of the chamber prior to the chamber being charged with the tritium. In embodiments where the pressurisable chamber is flushed with high purity inert gas, for example Argon gas, a vacuum is applied to the pressurisable chamber (e.g., to reduce the pressure of the chamber to a pressure of less than about 1 mTorr, for example less than about 0.1 mTorr, or about 1 μTorr or less) after flushing with inert gas and before the pressurisable chamber is charged with tritium.

In embodiments, tritium is supplied to the pressurisable chamber in the form of a tritium containing gas. In embodiments, the tritium containing gas comprises at least about 10 vol.% tritium, for example from about 10 vol.% up to about 90 vol.% tritium, for example from about 10 vol.% to about 90 vol.% tritium in Argon gas. In embodiments, the tritium (e.g. tritium-containing gas) charged to the pressurisable chamber contains no carbon source gas, for example no methane.

In embodiments, the process comprises charging the pressurisable chamber with tritium such that the pressure within the pressurisable chamber is at least about 5 Torr, for example at least about 10 Torr. In embodiments, the pressurisable chamber comprises tritium-containing gas at a pressure of at least about 5 Torr or at least about 10 Torr before the tritium containing gas is activated to form a tritium plasma.

In embodiments, activating the tritium to provide a tritium plasma comprises electrically activating the tritium to form a tritium plasma. Tritium may be electrically activated by applying an electric current across the tritium contained in the pressurisable chamber (e.g. employing a DC electric current) or by introducing electromagnetic radiation (for example having a radio frequency or a microwave frequency) to tritium in the pressurisable chamber activate the tritium. In embodiments, electrically activating the tritium to form a tritium plasma comprises generating an electric field of at least about 350 V/cm, for example an electric field in the range of about 350 V/cm to about 600 V/cm. The power of the electrical supply used to activate the tritium may be adjusted to control the temperature of the diamond substrate.

In embodiments, after tritium has been activated to form a tritium plasma, pressure in the pressurisable chamber is increased to greater than about 50 Torr, for example greater than about 100 Torr, greater than about 200 Torr or greater than about 500 Torr.

In embodiments, the tritium plasma is formed by electrical activation using a DC power supply. The power supplied by the DC power supply may be increased from at least about 50 W to greater than about 10kW after the tritium plasma has been formed. The power of the DC power supply may be adjusted to control the temperature of the diamond substrate.

In embodiments, infusing tritium into the diamond substrate comprises adjusting the temperature of the diamond substrate to at least about 800 K, for example at least about 850 K, at least about 900 K, at least about 950 K, at least about 1000 K, at least about 1050 °K, at least about 1100 °K, at least about 1150 °K, at least about 1200 °K, or at least about 1250 °K. The present inventors have found that temperatures of at least about 800K improve infusion of tritium into the diamond substrate.

In embodiments, the diamond substrate is exposed to tritium plasma for at least about 30 mins, for example at least about 60 mins, at least about 90 mins, or at least about 120 mins.

In embodiments, the process comprises providing the diamond containing tritium with a Schottky contact and/or an ohmic contact by forming a suitable metal layer(s) on a surface(s) of the diamond substrate containing tritium. Such metals may be provided on surfaces of the diamond substrate using physical vapour deposition, such as e-beam evaporation.

In embodiments, the process comprises depositing a layer of non-radioactive diamond (for example ^{12}C and/or ^{13}C diamond) on the diamond containing tritium. Non-radioactive diamond may be provided on the diamond containing tritium by CVD.

In embodiments, the process comprises encapsulating the diamond containing tritium, optionally encapsulating the diamond containing tritium comprises coating the diamond containing tritium with an insulating resin.

Using elevated temperature to infuse tritium into diamond

Described herein is a process for integrating tritium into diamond, the process comprising exposing the diamond substrate to elevated temperature and a tritium atmosphere.

In embodiments, infusing tritium into the diamond substrate comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber;

charging the pressurisable chamber with tritium to a pressure of at least about 1 bar; and

heating the pressurisable chamber to a temperature of at least about 800 °C.

The pressurisable chamber described in connection with figure 1 may also be employed in this process.

In embodiments, prior to charging the pressurisable chamber with tritium, a vacuum is applied to the pressurisable chamber to reduce the pressure of the chamber to a pressure of less than about 1m Torr, for example less than about 0.1 mTorr, or about 1 µTorr or less. In embodiments, after the vacuum has been applied, the pressurisable chamber is flushed with high purity inert gas, for example Argon gas. In embodiments where the pressurisable chamber is flushed with high purity inert gas, for example Argon gas, a vacuum is applied to the pressurisable chamber (e.g., to reduce the pressure of the chamber to a pressure of less than about 1 mTorr, for example less than about 0.1 mTorr, or about 1 µTorr or less) after flushing with inert gas and before the pressurisable chamber is charged with tritium. Suitably the chamber is evacuated to a pressure of about 5 µTorr or less prior to the chamber being purged with 500torr of argon gas to remove residual oxygen.

In embodiments, tritium is supplied to the pressurisable chamber in for form of a tritium containing gas. In embodiments, the tritium containing gas comprises at least about 10 vol.% tritium, for example from about 10 vol.% to about 90 vol.% tritium, for example from about 10 vol.% to about 90 vol.% tritium in argon gas.

In embodiments, the process comprises charging the pressurisable chamber with tritium such that the pressure within the pressurisable chamber is at least about 1 bar, for example a pressure in the range of about 1 bar to about 4 bar.

In embodiments, infusing of tritium into the diamond substrate comprises exposing the diamond substrate to a temperature of at least about 800 K, for example at least about 850 K, at least about 900 K, at least about 950 K, at least about 1000 K, at least about 1050 °K, at least about 1100 °K, at least about 1150 °K, at least about 1200 °K, or at least about 1250 °K.

In embodiments, the diamond substrate is exposed to tritium at a pressure of at least about 1 bar and a temperature of at least about 800 °C for at least about 30 mins, for example at least about 60 mins, at least about 90 mins, or at least about 120 mins.

In embodiments, the process comprises providing the diamond substrate (before or after tritium integration) with a Schottky contact and/or an ohmic contact by forming a suitable metal layer(s) on a surface(s) of the diamond substrate containing tritium. Such metals may be provided on surfaces of the diamond substrate using physical vapour deposition.

In embodiments, the process comprises depositing a layer of non-radioactive diamond (for example ^{12}C and/or ^{13}C diamond) on the diamond containing tritium. Non-radioactive diamond may be provided on the diamond containing tritium by CVD.

In embodiments, the process comprises encapsulating the diamond containing tritium, optionally encapsulating the diamond containing tritium comprises coating the diamond containing tritium with an insulating resin.

Using a tritium ion beam to implanting tritium into diamond

Described herein is a process for integrating tritium into diamond, the process comprising exposing the diamond substrate to a tritium containing ion beam.

In embodiments, infusing tritium into the diamond substrate comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber; and

irradiating the diamond substrate with the tritium ion beam having an energy of at least about 25 eV.

In embodiments, prior to charging the pressurisable chamber with tritium, a vacuum is applied to the pressurisable chamber to reduce the pressure of the chamber to a pressure of less than about 1 mTorr, for example less than about 0.1 mTorr, or about 1 µTorr or less. In embodiments, after the vacuum has been applied, the pressurisable chamber is flushed with high purity inert gas, for example Argon gas. In embodiments where the pressurisable chamber is flushed with high purity inert gas, for example Argon gas, a vacuum is applied to the pressurisable chamber (e.g., to reduce the pressure of the chamber to a pressure of less than about 1 mTorr, for example less than about 0.1 mTorr, or about 1 µTorr or less) after flushing with inert gas and before the pressurisable chamber is charged with tritium. Suitably the chamber is evacuated to a pressure of about 1 µTorr or less prior to purging the chamber with argon after which the chamber is re evacuated to high vacuum before being charged with the tritium.

In embodiments, the diamond substrate positioned in the pressurisable chamber is provided with a Schottky contact. In embodiments, the diamond substrate positioned in the pressurisable chamber is provided with an ohmic contact.

In embodiments, the process comprises irradiating the diamond substrate with the tritium ion beam having an energy of at least about 25 eV, for example at least about 250 eV. In embodiments, the process comprises irradiating the diamond substrate with the tritium ion beam having an energy of at in the range of about 25 eV to about 5000 eV, for example about 250 eV to about 5000 eV.

In embodiments, the ion mean has an ion current of at least about 20 mA, at least about 30 mA, or at least about 40 mA. In embodiments, an ion current of at least about 20 mA, at least about 30 mA, or at least about 40 mA is maintained as the diamond substrate is irradiated with the tritium ion beam.

In embodiments, the diamond substrate is irradiated with the tritium ion beam having an every of at least about 25 eV or at least about 250 eV for least about 800 °C for at least about 30 mins, for example at least about 60 mins, at least about 90 mins, or at least about 120 mins.

In embodiments, the ion flux at a surface of the diamond substrate is from about $1x10^{14}$ to about $1x\ 10^{19}$ $D.m^{-2}.s^{-1}$ during irradiation of the diamond substrate.

In embodiments, the process comprises providing the diamond substrate (before or after tritium integration) with a Schottky contact and/or an ohmic contact by forming a suitable metal layer(s) on a surface(s) of the diamond substrate containing tritium. Such metals may be provided on surfaces of the diamond substrate using physical vapour deposition.

In embodiments, the process comprises depositing a layer of non-radioactive diamond (for example ^{12}C and/or ^{13}C diamond) on the diamond containing tritium. Non-radioactive diamond may be provided on the diamond containing tritium by CVD.

In embodiments, the process comprises encapsulating the diamond containing tritium, optionally encapsulating the diamond containing tritium comprises coating the diamond containing tritium with an insulating resin.

The diamond containing tritium obtainable or obtained by the processes described herein contains tritium substitutionally or interstitially integrated into diamond. The tritium infused in this way may co-ordinate in interstitial positions to form clusters with included hydrogen present from the CVD diamond growth.

Also described herein is an electrical power source comprising a semiconductor, the semiconductor comprising diamond containing tritium obtainable or obtained by any of the processes described herein.

Also described herein, is a beta-voltaic battery comprising a semiconductor disposed between a first electrode and a second electrode, the semiconductor comprising diamond containing tritium obtainable or obtained by any of the processes described herein.

Examples

The following illustrates examples of the methods and related aspects described herein. Thus, these examples should not be considered to restrict the present disclosure but are merely in place to teach how to carry out the methods of the present disclosure.

Example 1

In this Example, deuterium was infused into diamond as part of an experiment to test the method of infusion. Deuterium was employed in this example in place of tritium due to it's ease of handling relative to tritium. The example could be repeated replacing deuterium with tritium to provide diamond containing tritium.

A semiconducting diamond substrate was provided (the diamond substrate in the form of a membrane having an upper surface area of 1 cm^2 and a thickness of 50 µm) and positioned in a CVD chamber largely composed of glass. The CVD chamber was configured with water-cooled electrical feedthroughs and cooled baseplate. Inside the CVD chamber is provided with plasma electrodes (a cathode and an anode). The diamond substrate was mounted on the anode electrode. The plasma electrodes are made primarily from oxygen-free copper with refractory metal ends to withstand the temperatures attained by the electrodes at the maximum plasma power used in this process. The CVD chamber was evacuated to high vacuum (5×10^{-6} torr). A deuterium-containing gas-was charged to the CVD chamber to a pressure of 10 Torr and electrically activated by applying an electric current between two electrodes in the CVD chamber. The voltage between the two electrodes, applied using a pulsed DC power supply, was arranged to generate a field exceeding 400 V/cm to enable an electron temperature of 250 000K to be achieved. Initially the pulsed DC power supply provided a power in the range of 50-100 W. Over a period of 120 minutes, the pressure of the deuterium-containing gas in the CVD chamber was increased to 350 Torr alongside power being adjusted in the range 2.5kW to 3kW to ensure that the plasma ball adequately covers the electrode surface area containing the diamond substrate. The diamond substrate working temperature was controlled by the plasma power dissipated at the anode and thermally conducted to the temperature-controlled electrical feedthrough. The plasma power is adjusted to allow the diamond substrate to reach 1000 °C. The plasma was then extinguished and the deuterium containing gas captured using a gas handling system connected to the CVD chamber exhaust. The diamond infused with deuterium was removed from the CVD chamber and loaded in to a PVD system for Schottky contact metallization and then encapsulated in an insulating resin.

Thermal desorption spectroscopy (TDS) was carried out on the deuterium infused diamond produced according to Example 1. The deuterium infused diamond was heated in a vacuum with a ramp rate of 10K/min from room temperature to 1300 K. The rolling averages of D_2, HD and total deuterium desorbed from the sample are shown in figure 2.

Figure 2 shows two peaks for each of D_2, HD and total deuterium rolling averages. The peak at around 780 K (peak temperatures shown on figure 2) is the result of desorption of deuterium that was bound to the surface of the diamond in a sp^3-like manner, while the peak around 1060K (peak temperatures shown on figure 2) is the result of desorption of deuterium that was bound in a sp^2 like manner within the bulk of the diamond. Therefore, figure 2 shows that deuterium was successfully infused into the diamond substrate. The deuterium infused into the diamond structure is bound at interstitial and/or substitutional atomic sites as well as being contained at grain boundary regions (although a lower amount of deuterium is found at grain boundaries compared to interstitial and/or substitutional atomic sites).

Prophetic Example 2

A semiconducting diamond substrate is provided (the diamond substrate in the form of a membrane having an upper surface area of 1 cm^2 and a thickness of 50 µm) and positioned in a CVD chamber largely composed of glass as described in Example 1. The CVD chamber was evacuated to high vacuum (5×10^{-6} torr). A tritium-containing gas is charged to the CVD chamber to a pressure of 10 Torr and electrically activated by applying an electric current between two electrodes in the CVD chamber. The voltage between the two electrodes, applied using a pulsed DC power supply, was arranged to generate a field exceeding 400 V/cm to enable an electron temperature of 250 000K to be achieved. Initially the pulsed DC power supply provides a power in the range of 50-100 W. Over a period of 120 minutes, the pressure of the tritium-containing gas in the CVD chamber is increased to 350 Torr alongside power being adjusted in the range 2.5kW to 3kW to ensure that the plasma ball adequately covers the electrode surface area containing the diamond substrate. The diamond substrate working temperature is controlled by the plasma power dissipated at the anode and thermally conducted to the temperature-controlled electrical feedthrough. The plasma power is adjusted to allow the diamond substrate to reach 1000 °C. The plasma is then extinguished and the tritium containing gas captured using a gas handling system connected to the CVD chamber exhaust. The diamond infused with tritium is removed from the CVD chamber.

The tritium infused diamond produced according to Example 2 can be metallised with diode contacts in order to operate as a beta-voltaic diamond battery. After metallization the beta-voltaic diamond battery is encapsulated in an insulating resin.

Prophetic Example 3

A semiconducting diamond substrate is provided (the diamond substrate in the form of a membrane having an upper surface area of 1 cm^2 and a thickness of 50 µm). On one surface of the diamond substrate a metal layer is deposited to form a Schottky contact. An ohmic contact may also be formed using iridium or titanium. The diamond substrate comprising the Schottky contact is mounted in a glass tube with an internal diameter exceeding the width of the diamond substrate. A sorbing getter (such as SAES Getters St707) is also inserted in the glass tube that can efficiently pump tritium when activated at a temperature of 850 °C with radio frequency eddy-current heating or laser heating. The tube is then sealed at one end and the other end is connected to a gas handling system that allows the tube to be evacuated to high vacuum and back-filled with tritium to typical pressure of 1 to 4 bar. The glass tube is sealed off from the gas handling system to form a small gas enclosure with a volume (e.g. 3 cm^3) that accommodates the diamond diode with the getter placed as far away as possible from the diode. The tube is placed in a small furnace where it may be heated to in excess of 800 °C for 120 minutes to infuse the tritium radioisotope into the exposed diamond surfaces of the device. The tube is then removed from the furnace and the getter is activated to pump tritium, excess free tritium radioisotope is safely captured in the getter. Once the tube has cooled to room temperature and the getter has completed its predetermined tritium pump cycle, the glass enclosure is ruptured in a fume cupboard equipped to handle active gases. The infused diamond diode is removed from the fume cupboard and electrical lead connections are made by wire bonding. A resin-based encapsulant is spray coated onto the diode to envelope the device to provide electrical insulation and to make it impervious to vapors and liquids that may otherwise short-circuit the battery device, typically a metal encapsulation completes the beta battery fabrication.

Prophetic Example 4

A semiconducting diamond substrate is provided (the diamond substrate in the form of a membrane having an upper surface area of 1 cm^2 and a thickness of 50 µm). On one surface of the diamond substrate a metal layer is deposited to form a Schottky contact. An ohmic contact may also be formed using iridium or titanium. The diamond substrate comprising the Schottky contact is mounted in a vacuum system equipped with an ion gun with the rectifying contact surface exposed for ion irradiation. The ion implantation system is pumped to high vacuum. The ion gun is energised to

irradiate the exposed metal diamond contact with tritium using accelerating voltages. The voltage applied to the ion gun is increased in 500V steps from 250V to 3750V to irradiate the diamond substrate with ions having incident energies of 250eV, 750eV, 1250eV, 1750eV, 2250eV, 2750eV, 3250eV and 3750eV. The ion current is maintained at 40mA. Ion flux is at least 3.04×10^{17} $D.m^{-2}.s^{-1}$ to enable tritium to diffuse to different depths below the Schottky contact. For each voltage step the tritium ion-irradiation is continued for typically 30 minutes, this is dependent on the activity or battery charge required and a minimum of four voltage steps are completed during the 120 minute process cycle to match the depth of the semiconductor depletion or active layer. Following implantation, the device is removed and electrical leads and encapsulation as described in Example 3.

The methods described in Examples 3 and 4 provide an advantage over Examples 1 and 2 insofar that the processes exemplified in Examples 3 and 4 can be used to infuse tritium into a diamond semiconductor comprising a Schottky content (and optionally an Ohmic contact). Therefore, the products resulting from the infusion/implantation of tritium according to the processes exemplified in Examples 3 and 4 can be a beta-voltaic battery, whereas the products resulting from the tritium infusion process exemplified in Example 2 (see also Example 1) must be metallised after tritium infusion to from a beta-voltaic battery.

Advantages of the methods described in Examples 1 and 2 include being able to carry out tritium infusion in a CVD chamber that was used to grow the diamond substrate, and/or being able to deposit a non-radioactive layer of diamond (for example a layer of ^{12}C or ^{13}C containing diamond) on the diamond containing tritium in the CVD chamber.

It is also envisaged that beyond the processes, diamond containing tritium, semiconductors and beta-voltaic devices as described herein, other diamond products can be provided. The diamond containing tritium can then be utilized in a range of applications as is known in the art.

While this invention has been described in relation to certain embodiments it will be appreciated that various alternative embodiments can be provided without departing from the scope of the invention which is defined by the appending claims.

Unless otherwise stated, the features of any dependent claim can be combined with the features of any of the other dependent claims, and any other independent claim.

Additional Description

This invention relates to an infusion method of Tritium (H_3) for the purpose of Diamond Beta Battery fabrication or manufacture, this is an alternative to an expensive transmutation process of a pre-prepared diamond device. The processes included in the method cover a direct plasma infusion of the radioisotope Tritium (H_3) into a diamond surface and through in the making of a Diamond Beta Battery or semiconductor device, Tritium ion implantation with use of an electric field or simply the Chemical Vapour Deposition (CVD) of diamond in the presence of Tritium (H_3) and other elements to achieve an infusion of the radioisotope within the diamond semiconductor to fabricate a beta battery or component part. These processes utilise standard low pressure or vacuum systems and provide for a multi-micron infusion, various depths of infusion to gain higher device efficiencies. This invention and the infusion processes described here make use of waste Tritium from the Nuclear Industry and provide a viable path for processing and repurposing of nuclear waste and support the nuclear decontamination and decommission of end-of-life nuclear power stations. The decommissioned UK Magnox, the operating Canadian CANDU power stations and UKAEA H3AT are excellent sources of waste radioisotopes which can be utilised with the infusion methods described. A standard plasma or microwave plasma CVD system can be modified to use these radioisotope infusion processes and can be viewed as an additional step in the manufacture of a diamond battery. This invention has synergy with the previous patents on diamond batteries, reference UK Patents WO2018/206958 (1) and WO2021 044140A2 (2).

This invention relates to an improved method of Diamond Beta Battery (DBB) fabrication or manufacture and follows on from the earlier patents WO2018/206958 and WO2021 044140A2. This invention is centred on the method of infusion or incorporation of a radioisotope into a diamond semiconductor, the primary radioisotope is Tritium or the Hydrogen-3, a radioactive isotope of Hydrogen which is a pure beta emitter and suitable material for incorporation into beta batteries with low radiation penetration depth, the beta or high energy electrons are confined within the diamond battery and do not pose a risk or hazard to the user or in the application of Diamond Beta Batteries (DBB).

Tritium or the $Hydrogen_3$ isotope is a very suitable beta radioisotope for diamond infusion being of low mass, a compatible energy spectrum of the emitted beta particles on decay with an average energy of 5.6keV and is readily available as a waste product from the nuclear industry. Other heavier beta radioisotopes, as in claim 6, are not excluded in this invention, and alternative infusion processes for example ion implantation as in claim 2 or Chemical Vapour Deposition (CVD) diamond growth to incorporate a radioisotope.

These are all scalable infusion processes which are in development and test, two infusion processes are an additional or separate step in the diamond battery fabrication the other is fundamental to the diamond growth stage or Chemical Vapour Deposition (CVD) in the presence of a suitable beta radioisotope. Beta batteries are essentially a semiconductor device with a beta radioisotope in close proximity, the radioisotope provides a source of high energy electrons which can generate power or electrical current, and this is very similar to photovoltaic (PV) cells/panels which make use of light to generate power, for a full description of this battery technology refer to references (8) & (9). Diamond Beta Batteries (DBB) also make use of a semiconductor junction, an example is a simple Schottky Diode with the appropriate material doping and electric connections designed to produce an internal device voltage or built-in potential, this allows for the collection of mobile secondary electrons created by beta radiation to generate electrical power.

With Beta-Voltaic devices the efficiency or conversion of beta electrons to useful electrical power is very dependent on the coupling of the radioisotope to the semiconductor. High collection efficiencies, of the order of 0.95 can be achieved if beta electrons are injected directly into the depletion area of the semiconductor. This semiconductor depletion area is where electrical charge exists, this in-built device voltage or potential gradient provides a drift zone for the movement and efficient collection of electrons. If the radioisotope is external to the semiconductor or in a separate layer then self-absorption losses or sub-optimal beta paths or trajectories result in much reduced battery efficiencies, this increases manufacture costs and reduces the power output of devices. Essentially each beta decay releases an electron of high energy, in the case of Tritium an average energy of 5690eV, this immediately interacts with the electrons of the material, in the case of a semiconductor, electron energy states are engineered to receive this energy by moving electrons up in energy to the conduction band, higher energies in which they are free to move or drift in the presence of the internal potential within the device. This is the same mechanism utilised in a photovoltaic cell, the difference being that light is the energy source, a single photon to

elevate an electron into the conduction band and charge collection provides power generation. The other difference is that each beta particle or high energy electron in a beta-voltaic device can elevate many electrons to the conduction band for energy generation as per equation (1) & (2), provided by theoretical and proven experimentally, reference (4) & (5).

$$e = 2.8Eg + 0.5eV \quad \text{equation (1)} \quad \text{(Klien 1968)}$$

where e is the average energy dissipated to generate one electron hole pair, or elevate an electron to the conduction band, Eg is the band gap of the material or semiconductor, for diamond this is 5.47eV.

$$e_n = 5690eV / (2.8Eg + 0.5eV) \quad \text{equation (2)}$$

So, for a Diamond Schottky Diode favoured in our device fabrications, with Tritium as the active energy source, each beta decay provides an e_n of approximately 360 electrons, measured at slightly higher Canali et al (4), this invention provides for maximal device efficiency in that these electrons elevated to the conduction band are in the drift region of the semiconductor for maximum collection and providing increased power generation and efficiency. The radioisotope, in this invention, can be described as intrinsic to the diamond crystal providing the highest theoretical device efficiency using one of these three infusion processes. There are many granted patents focused on various geometries of beta-voltaic batteries to improve the efficiency of devices, this invention is a novel use of radioisotope infusion resulting in an atomic-level integration of the beta radioisotope directly into the diamond.

With conventional beta-voltaic device-layered geometries the efficiency is affected by the backscattering coefficient, primary electrons being deflected back by collisions within the semiconductor crystal as secondary electrons are propagated. Backscatter is low for diamond and helps with confinement of the primary beta particles, however in this invention the radioisotope is intrinsic to the semiconductor reducing backscatter and self-absorption losses to the theoretical minimum.

Diamond is an excellent material for beta-voltaics, one important material parameter is the minimum energy for atomic displacement and is directly related to the high bond strength. Diamond has the highest bond strength of any semiconductor used in beta-voltaics, measured at 35eV and thereby providing the highest radiation resistance. The threshold for lattice damage is 200keV which is an order of magnitude above the maximum Tritium (H_3) beta energies and energy spectrum upto 20keV.

The cost of Diamond Beta Batteries is dominated by the CVD growth of diamond with expensive plant, running costs and the handling of radioisotopes in their fabrication to maximise the efficiency of the final battery. There are great advantages to the intrinsic incorporation within the diamond device, inside the depletion layer of the semiconductor where primary beta electronics can generate the maximum secondary electrons and at the greatest collection efficiency. This invention allows for the infusion of the radioisotope

directly into the device as an additional step within the CVD process or an integrated part of the diamond growth phase. This has major cost savings in a single fabrication process of the diamond beta battery and aids the safe handling of radioisotopes within the low-pressure vacuum system using a sealed CVD diamond reactor process.

A basic plasma CVD system is illustrated in figure 1, the CVD process is normally housed within a low-pressure vessel or vacuum chamber [1]. For high quality deposition of crystalline diamond (sp_3) high electron and gas temperatures are needed to promote the presence of energetic atomic hydrogen typically in a gas-plasma to promote only the strongest carbon atomic bonding to form diamond, for a full description of the Chemical Vapour Deposition (CVD) methods, operation and setup see references (4) & (5). The CVD environment provides a predisposition for diamond/SP_3 bonding, and the pressures, temperatures, gases and gas-ratios are tuned for high quality diamond growth. The CVD system of figure 1 is a typical DC plasma system whereby electrical power is provided to the Anode [5] and Cathode [2] in order to strike an Inter-Electrode Plasma [7] at the correct pressure levels and gas mix to attain the desired diamond deposition. Typically, a pulsed direct current is supplied to the electrodes to improve the quality of the diamond CVD onto the substrate. The gas mix is also important in achieving high quality diamond growth, references (4) & (5), this is achieved in combination with the Vacuum Pump [9] to evacuate the air and a Gas Board [6] that control a number of gases for input into the Vacuum Chamber [1] typically using Mass Flow Controllers, for diamond CVD these gases are typically Hydrogen, Methane and Oxygen in an approximate ratio of 97:2:1 at various set point pressures. Typical vacuum pressure for CVD diamond growth is between 100 to 200 Torr at plasma and electrode temperatures between 800 to 1000^{o}C at power levels between 3 to 5kW on this scale. In a conventional CVD the diamond is deposited directly onto the Anode [5] or Substrate which imposes certain conditions and preparation in terms of providing a diamond seed, references (4) & (5).

The radioisotope diamond infusion of this invention can be achieved by the introduction of Tritium, or alternative radioisotope as per claim 6, into the fabrication chamber with an electrically biased substrate plasma or microwave plasma or other heating mechanism, infusing the radioisotope directly into the diamond semiconductor to a typical depth of several microns in the making of a Diamond Beta Battery. All three methods can be integrated into the overall battery fabrication, the infusion mechanism differs slightly as does the granularity or scale, however the principle mechanism remains the same. With the ion infusion process, or ion implantation, the radioisotope needs to be ionised and a suitable electrical field provided across the diamond substrate, it is worth noting that plasma CVD systems do provide gas ionisation as part of the diamond growth process.

The amount of Tritium absorbed and held by the diamond is dependent on the semiconductor doping levels, the level of crystal defects and other material choices, and by example, on a P-type Schottky Diode in diamond a fivefold infusion above the doping level is feasible. The final beta-voltaic battery fabricated using these processes will have an intrinsic radioisotope integrated directly into the diamond crystal or device at the atomic level with all the efficiency benefits this brings to the product.

Care needs to be taken on radioisotope safety handling, the diamond acts as a getter for the radioisotope and the mass used in the fabrication needs to be matched to the device infusion to avoid excessive discharge and necessary capture of Tritium in the exhaust gases of the fabrication or vacuum chamber. A sealed diamond growth process, described in reference [2], and tandem Tritium infusion has important environmental benefits in the diamond beta-battery fabrication process, separate Tritium infusion and dedicated diamond growth facilities have many safety and certification advantages.

REFERENCES and REVIEW PAPERS

WO2018/206958 - RADIATION POWERED DEVICES COMPRISING DIAMOND MATERIAL AND ELECTRICAL POWER SOURCES FOR RADIATION POWERED DEVICES

WO2021044140A2 - CHEMICAL VAPOUR DEPOSITION PROCESS FOR PRODUCING DIAMOND

US 8,153,453 B2 - BETAVOLTAIC BATTERY WITH A SHALLOW JUNCTION AND A METHOD FOR MAKING SAME, M. Spencer and M. Chandrashekhar, Apr. 10, 2012.

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Spencer et al. 2019 - Spencer, M. G. and Alam T., 'High power direct energy conversion by nuclear batteries', Appl. Phys. Rev. 6, 031305 (2019); https://doi.org/10.1063/1.5123163, 13 September 2019.

The following paragraphs (paras) provide additional description of the processes described herein.

[1] The use of an infusion process utilising a plasma or other energy source to move or incorporate the radioisotope of Tritium (H_3) inside or become intrinsic to a diamond device in the making of a Diamond Beta Battery.

[2] As per para 1, using an alternative ion implantation infusion process for the radioisotope of Tritium (H_3) in the making of a Diamond Beta Battery.

[3] As per para 1, whereby the infusion is at the Chemical Vapour Deposition (CVD) diamond growth stage in the presence of the radioisotope of Tritium (H_3) as a fabrication process in the making of a Diamond Beta Battery.

[4] As per para 1, 2 and 3 to infuse a diamond structure, diamond material or diamond device with a beta radioisotope in the making of a Diamond Beta Battery.

[5] As per para 1, 2, 3 and 4 using an alternative to a vacuum system, some other enclosed vessel, at different operating pressures and temperatures.

[6] As per para 1, 2, 3, 4 and 5 using a different beta radioisotope in the making of a Diamond Beta Battery.

Claims:

1. A process for integrating tritium into diamond, the process comprising:

providing a diamond substrate; and

infusing or implanting tritium into the diamond substrate to provide diamond containing tritium, wherein tritium is substitutionally and/or interstitially integrated into the diamond substrate,

wherein infusing or implanting tritium into the diamond substrate comprises exposing the diamond substrate to tritium and an energy source.

2. The process of claim 1, wherein infusing or implanting tritium into the diamond substrate comprises exposing the diamond substrate to:

a tritium plasma;

elevated temperature and a tritium atmosphere; or

a tritium containing ion beam.

3. The process of claim 1, wherein infusing or implanting tritium into the diamond substrate comprises exposing the diamond substrate to:

a tritium plasma;

a tritium atmosphere and a temperature of at least about 800 K;or

a tritium ion beam having an energy of at least about 25 eV.

4. The process of claim 1, wherein infusing or implanting tritium into the diamond substrate comprises exposing the diamond substrate to:

a tritium plasma and a temperature of at least about 800 K;

a tritium atmosphere having a pressure of at least about 1 bar and a temperature of at least about 800 K; or

a tritium ion beam having an energy in the range of about 25 eV to about 5000 eV.

5. The process of any of claims 1-4, wherein infusing or implanting tritium into the diamond substrate comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber; and

exposing the diamond substrate to tritium and an energy source.

6. The process of any of claims 1-5, wherein infusing tritium into the diamond substrate comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber;

charging the pressurisable chamber with tritium to a pressure of at least about 1 bar; and

heating the pressurisable chamber to a temperature of at least about 800 K.

7. The process of any of claims 1-5, wherein infusing tritium into the diamond substrate comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber;

charging the pressurisable chamber with tritium; and

activating the tritiumto provide a tritium plasma.

8. The process of claim 7, wherein activating the tritium comprises electrically activating the tritium, optionally by applying an electrical current.

9. The process of any of claims 1-5, wherein implanting tritium into the diamond substrate comprises:

positioning the diamond substrate in a pressurisable chamber;

applying a vacuum to the pressurisable chamber; and

irradiating the diamond substrate with the tritium ion beam having an energy of at least about 25 eV, optionally at least about 250 eV.

10. The process of any of the preceding claims, wherein the diamond substrate comprises an exposed Schottky contact, optionally the Schottky contact being formed by a metal layer on a surface of the diamond of the diamond substrate.

11. The process of any of the preceding claims, wherein the diamond substrate comprises an Ohmic contact formed on a surface of the diamond of the diamond substrate, optionally the ohmic contact being formed by a metal layer on a surface of the diamond of the diamond substrate.

12. The process of any of the preceding claims comprising providing a layer of non-radioactive diamond on the diamond containing tritium.

13. The process of any of the preceding claims comprising encapsulating the diamond containing tritium with an insulating resin.

14. An electrical power source comprising a semiconductor, the semiconductor comprising diamond containing tritium obtainable or obtained by the process of any of claims 1 to 13, wherein the diamond containing tritium contains tritium substitutionally or interstitially integrated into diamond.

15. A beta-voltaic battery comprising a semiconductor disposed between a first electrode and a second electrode, the semiconductor comprising diamond containing tritium obtainable or obtained by the process of any of claims 1 to 13, wherein the diamond containing tritium contains tritium substitutionally or interstitially integrated into diamond.

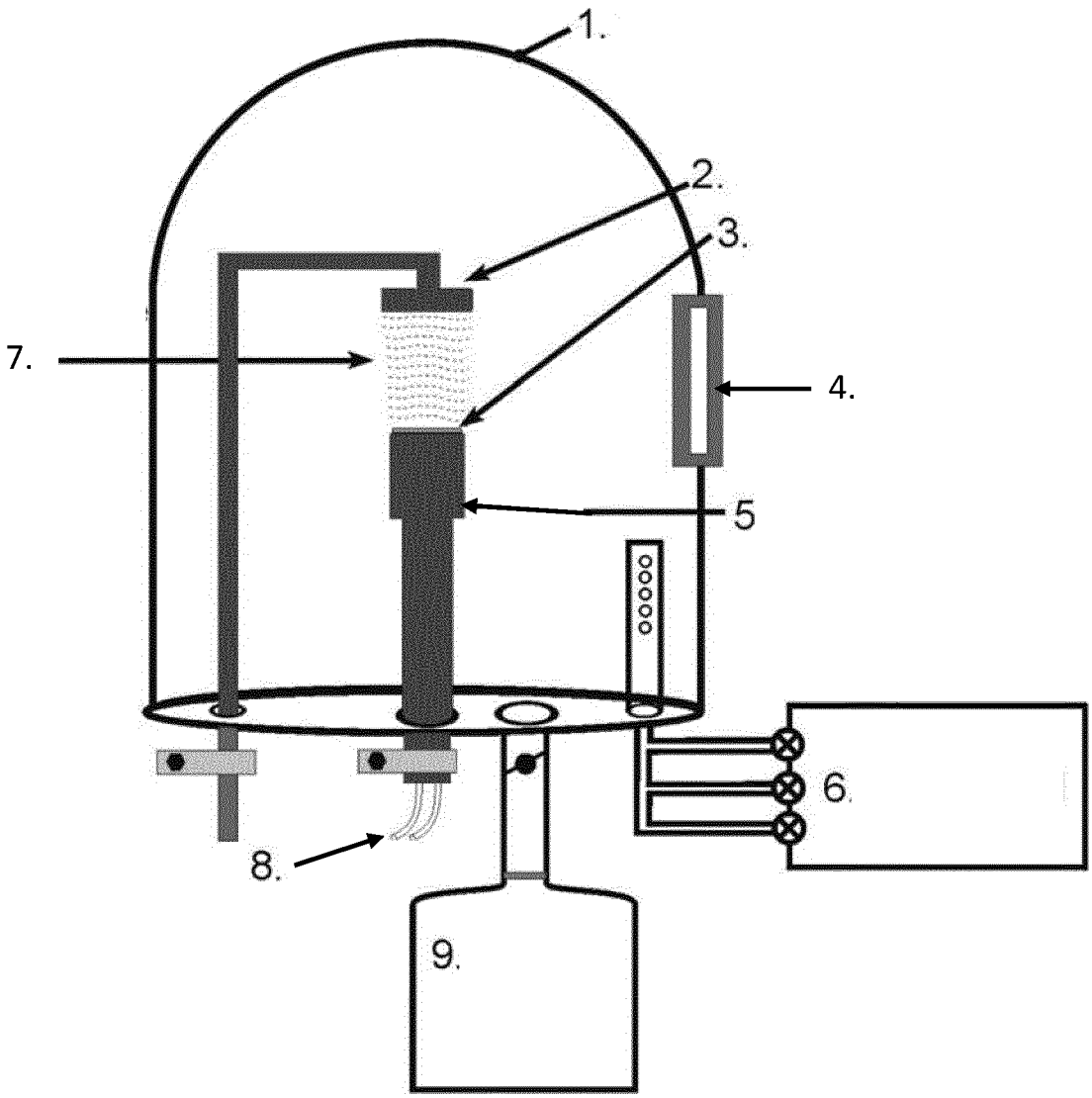

Fig. 1

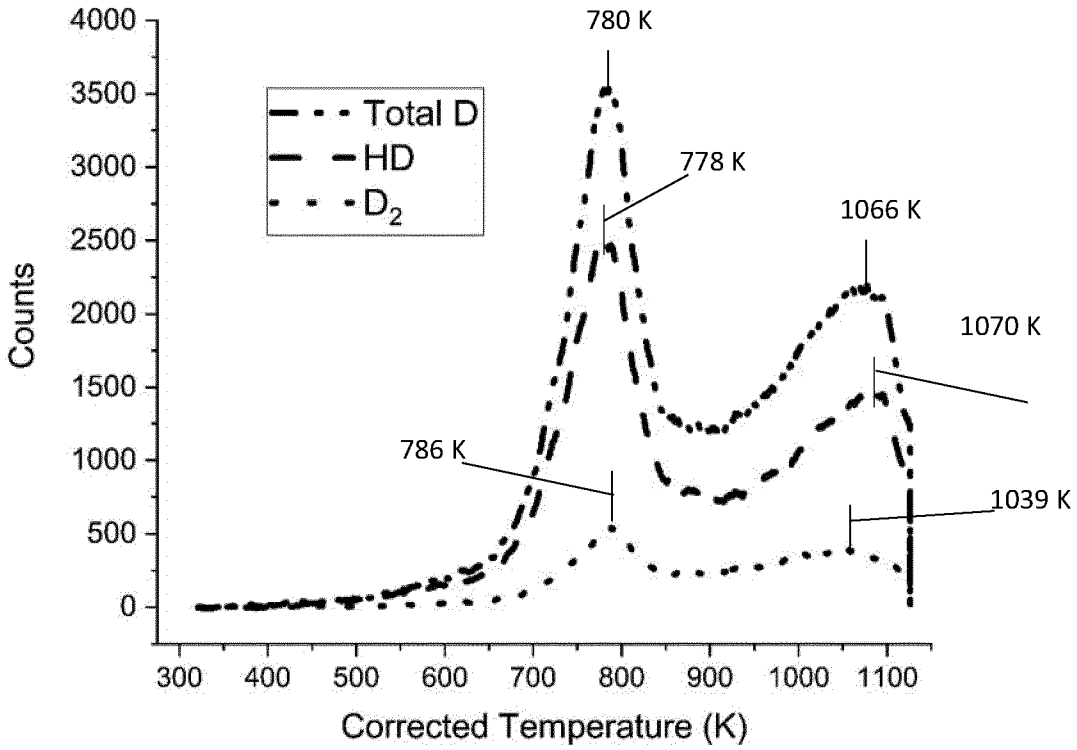
4000
3500
3000
2500
2000
1500
1000
500
0
Counts
300
400
500
600
700
800
900
1000
1100
Corrected Temperature (K)
Total D
HD
D2
780 K
778 K
1066 K
1070 K
786 K
1039 K

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/068196

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B32/26 G21H1/02 H01J37/32 H01J37/317 H01L21/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B G21H H01J H01L

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RU 2 668 229 C1 (FEDERALNOE GOSUDARSTVENNOE BYUDZHETNOE NAUCHNOE UCHREZHDENIE TEKH INST) 27 September 2018 (2018-09-27)	1-5,7-15
A	paragraphs [0038], [0042], [0043], [0022]; claims; figures	6
X	US 2020/203033 A1 (SCOTT THOMAS [GB] ET AL) 25 June 2020 (2020-06-25) paragraphs [0067] - [0069]; claims; figures	1
X	US 2017/287572 A1 (KLEY VICTOR B [US]) 5 October 2017 (2017-10-05) claims	1

☐ 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

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Date of the actual completion of the international search	Date of mailing of the international search report
17 October 2022	24/10/2022

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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