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(54) **SEMICONDUCTOR BETAVOLTAIC BATTERY WITH INTEGRATED BETA EMITTER**

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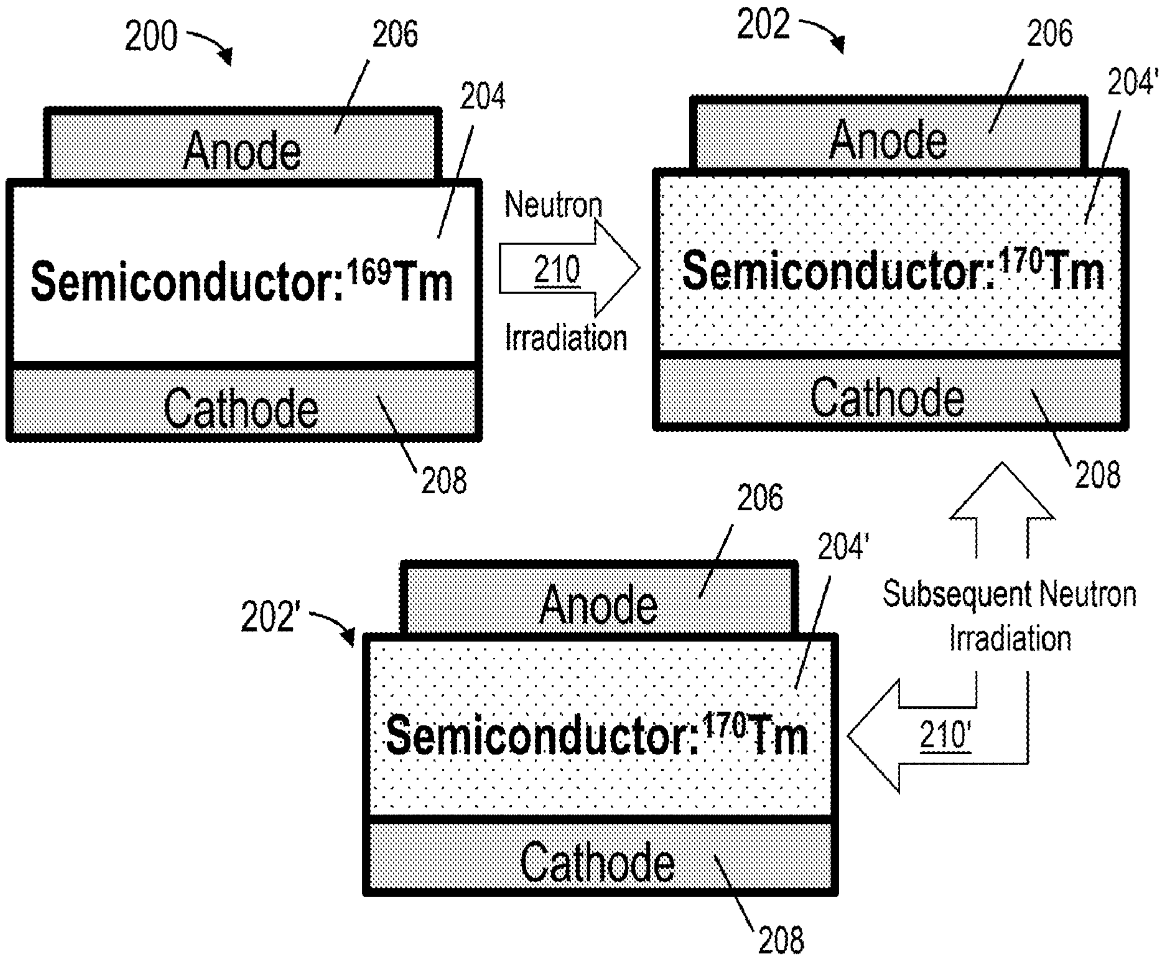
(57) **ABSTRACT**

An electrically inactive betavoltaic battery, an electrically active betavoltaic battery, and methods of making the same are provided. In implementations, a method of making an electrically active betavoltaic battery includes: providing an electrically inactive betavoltaic battery device having one or more diodes incorporating a semiconductor material layer having a stable non-radioactive isotope; and irradiating the electrically inactive betavoltaic battery device with thermal neutrons, thereby causing the conversion of at least a portion of the stable non-radioactive isotope to a radionuclide and creating the electrically active betavoltaic battery, wherein the semiconductor material layer acts as both an electron emitter and an electron absorber simultaneously.



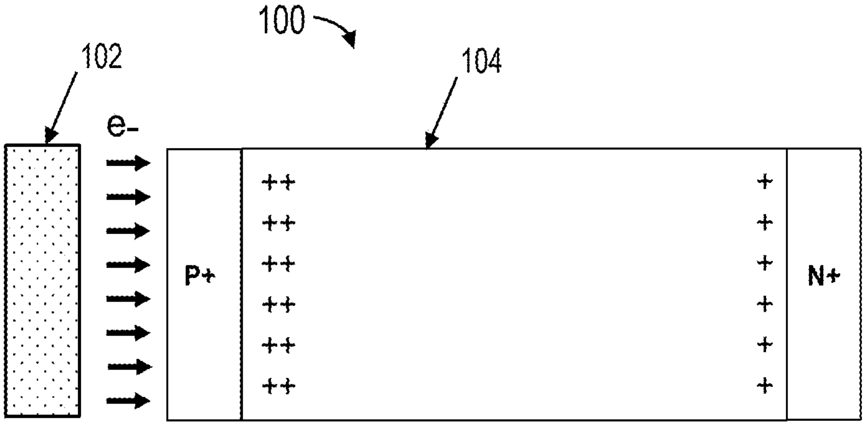


FIG. 1
(Prior Art)

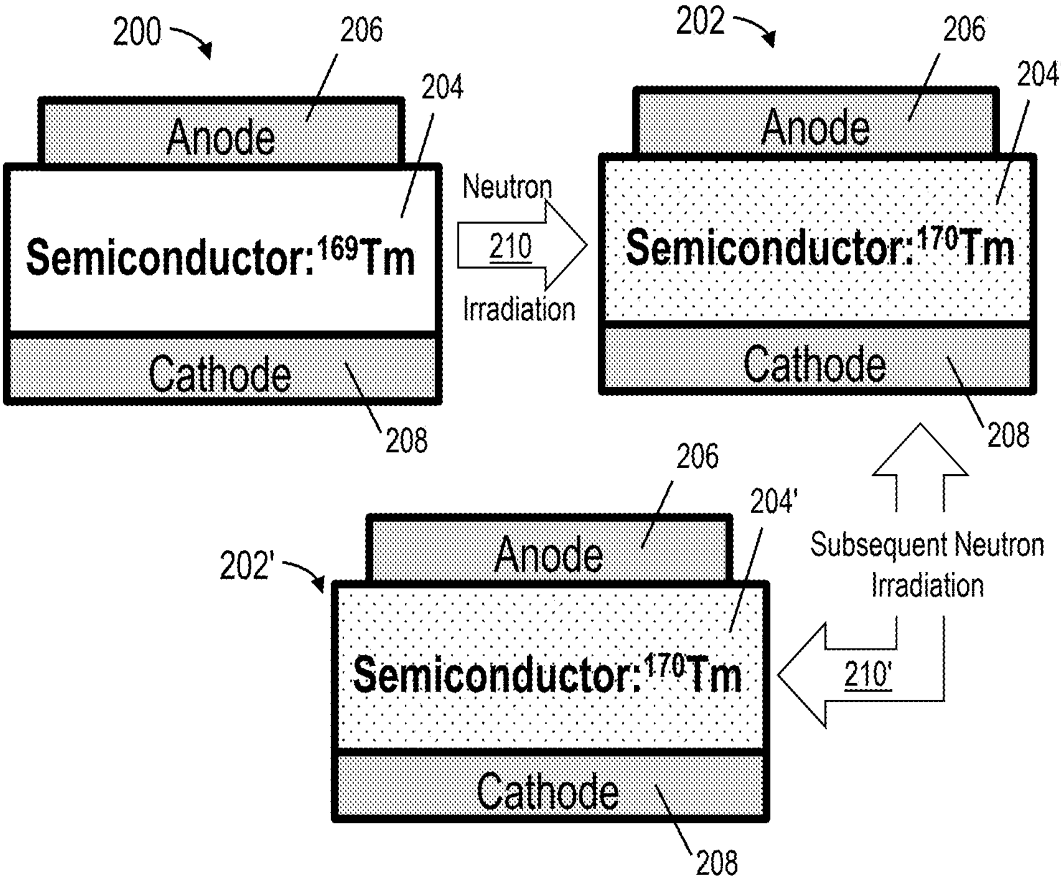


FIG. 2A

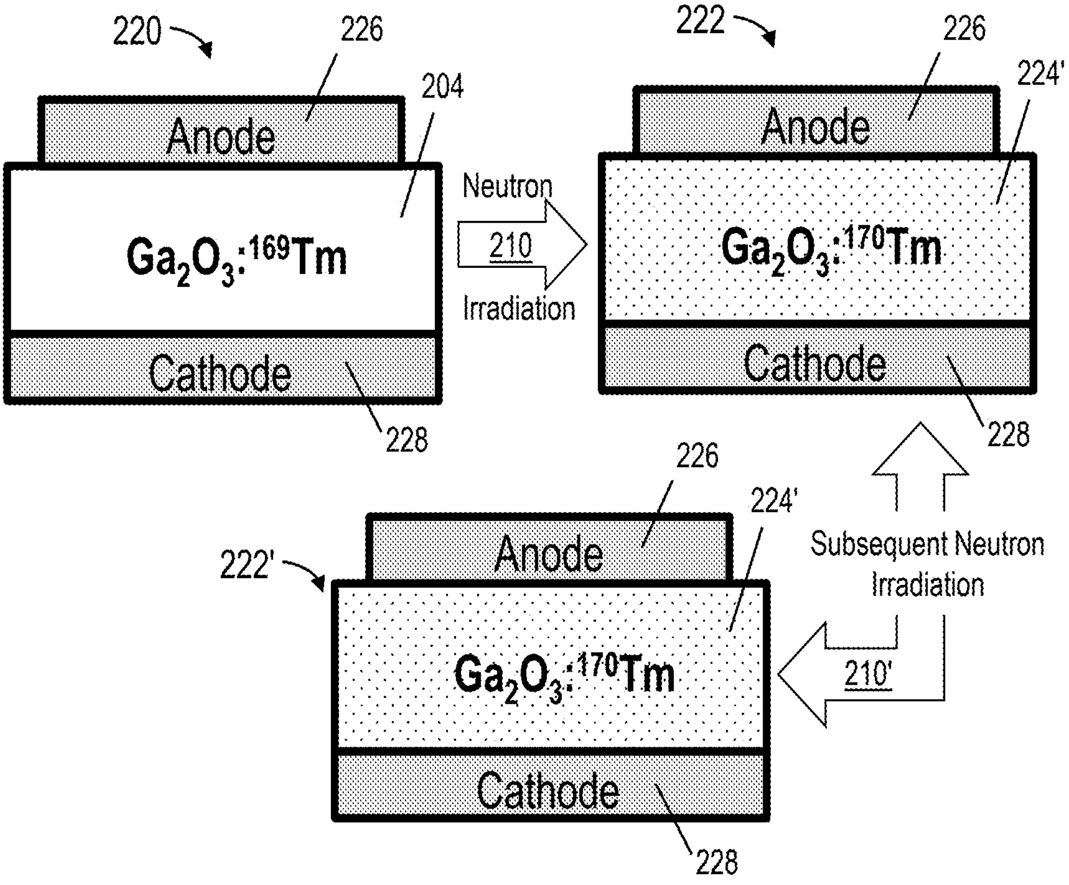

220
226
204
Anode
Ga$_2$O$_3$:^{169}Tm
Cathode
228
Neutron
210
Irradiation
222
226
224'
Anode
Ga$_2$O$_3$:^{170}Tm
Cathode
228
Subsequent Neutron
Irradiation
210'
222'
226
224'
Anode
Ga$_2$O$_3$:^{170}Tm
Cathode
228

FIG. 2B

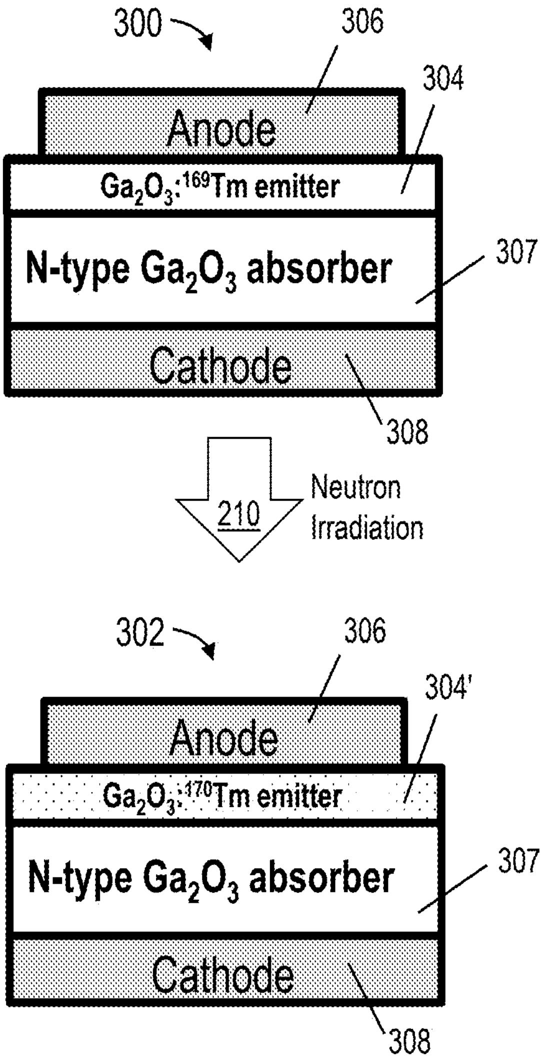

300
306
304
Anode
Ga_2O_3:^{169}Tm emitter
N-type Ga_2O_3 absorber
307
Cathode
308
210
Neutron Irradiation
302
306
304'
Anode
Ga_2O_3:^{170}Tm emitter
N-type Ga_2O_3 absorber
307
Cathode
308

FIG. 3A

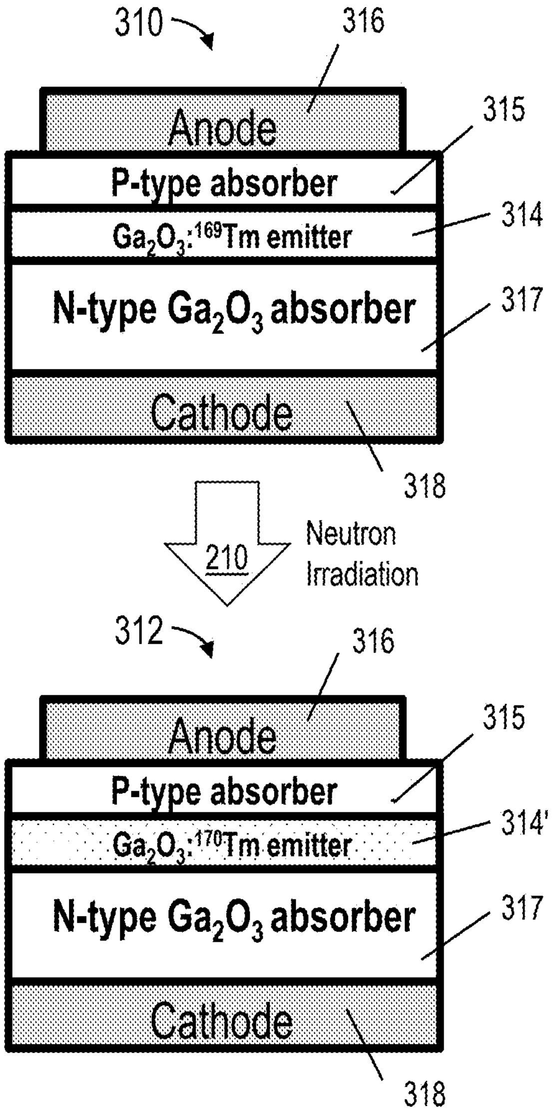

310
316
Anode
315
P-type absorber
Ga_2O_3:^{169}Tm emitter
314
N-type Ga_2O_3 absorber
317
Cathode
318
210
Neutron Irradiation
312
316
Anode
315
P-type absorber
Ga_2O_3:^{170}Tm emitter
314'
N-type Ga_2O_3 absorber
317
Cathode
318

FIG. 3B

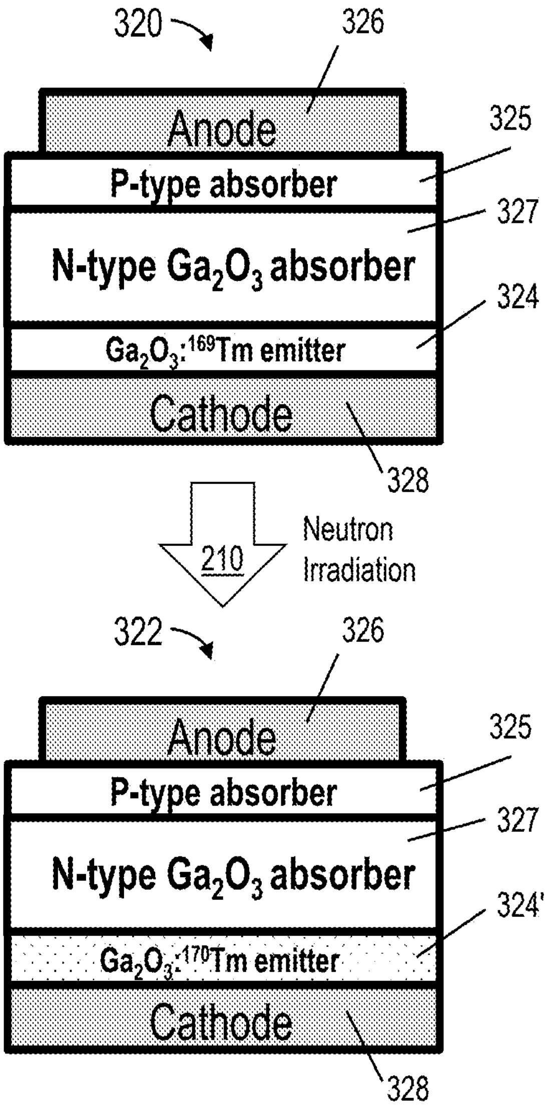

320
326
Anode
325
P-type absorber
327
N-type Ga_2O_3 absorber
324
Ga_2O_3:^{169}Tm emitter
Cathode
328
210
Neutron Irradiation
322
326
Anode
325
P-type absorber
327
N-type Ga_2O_3 absorber
324'
Ga_2O_3:^{170}Tm emitter
Cathode
328

FIG. 3C

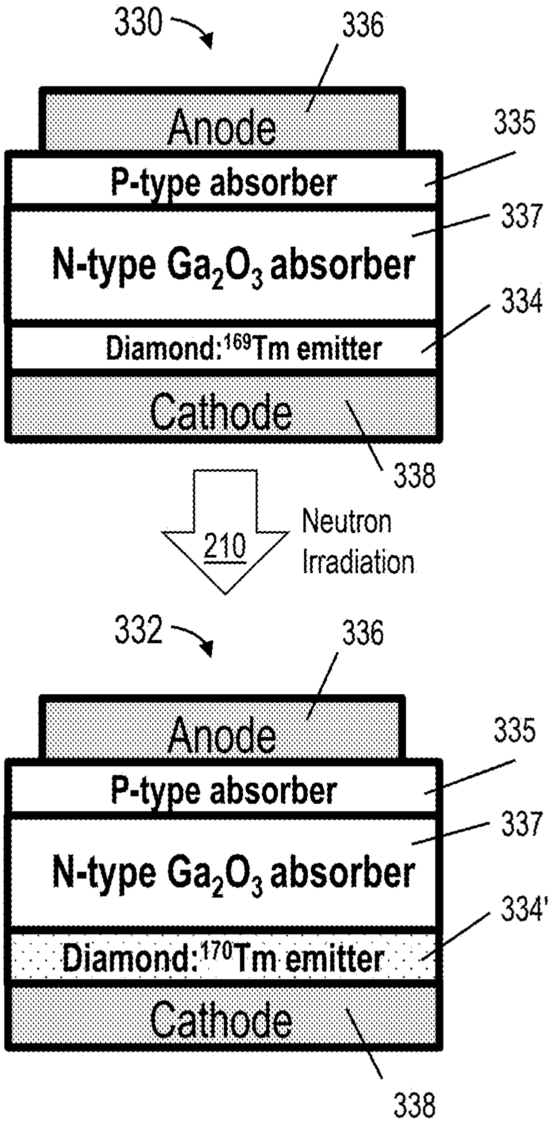

330
336
Anode
335
P-type absorber
337
N-type Ga_2O_3 absorber
334
Diamond:^{169}Tm emitter
Cathode
338
210
Neutron Irradiation
332
336
Anode
335
P-type absorber
337
N-type Ga_2O_3 absorber
334'
Diamond:^{170}Tm emitter
Cathode
338

FIG. 3D

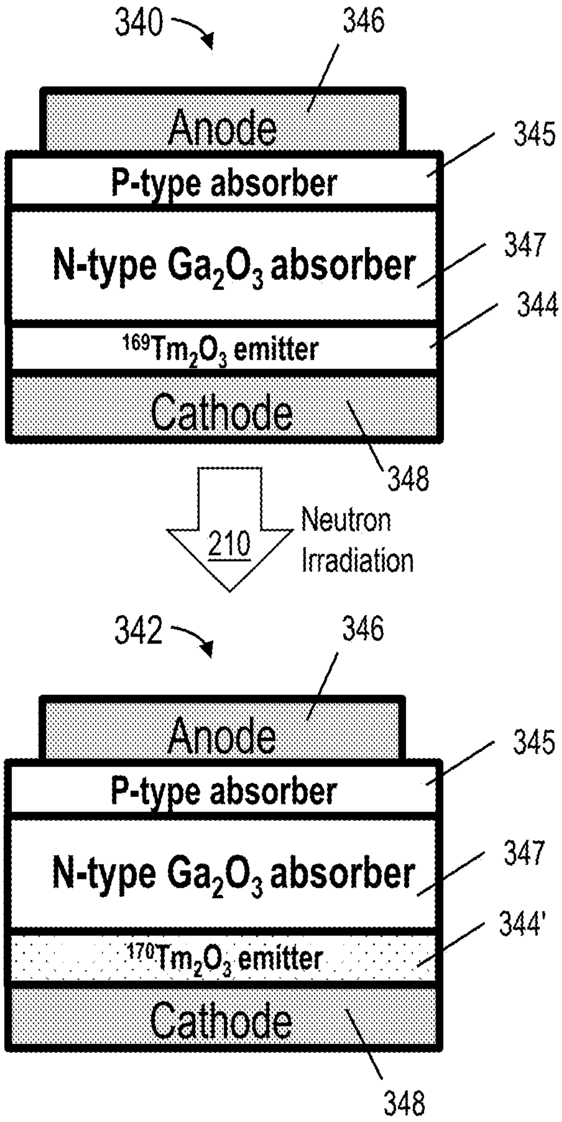

340
346
Anode
345
P-type absorber
347
N-type Ga_2O_3 absorber
344
$^{169}Tm_2O_3$ emitter
Cathode
348
210
Neutron Irradiation
342
346
Anode
345
P-type absorber
347
N-type Ga_2O_3 absorber
344'
$^{170}Tm_2O_3$ emitter
Cathode
348

FIG. 3E

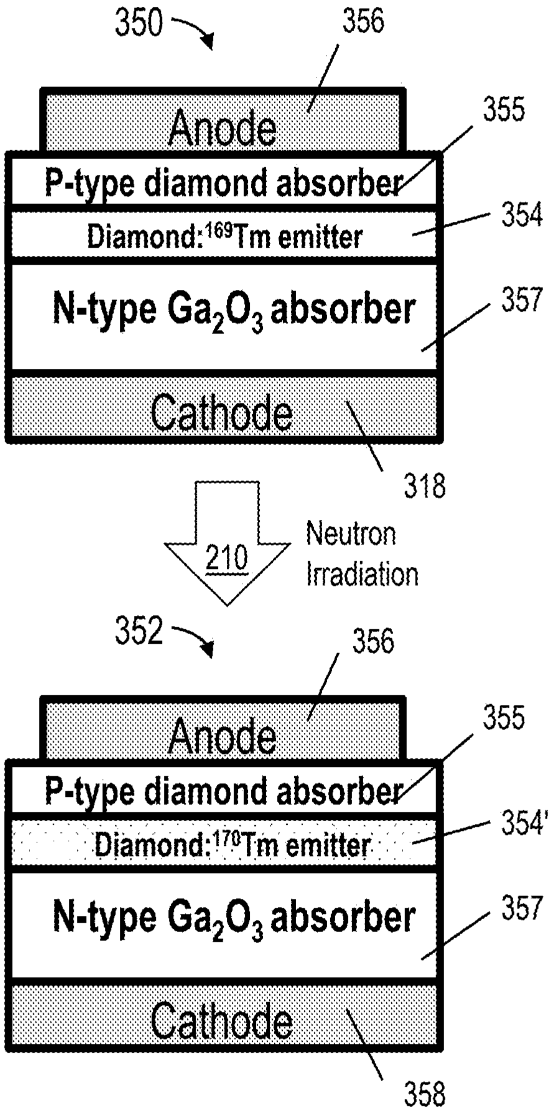

350
356
Anode
355
P-type diamond absorber
354
Diamond:^{169}Tm emitter
357
N-type Ga_2O_3 absorber
Cathode
318
210
Neutron Irradiation
352
356
Anode
355
P-type diamond absorber
354'
Diamond:^{170}Tm emitter
357
N-type Ga_2O_3 absorber
Cathode
358

FIG. 3F

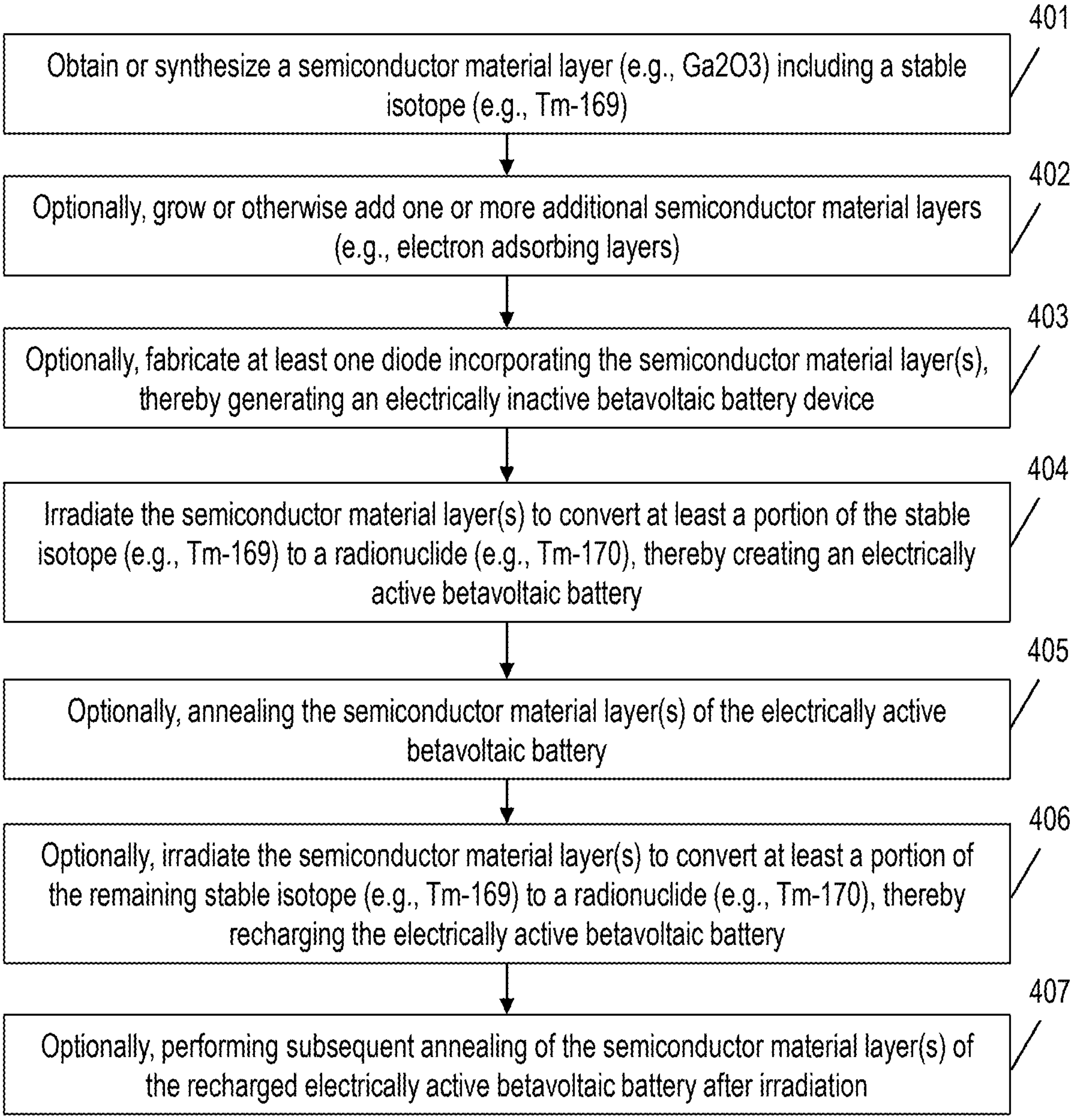

401
Obtain or synthesize a semiconductor material layer (e.g., Ga2O3) including a stable isotope (e.g., Tm-169)
402
Optionally, grow or otherwise add one or more additional semiconductor material layers (e.g., electron adsorbing layers)
403
Optionally, fabricate at least one diode incorporating the semiconductor material layer(s), thereby generating an electrically inactive betavoltaic battery device
404
Irradiate the semiconductor material layer(s) to convert at least a portion of the stable isotope (e.g., Tm-169) to a radionuclide (e.g., Tm-170), thereby creating an electrically active betavoltaic battery
405
Optionally, annealing the semiconductor material layer(s) of the electrically active betavoltaic battery
406
Optionally, irradiate the semiconductor material layer(s) to convert at least a portion of the remaining stable isotope (e.g., Tm-169) to a radionuclide (e.g., Tm-170), thereby recharging the electrically active betavoltaic battery
407
Optionally, performing subsequent annealing of the semiconductor material layer(s) of the recharged electrically active betavoltaic battery after irradiation

FIG. 4

SEMICONDUCTOR BETAVOLTAIC BATTERY WITH INTEGRATED BETA EMITTER

FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

[0001] The United States Government has ownership rights in this invention. Licensing inquiries may be directed to Office of Technology Transfer, US Naval Research Laboratory, Code 1004, Washington, D.C. 20375, USA; +1.202.767.7230; techtran@nrl.navy.mil, referencing Navy Case No. 211590-US1.

BACKGROUND OF THE INVENTION

[0002] Aspects of the present invention relate generally to betavoltaic power sources and, more particularly, to a semiconductor betavoltaic battery.

[0003] In general, a battery is a source of electric power derived from chemical energy. A betavoltaic device or betavoltaic battery is a type of nuclear battery which generates electric current from beta particles (electrons) emitted from a radioactive source (i.e., the emitter), using semiconductor junctions (i.e., the absorber). Betavoltaic semiconductor devices use a non-thermal conversion process, ionizing electron-hole pairs produced by beta particles traversing the semiconductor absorber.

[0004] Monoclinic beta (β) Ga_2O_3 technology has experienced rapid development in recent years. After initial growth demonstrations, melt grown 100 millimeter (mm) diameter substrates have been commercialized using techniques such as edge-defined film-fed (EFG) growth, Czochralski (CZ), float-zone (FZ), and vertical Bridgman (VB). Commercial epitaxial growth techniques have also resulted in 1-10 micron (μm) thick epitaxial layers of high quality, suitable for vertical diode demonstrations in the 5-8 kilovolt (kV) breakdown voltage range. Domestic production of semi-insulating (010) Ga_2O_3 substrates has been scaled up to 2 inches using Czochralski and EFG techniques, respectively. The ultra-wide bandgap of β-Ga_2O_3 (4.6-4.9 electron volts (eV)) results in a high critical field of 6-8 Megavolts per centimeter (MV/cm) and has also enabled lateral and vertical rectifier and transistor devices potentially suitable for radio frequency and high voltage power switching. In the frequency domain, Ga_2O_3 devices face performance challenges due to the low mobility and low thermal conductivity of Ga_2O_3. For high power electronics, the main challenge is the absence of p-type conductivity in Ga_2O_3 due to hole self-trapping originating from strong polaron effects[1].

SUMMARY OF THE INVENTION

[0005] In a first aspect of the invention, there is method of making an electrically active betavoltaic battery comprising: providing an electrically inactive betavoltaic battery device having one or more diodes incorporating a semiconductor material layer including a stable non-radioactive isotope; and irradiating the electrically inactive betavoltaic battery device with thermal neutrons, thereby causing the conversion of at least a portion of the stable non-radioactive isotope to a radionuclide and creating an electrically active betavoltaic battery, wherein the semiconductor material layer acts as both an electron emitter and an electron absorber simultaneously. In implementations, the semiconductor material is gallium oxide (Ga_2O_3). In embodiments, the stable non-radioactive isotope is thulium-169 (Tm-169) and the radionuclide is thulium-170 (Tm-170).

[0006] In another aspect of the invention, there is a method of making an electrically inactive betavoltaic battery device comprising: fabricating a semiconductor material layer containing a stable isotope9; and fabricating one or more diodes such that the one or more diodes incorporate the semiconductor material layer, thereby creating the electrically inactive betavoltaic battery device, wherein the electrically inactive betavoltaic battery device is configured to be transformed into an electrically active betavoltaic battery upon irradiation with thermal neutrons. In embodiments, the stable non-radioactive isotope is Tm-169 and the radionuclide is Tm-170.

[0007] In another aspect of the invention, there is an inactive betavoltaic battery device comprising: a semiconductor material layer including a stable isotope; and one or more diodes incorporating the semiconductor material layer, wherein the electrically inactive betavoltaic battery device is configured to be transformed into an electrically active betavoltaic battery upon irradiation with thermal neutrons. In embodiments, the stable non-radioactive isotope is Tm-169 and the radionuclide is Tm-170.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Aspects of the present invention are described in the detailed description which follows, in reference to the noted plurality of drawings by way of non-limiting examples of exemplary embodiments of the present invention.

[0009] FIG. **1** depicts a prior art betavoltaic semiconductor device according to an embodiment of the present invention.

[0010] FIG. **2**A shows an exemplary inactive betavoltaic battery device, an active betavoltaic battery, and a recharged betavoltaic battery in accordance with embodiments of the invention.

[0011] FIG. **2**B shows the device and batteries of FIG. **1** in accordance with embodiments of the invention, wherein the semiconductor is gallium (III) oxide.

[0012] FIGS. **3**A-**3**F show alternative embodiments of the inactive betavoltaic battery device and active betavoltaic battery of FIG. **2**A.

[0013] FIG. **4** shows a flowchart of an exemplary method in accordance with aspects of the present invention.

DETAILED DESCRIPTION

[0014] Aspects of the present invention relate generally to betavoltaic power sources and, more particularly, to a semiconductor betavoltaic battery. In implementations, a semiconductor material (e.g., gallium (III) oxide (Ga_2O_3)) is doped with an appropriate radioisotope which, once irradiated with thermal neutrons, becomes a beta source within the semiconductor material. Embodiments of the invention provide a betavoltaic battery using a radioisotope "host" crystal (semiconductor material) as both a beta particle emitter and an electron absorber simultaneously.

[0015] For years, betavoltaic sources have relied on silicon (Si) and more recently silicon carbide (SiC) coated with nickel-63 as the most accessible, reliable, and energetic beta source. Recent efforts in demonstrating Ga_2O_3 betavoltaic devices with separate embedding and emitting layers limit the beta source to the relatively low energy helium-3, carbon-14, and nickel-63, due to crystal lattice damage, limiting absorber efficiency at higher irradiation energies.

[0016] Ga_2O_3 bulk and epitaxial growth has the capability to incorporate a variety of impurities, both intentional and unintentional. When irradiated with thermal neutrons, appropriate impurities in Ga_2O_3 will transmute to radioactive nuclides with beta emission decay paths, effectively providing an in situ electron irradiation source embedded within the Ga_2O_3 crystal. One example of such an impurity is iridium (Ir), which is the scarcest metal in the Earth's crust but a common unintentional impurity in Ga_2O_3 crystals synthesized via the edge-defined film-fed growth (EFG) and Czochralski (CZ) techniques relying on the use of an Ir crucible. Upon neutron irradiation, the radioisotope Ir-192 will be produced via neutron capture. With a half-life of 73 days for the gamma rays resulting, Ir-192 is a strong gamma emitter and is thus undesirable from an electronic device safety perspective. From a betavoltaic perspective, however, Ga_2O_3 is attractive because of its relatively good tolerance to gamma irradiation and potentially good tolerance to beta irradiation at 1.5 Megaelectron volt (MeV) and 2.5 MeV energies[2, 3].

[0017] FIG. **1** depicts a prior art multi-layer betavoltaic semiconductor device **100**. As illustrated in FIG. **1**, device **100** relies on beta particle (electron) emission from an emitter layer **102** deposited on a semiconductor absorber device **104**, typically a p-n junction. This limits the generation current to the vicinity of the metallurgical junction. Unlike such devices, implementations of the invention utilize a semiconductor device as both a beta particle emitter and an electron absorber. More specifically, embodiments of the invention utilize beta emissions from dopants distributed within a semiconductor crystal, which increase the emission volume and the overall power produced by a betavoltaic battery of the present invention as compared to previous multi-layer betavoltaic semiconductor devices.

[0018] FIG. **2**A shows an exemplary electrically inactive betavoltaic battery device **200**, an electrically active betavoltaic battery **202** and a recharged electrically active betavoltaic battery **202'** in accordance with embodiments of the invention. The exemplary electrically inactive betavoltaic battery device **200** of FIG. **1** includes at least one semiconductor material **204** doped with the only stable (observationally stable) isotope of thulium (Tm), Tm-169, and at least one diode comprising at least one anode **206**, and at least one cathode **208**. In implementations, the electrically inactive betavoltaic battery device **200** is exposed to thermal neutron irradiation at **210**, which converts at least a portion of the Tm-169 in the semiconductor material **204** to the radioisotope Tm-170, resulting in the electrically active betavoltaic battery **202** including an emissive semiconductor substrate **204'**. In implementations, the semiconductor **204** comprises Ga_2O_3. See, for example, FIG. **2**B.

[0019] FIG. **2**B shows an exemplary electrically inactive betavoltaic battery device **220**, an electrically active betavoltaic battery **222** and a recharged electrically active betavoltaic battery **222'** in accordance with embodiments of the invention. The exemplary electrically inactive betavoltaic battery device **220** of FIG. **2**B includes at least one semiconductor material **224** comprising Ga_2O_3 doped with the only stable (observationally stable) isotope of thulium (Tm), Tm-169, and at least one diode comprising at least one anode **226**, and at least one cathode **228**. In implementations, the electrically inactive betavoltaic battery device **220** is exposed to thermal neutron irradiation at **210**, which converts at least a portion of the Tm-169 in the semiconductor material **224** to the radioisotope Tm-170, resulting in the electrically active betavoltaic battery **222** including an emissive Ga_2O_3 substrate **224'**. Electron-hole pair generation originates from in situ beta particle emission within the semiconductor Ga_2O_3 crystal, which acts both as an electron emitter and an absorber simultaneously. Rather than an ex situ deposited beta irradiation coating over the semiconductor absorber layer, embodiments of the invention leverage intentional dopants and/or unintentional impurities within a large-volume bulk Ga_2O_3 crystal.

[0020] Advantageously, implementations of the invention enable production of a stable electrically inactive betavoltaic battery device (e.g., **200**, **220**) in a conventional cleanroom without any special measures necessary to accommodate electronic device fabrication using radioactive semiconductor materials. The electrically inactive betavoltaic battery device (e.g., **200**, **220**) may then be transported to another location for irradiation to transform at least some of a stable isotope to a radionuclide, resulting in the electrically active betavoltaic battery (e.g., **202**, **222**).

[0021] The term radionuclide refers to a nuclide that has excess nuclear energy, making it unstable. This excess energy may be: emitted from the nucleus as gamma radiation; transferred to one of its electrons to release the energy as a conversion electron; or used to create and emit a new particle from the nucleus. In implementations, second and subsequent irradiation **210'** of the electrically active betavoltaic battery (e.g., **202**, **222**) may be implemented to generate the recharged electrically active betavoltaic battery (e.g., **202'**, **222'**) via the same mechanism, as will be discussed in more detail below. Although the exemplary electrically inactive betavoltaic battery device **220** utilizes Ga_2O_3 as a host crystal for the stable isotope, it should be understood that embodiments of the invention may utilize different semiconductor materials or host crystals and/or stable isotopes, and the invention is not intended to be limited to the examples described herein.

[0022] FIGS. **3**A-**3**F show alternative embodiments of the electrically inactive betavoltaic battery device and electrically active betavoltaic battery of FIG. **2**A. More specifically, FIG. **3**A depicts an electrically inactive betavoltaic battery device **300** in accordance with embodiments of the invention, including: a first semiconductor layer **304** comprising Ga_2O_3 doped with Tm-169, at least one diode comprising at least one anode **306** and at least one cathode **308**, and a second semiconductor layer **307** comprising N-type Ga_2O_3 (an electron absorbing layer, a.k.a., absorber). In implementations, the electrically inactive betavoltaic battery device **300** is exposed to thermal neutron irradiation **210**, which converts at least a portion of the Tm-169 in the first semiconductor layer **304** to the radioisotope Tm-170, resulting in an electrically active betavoltaic battery **302** including an electron (beta particle) emissive first semiconductor layer **304'** (an electron emitting and absorbing layer) adjacent an electron absorbing semiconductor layer **307**.

[0023] FIG. **3**B depicts an electrically inactive betavoltaic battery device **310** in accordance with embodiments of the invention, including: a first semiconductor layer **314** comprising Ga_2O_3 doped with Tm-169, at least one diode comprising at least one anode **316** and at least one cathode **318**, a second semiconductor layer **317** comprising N-type Ga_2O_3 (a first electron absorbing layer), and a third semiconductor layer **315** comprising a P-type semiconductor material (a second electron absorbing layer). In implementations, the electrically inactive betavoltaic battery device **310** is exposed to thermal neutron irradiation **210**, which converts at least a portion of the Tm-169 in the first semiconductor layer **314** to the radioisotope Tm-170, resulting in an electrically active betavoltaic battery **312** including an electron (beta particle) emissive first semiconductor layer **314'** (an electron emitting and absorbing layer) between the first and second electron absorbing layers **315** and **317**.

[0024] FIG. **3**C depicts an electrically inactive betavoltaic battery device **320** in accordance with embodiments of the invention, including: a first semiconductor layer **324** comprising Ga_2O_3 doped with Tm-169, at least one diode comprising at least one anode **326** and at least one cathode **328**, a second semiconductor layer **325** comprising a P-type semiconductor material (a first electron absorbing layer), and a second semiconductor layer **327** comprising N-type Ga_2O_3 (a second electron absorbing layer). In the example shown, the first semiconductor layer **324** is positioned below the first and second electron absorbing layers (layers **325** and **327**). In implementations, the electrically inactive betavoltaic battery device **320** is exposed to thermal neutron irradiation **210**, which converts at least a portion of the Tm-169 in the first semiconductor layer **324** to the radioisotope Tm-170, resulting in an electrically active betavoltaic battery **322** including an electron (beta particle) emissive first semiconductor layer **324'** (an electron emitting and absorbing layer).

[0025] FIG. **3**D depicts an electrically inactive betavoltaic battery device **330** in accordance with embodiments of the invention, including: a first semiconductor layer **334** comprising diamond doped with Tm-169, at least one diode comprising at least one anode **336** and at least one cathode **338**, a second semiconductor layer **335** comprising a P-type semiconductor material (a first electron absorbing layer), and a third semiconductor layer **337** comprising N-type Ga_2O_3 (a second electron absorbing layer). In the example shown, the first semiconductor layer **334** is positioned below the first and second electron absorbing layers (layers **335** and **337**). In implementations, the electrically inactive betavoltaic battery device **330** is exposed to thermal neutron irradiation **210**, which converts at least a portion of the Tm-169 in the first semiconductor layer **334** to the radioisotope Tm-170, resulting in an electrically active betavoltaic battery **332** including an electron (beta particle) emissive first semiconductor layer **334'** (a beta particle emitting and absorbing layer).

[0026] FIG. **3**E depicts an electrically inactive betavoltaic battery device **340** in accordance with embodiments of the invention, including: a first semiconductor layer **344** comprising thulium oxide (Tm_2O_3) including Tm-169, at least one diode comprising at least one anode **346** and at least one cathode **348**, a second semiconductor layer **345** comprising a P-type semiconductor material (a first electron absorbing layer) a third semiconductor layer **347** comprising N-type Ga_2O_3 (a second electron absorbing layer). In the example shown, the first semiconductor layer **344** is positioned below the first and second electron absorbing layers (layers **345** and **347**). In implementations, the electrically inactive betavoltaic battery device **340** is exposed to thermal neutron irradiation **210**, which converts at least a portion of the Tm-169 in the first semiconductor layer **344** to the radioisotope Tm-170, resulting in an electrically active betavoltaic battery **342** including an electron (beta particle) emissive first semiconductor layer **344'** (an electron emitting and absorbing layer).

[0027] FIG. **3**F depicts an electrically inactive betavoltaic battery device **350** in accordance with embodiments of the invention, including: a first semiconductor layer **354** comprising diamond including Tm-169, at least one diode comprising at least one anode **356** and at least one cathode **358**, a second semiconductor layer **355** comprising a P-type diamond material (a first electron absorbing layer) a third semiconductor layer **357** comprising N-type Ga_2O_3 (a second electron absorbing layer). In the example shown, the first semiconductor layer **354** is positioned between the first and second electron absorbing layers (layers **355** and **357**). In implementations, the electrically inactive betavoltaic battery device **350** is exposed to thermal neutron irradiation **210**, which converts at least a portion of the Tm-169 in the first semiconductor layer **354** to the radioisotope Tm-170, resulting in an electrically active betavoltaic battery **352** including an electron (beta particle) emissive first semiconductor layer **354'** (an electron emitting and absorbing layer).

[0028] FIG. **4** illustrates method steps in accordance with embodiments of the invention. The method of FIG. **4** references the electrically inactive betavoltaic battery device **200**, the electrically active betavoltaic battery **202**, and the recharged betavoltaic battery **202'** of FIG. **2**A, but is not intended to be limited to the devices of FIG. **2**A.

[0029] At step **401**, a manufacturer obtains or synthesizes a semiconductor material layer (e.g., **204** of FIG. **2**A) in the form of a substrate or an epitaxial layer either extrinsically doped with or naturally containing a stable isotope. In implementations, the stable isotope is Tm-169. In embodiments, the semiconductor material layer is selected from Ga_2O_3, diamond, Tm_2O_3, gallium nitride (GaN), SiC, aluminum nitride (AlN), Si, or other semiconductors appropriate for the stable isotope utilized. For example, those skilled in the art will recognize that it is not possible to dope some semiconductors with Tm-169, and some semiconductors would not be able to tolerate (would be excessively damaged by) beta irradiation arising from Tm-170.

[0030] In implementations, step **401** comprises growing Ga_2O_3 crystals utilizing existing techniques. In embodiments, beta (β) Ga_2O_3 is grown from a melt source using iridium (Ir) crucibles by the EFG method or the Cz method. However, Ir-192 is a known source of undesirable gamma-ray emission. Accordingly, in other embodiments of the invention, Ir-free Ga_2O_3 is grown via the float-zone (zone melting) method or vertical Bridgman method, another crucible-free or non-Ir crucible method, or another EFG or CZ technique where Ir incorporation in the Ga_2O_3 crystal is suppressed.

[0031] In implementations, the stable isotopes are introduced into the at least one host semiconductor material layer (e.g., **204**) with precise quantity via doping near carrier generation sites where the beta electrons are actually needed, eliminating the need for coating the device with a beta irradiation source and improving the conversion efficiency of the resulting electrically active betavoltaic battery device (e.g., **202**) by suppressing self-absorption effects.

[0032] Thermal neutron reactions by the stable isotopes of nitrogen-14, nickel-62, krypton-84, strontium-88, cadmium-112, iridium-191, and potentially other stable isotopes, can produce radionuclides such as carbon-14, nickel-63, krypton-85, strontium-90, cadmium-113 and iridium-192, respectively. Both carbon-14 and nickel-63 are known pure beta emitters with reasonably low energy. Krypton-85 and strontium-90 are also beta emitters but are commonly dismissed for betavoltaics as being too energetic for use with common semiconductors (e.g., Si and SiC). Cadmium-113 and iridium-192 have high energy beta decay but are also gamma emitters, to which Ga_2O_3 may exhibit reasonable tolerance, especially in the case of cadmium-113 whose gamma decay is only due to an isomeric transition. To date, no known technology exists that can harness the potentially ~10× higher beta decay energy of cadmium-113 (E_{avg}=185.4 keV) and strontium-90/yttrium-90 (E_{avg}=195.8 keV), compared to commonly used beta sources of hydrogen-3 (E_{avg}=5.7 keV), carbon-14 (E_{avg}=49.5 keV) and nickel-63 (E_{avg}=17.4 keV).

[0033] At the 185.4 and 195.8 keV beta decay energies of cadmium-113 and strontium-90/yttrium-90, respectively, Ga_2O_3 should be tolerant to electron irradiation. Electron irradiation at 1.5-2 MeV energy levels have been shown via electron paramagnetic resonance techniques to induce Ga vacancy related defects and result in degradation in Schottky barrier diode performance (on-resistance, on/off ratio, etc.). However, a betavoltaic cell operates in reverse bias mode and thus any Ga vacancy and related point defects generated by the radionuclide decay paths will cause degradation to the absorption efficiency of the betavoltaic cell if it captures generated electrons at a significantly higher rate than the electron-hole pair generation rate.

[0034] With respect to betavoltaic cells, the main disadvantage of the aforementioned isotopes is their natural occurrence in multiple stable isotopes. This would require doping of the host semiconductor material layer with isotopically pure elements, which is extremely expensive. From this standpoint, it is desirable to utilize an element which occurs naturally in only one stable isotope and can undergo a single-neutron capture reaction to produce a radionuclide without fissuring in the process (eliminating beryllium from consideration), which then decays only through beta particles directly into a stable isotope. One element that comes close to this specification is thulium (Tm). The only stable isotope of Tm, Tm-169, forms Tm-170 upon single neutron capture, which has a 99.86% probability of decaying to stable ytterbium-170 (Yb-170) via pure beta (β^-) emission with a reasonably long half-life of 128.6 days. The remaining 0.14% emission decays to stable erbium-170 via electron recapture consisting of 0.11% ground state decay and 0.03% photon emission to the first excited state. Therefore, for every 10000 decays worth of energy there will be three (3) photons emitted with 78 keV of energy. Tm also exhibits a large neutron capture cross section. Furthermore, any double neutron capture resulting in Tm-171 also decays via beta emission (1.92 year half-life) to stable Yb-171. This makes Tm an excellent candidate for betavoltaic applications if only neutron capture reactions are considered.

[0035] Accordingly, in implementations, a host semiconductor material layer (e.g., Ga_2O_3) is doped with or naturally contains the stable isotope Tm-169. In general, isotopically-pure elements are very expensive. Advantageously, Tm has a single stable isotope (Tm-169), and does not require costly isotope enrichment; provides a large neutron capture cross section (100 barns); and becomes a pure beta emitter, Tm-170 (max beta energy 968 KeV), upon single neutron capture. Specifically, Tm-170 is a 99.97% beta-emitter decaying to stable ytterbium-170 (Yb-170) and erbium (Er), with no further decay, and requires little gamma shielding (0.03% gamma rays). In implementations, Tm_2O_3 is used as a source of Tm for doping of the host semiconductor material layer (e.g., Ga_2O_3) or as the host semiconductor material layer. Tm_2O_3 is a low-cost oxide powder available commercially with four nines (4N) purity and can be alloyed into a host crystal of a semiconductor material layer (e.g., **204**) during melt growth.

[0036] Certain advantages may be obtained when Ga_2O_3 is utilized as the host semiconductor material layer. The strong polaron effects in Ga_2O_3 leading to the self-trapping of holes means that any generated holes will be trapped almost immediately, resulting in excess electron concentration available for transport upon the application of an electric field. Additionally, the ability to generate relatively large diameter Ga_2O_3 wafers and thick epitaxial layers of Ga_2O_3 offer significant technological advantages in that Ga_2O_3 can be utilized to create a relatively large collection area for a battery, as compared to a battery made from another crystalline material. Accordingly, embodiments of the invention utilize Ga_2O_3 as a host semiconductor material layer.

[0037] In implementations, the Tm metal organic chemical vapor deposition (MOCVD) precursor thulium (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) is utilized to grow Ir-free Ga_2O_3 via the float-zone method. Various doping methods may be used in accordance with embodiments of the invention. In one implementation, a Ga_2O_3 layer is doped with Tm-169 deposited via an epitaxial growth doping method, such as metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), halide vapor phase deposition (HVPE), pulsed laser deposition (PLD), etc. In embodiments, an annealing step is performed after doping of the Ga_2O_3 semiconductor material layer, particularly for the purpose of lattice damage recovery if ion implantation of Tm-169 is used. Various annealing methods may be utilized in accordance with embodiments of the invention.

[0038] With continued reference to FIG. **4**, optionally at step **402**, a manufacturer grows or otherwise adds one or more additional semiconductor material layers (e.g., electron absorbing layers of either p-type or n-type conductivity) to the host semiconductor material layer including the stable isotope of step **401**. See, for example, the semiconductor layers **315** and **317** of FIG. **3**B.

[0039] At step **403**, a manufacturer fabricates at least one diode (e.g., comprising an anode **206** and a cathode **208**) incorporating the semiconductor material layer(s) (e.g., **204** of FIG. **2**A). Various methods may be utilized to fabricate the at least one diode, and the present invention is not intended to be limited to a particular method of diode fabrication. Alternatively, the user may obtain a pre-fabricated semiconductor device at step **401** having at least one diode incorporating the semiconductor material layer(s). In implementations an anode (e.g., **206**) and cathode (e.g., **208**) are fabricated on opposing surfaces of the host semiconductor material layer (e.g., **204** of FIG. **2**A) doped with a stable isotope (e.g., Tm-169). The diode may comprise a Ga_2O_3 substrate, a Ga_2O_3 epitaxial layer, another semiconductor substrate or epitaxial layer, or a junction of a heteroepitaxial semiconductor layer on a dissimilar semiconductor substrate, for example.

[0040] At step **404**, a manufacturer irradiates the semiconductor material layer(s) (e.g., **204** of FIG. **2**A) of the electrically inactive betavoltaic battery device (e.g., **200**) to convert at least a portion of the stable isotope (e.g., Tm-169) therein to a radionuclide (e.g., Tm-170), thereby creating an electrically active betavoltaic battery (e.g., **202**). In implementations, step **404** (thermal neutron irradiation) is performed at a nuclear reactor physically or geographically remote from the semiconductor fabrication location of steps **401-403**, thereby enabling special safety precautions to be taken only at the irradiation stage, without the need for special safety precautions at the manufacturing stages (steps **401-403**).

[0041] In implementations, the initial doping agent is Tm-169, resulting in minimal gamma-ray emissions from a Tm-170 electron capture process in the electrically active betavoltaic battery (e.g., **202**), where the minimal gamma-ray emission can be shielded in a relatively straightforward and safe manner by the semiconductor diode package. Simulations indicate about 100-200 microns (μm) of beta electron penetration in Ga_2O_3 from Tm-170 decay. Advantageously, implementations of the invention require minimal thermal neutron irradiation in the range of minutes or a few hours rather than days (as compared to betavoltaic battery devices utilizing other radionuclides), due to the large neutron capture cross section of Tm-170. In general, Ga_2O_3 devices have shown high on-state current density and low reverse bias current, making Ga_2O_3 devices appropriate semiconductor absorbers for beta-emitter dopants in the drift region. Moreover, Ga_2O_3 is tolerant to beta irradiation, and the high energy of beta electrons from Tm-170 is not expected to result in significant Ga_2O_3 crystal damage over the life of active Ga_2O_3 betavoltaic batteries in accordance with embodiments of the invention.

[0042] Optionally, at step **405**, annealing of the semiconductor material layer(s) (e.g., **204**) of the active betavoltaic battery (e.g., **202**) is performed. In implementations, the annealing step repairs damage to the crystals (e.g., Ga_2O_3) in the semiconductor material layer(s) that occurs during the irradiation step **404**. Various annealing processes may be utilized, and the invention is not intended to be limited to a particular type of annealing method.

[0043] Optionally, at step **406**, a manufacturer performs a second or subsequent irradiation of the semiconductor material layer(s) (e.g., **204**) of the electrically active betavoltaic battery (e.g., **202**) to convert at least a portion of the remaining stable isotope (e.g., Tm-169) into a radionuclide (e.g., Tm-170), resulting in a recharged active betavoltaic battery (e.g., **202'** of FIG. **2**A). In embodiments utilizing Tm-169, after a period of time, a significant portion of the Tm-170 in the active betavoltaic battery (e.g., **202**) will have degraded to ytterbium-170 (Yb-170) and erbium (Er) (i.e., the active betavoltaic battery will be in a degraded state), slowing energy production of the battery. By converting any remaining stable isotope (Tm-169) in the active betavoltaic battery to a radionuclide (Tm-170) via irradiation, the active betavoltaic battery will be recharged and will generate more energy than in the degraded state. In implementations, the second or subsequent irradiation of a semiconductor material layer (e.g., **204** of FIG. **2**A) originally doped with Tm-169 will result in conversation of at least some of the remaining stable isotope Tm-169 to Tm-170, and will convert at least a portion of any remaining Tm-170 to Tm-171 (having a half-life of 1.92 years), resulting in a recharged electrically active betavoltaic battery **202**. At the end of battery life, implementations of the invention originally doped with Tm-169 will result in class A waste, which is the least radioactive level of any nuclear waste.

[0044] Optionally, at step **407**, subsequent annealing of the semiconductor material layer(s) (e.g., **204**) of the recharged electrically active betavoltaic battery (e.g., **202**) is performed. In implementations, the annealing step repairs damage to the crystals in the semiconductor material layer(s) (e.g., Ga_2O_3) that occurs during the second or subsequent irradiation steps. Various annealing processes may be utilized, and the invention is not intended to be limited to a particular type of annealing method.

[0045] In use, an electrically active betavoltaic battery of the present invention (e.g., **202'** of FIG. **2**A) produces electron hole pairs from energetic beta particles emitted from one or more radionuclides (e.g., Tm-170, Tm-171) within the host semiconductor material layer (e.g., **204'**) positioned between an anode (e.g., **206**) and a cathode (e.g., **208**). The electron hole pairs are mobile under the effect of an electric field existing between the anode and cathode, thereby generating electrical energy.

[0046] The descriptions of the various embodiments of the present invention have been presented for purposes of illustration, but are not intended to be exhaustive or limited to the embodiments disclosed. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope and spirit of the described embodiments. The terminology used herein was chosen to best explain the principles of the embodiments, the practical application or technical improvement over technologies found in the marketplace, or to enable others of ordinary skill in the art to understand the embodiments disclosed herein.

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What is claimed is:

1. A method of making an electrically active betavoltaic battery comprising:

providing an electrically inactive betavoltaic battery device having one or more diodes incorporating a semiconductor material layer including a stable non-radioactive isotope; and

irradiating the electrically inactive betavoltaic battery device with thermal neutrons, thereby causing the conversion of at least a portion of the stable non-radioactive isotope to a radionuclide and creating the electrically active betavoltaic battery, wherein the semiconductor material layer acts as both an electron emitter and an electron absorber simultaneously.

2. The method of claim **1**, wherein the stable non-radioactive isotope is thulium-169 and the radionuclide is thulium-170.

3. The method of claim **1**, wherein the semiconductor material layer is selected from the group consisting of: diamond, thulium oxide, aluminum nitride, aluminum gallium nitride, gallium nitride, silicon carbide, gallium oxide, aluminum gallium oxide, zinc oxide, and silicon.

4. The method of claim **3**, wherein the semiconductor material layer comprises gallium oxide, and the method further comprises growing the semiconductor material layer with the stable non-radioactive isotope using an epitaxial growth doping method.

5. The method of claim **3**, wherein the semiconductor material layer comprises iridium-free β-gallium oxide.

6. The method of claim **1**, further comprising irradiating the electrically active betavoltaic battery after a period of time has elapsed since the irradiating the electrically inactive betavoltaic battery device with thermal neutrons and a portion of the radionuclide has been converted into one or more stable isotopes thus depleting an electrical charge in the electrically active betavoltaic battery, thereby converting at least a portion of remaining stable non-radioactive isotope in the electrically active betavoltaic battery to the radionuclide, resulting in a recharged electrically active betavoltaic battery.

7. The method of claim **1**, wherein the electrically inactive betavoltaic battery device includes one or more additional semiconductor material layers, different from the semiconductor material layer including the stable non-radioactive isotope, that act as electron absorbers.

8. The method of claim **1**, further comprising fabricating the one or more diodes such that the one or more diodes incorporate the semiconductor material layer including the stable non-radioactive isotope.

9. The method of claim **8**, wherein the one or more diodes comprise an anode fabricated at a first surface of the semiconductor material layer and a cathode fabricated at a second surface of the semiconductor material layer.

10. The method of claim **1**, further comprising annealing the electrically active betavoltaic battery to repair crystal damage in the semiconductor material layer caused by the irradiation.

11. A method of making an electrically inactive betavoltaic battery device comprising:

fabricating a semiconductor material layer containing a stable isotope; and

fabricating one or more diodes such that the one or more diodes incorporate the semiconductor material layer, thereby creating the electrically inactive betavoltaic battery device, wherein the electrically inactive betavoltaic battery device is configured to be transformed into an electrically active betavoltaic battery upon irradiation with thermal neutrons.

12. The method of claim **11**, wherein the stable isotope is thulium-169, which converts to thulium-170 upon irradiation with thermal neutrons.

13. The method of claim **11**, wherein the semiconductor material layer is selected from the group consisting of: diamond, thulium oxide, aluminum nitride, aluminum gallium nitride, gallium nitride, silicon carbide, gallium oxide, aluminum gallium oxide, zinc oxide, and silicon.

14. The method of claim **11**, wherein the fabricating the semiconductor material layer containing a stable isotope comprises doping the semiconductor material layer with the stable isotope.

15. The method of claim **14**, wherein the semiconductor material layer comprises iridium-free β-gallium oxide.

16. The method of claim **11**, wherein the one or more diodes comprise an anode fabricated at a first surface of the semiconductor material layer and a cathode fabricated at a second surface of the semiconductor material layer.

17. The method of claim **11**, further comprising annealing the semiconductor material layer.

18. An electrically inactive betavoltaic battery device comprising:

a semiconductor material layer including a stable isotope; and

one or more diodes incorporating the semiconductor material layer, wherein the electrically inactive betavoltaic battery device is configured to be transformed into an electrically active betavoltaic battery upon irradiation with thermal neutrons.

19. The electrically inactive betavoltaic battery device of claim **18**, wherein the stable isotope is thulium-169, which converts to thulium-170 upon irradiation with thermal neutrons.

20. The electrically inactive betavoltaic battery device of claim **18**, wherein the semiconductor material layer comprises iridium-free β-gallium oxide.

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