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(54) Device and method for thermoelectronic energy conversion

(57) A thermoelectronic energy conversion device (100) comprises an electron emitter (10), which is adapted for a temperature-dependent release of electrons (1), an electron collector (20), which is adapted for a collection of the electrons (1), wherein the electron collector (20) and the electron emitter (10) are spaced from each other by a gap (2), and a gate electrode (30), which is arranged between the electron emitter (10) and the electron collector (20), wherein the gate electrode (30) is adapted for subjecting the electrons (1) in the gap (2) to

an electrical potential, wherein the gate electrode (30) comprises at least one membrane-shaped, electrically conductive or semiconductive electrode layer (31), which is at least partially transparent for the electrons (1). The electrode layer (31) is e. g. graphene or a similar two-dimensional material. Furthermore, a power source device including at least one energy conversion device and a method of converting energy using the thermoelectronic energy converter device (100) are described.





Description

[0001] The present invention relates to a thermoelectronic energy conversion device (or: thermoelectronic generator) comprising at least one electron emitter, at least one electron collector and at least one gate electrode. The thermoelectronic energy converter device is adapted for converting heat into a consumable electric current. Furthermore, the present invention relates to a power source device, which is adapted for converting heat into a consumable electric current, which includes at least one thermoelectric energy converter device. Furthermore, the present invention relates to a method of thermoelectronic energy conversion of thermal energy, e. g. solar energy, to electric energy, wherein the thermoelectronic energy converter device is used. Applications of the invention are available in the fields of generating electric power, in particular on the basis of solar energy or thermal energy from nuclear reactions, combustion, or industrial fabrication processes.

[0002] For illustrating background art relating to thermoelectronic energy conversion and to two-dimensional materials, like e.g. graphene, reference is made to the following prior art:

[1] WO 2014/019594;

[2] S. Meir, C. Stephanos, T. H. Geballe, J. Mannhart, High-ly-efficient thermoelectronic conversion of solar energy and heat into electric power, Journal of Renewable and Sustainable Energy 5, 043127 (2013);

[3] S. Meir, Highly-Efficient Thermoelectronic Conversion of Heat and Solar Radiation to Electric Power, Doctoral thesis (2012);

[4] C. Stephanos, Thermoelectronic Power Generation from Solar Radiation and Heat, Doctoral thesis (2012);

[5] J.-N. Longchamp,T. Latychevskaia, C. Escher, H.-W. Fink, Low-energy electron transmission imaging of clusters on freestanding graphene, Applied Physics Letters 101, 113117 (2012);

[6] B. Guo, L. Fang, B. Zhang, J. R. Gong, Graphene Doping: A Review, Insciences Journal 1 (2), 80 (2011);

[7] H. Liu, Y. Liu and D. Zhu, Chemical doping of graphene, Journal of Materials Chemistry 21, 3253 (2011);

[8] C. Li, M. T. Cole, W, Lei, K. Qu, K. Ying, Y. Zhang,
A. R. Robertson, J. H. Warner, S. Ding, X. Zhang,
B. Wang, W. I. Milne, Highly Electron Transparent
Graphene for Field Emission Triode Gates, Advanced Functional Materials 24, 1218 (2014);

[9] C. Lee, X. Wei, J. Kysar, J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, Science 321, 385 (2008);

[10] A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, Superior Thermal Conductivity of Single-Layer Graphene, Nano Let-

ters 8, 902 (2008); and

[11] J. Schwede, I. Bargatin, D. C. Riley, B. E. Hardin, S. J. Rosenthal, Y. Sun, F. Schmitt, P. Pianetta, R. T. Howe, Z.-X. Shen, N. A. Melosh, Photon-enhanced thermionic emission for solar concentrator systems, Nature Materials 9, 762 (2010).

[0003] Thermoelectronic generators and the related thermionic generators produce electric power directly
 ¹⁰ from a temperature gradient between an electron emitter and an electron collector, which are spaced by a gap. Typically, they are used as sources of electricity provided from thermal and/or solar energy (see [1] and references cited therein).

¹⁵ [0004] An example of a conventional thermoelectronic generator 100' is schematically illustrated in Figure 6 (prior art, see [1]). The thermoelectronic generator 100' comprises the electron emitter 10', the electron collector 20' and a gate electrode 30', which is arranged in the gap 2'

²⁰ between the electron emitter 10' and the electron collector 20'. The work function of the electron collector 20' is lower compared to the work function of the electron emitter 10'. With a temperature difference between the emitter 10' and the collector 20', electrons 1' are emitted into

the gap 2' and collected with the collector 20'. The difference between the work functions of the emitter 10' and the collector 20' determines the maximum efficiency of the thermoelectronic generator (see [2 - 4]). The gate electrode 30' generates an accelerating electric field,
which accelerates the electrons 1' towards the collector 20'. Simultaneously, space charges at the emitter 10' are avoided.

[0005] The gate electrode 30' of the conventional thermoelectronic generators is made of a metal grid or a 35 structured, electrically conducting sheet, made e.g. of Si, having holes for passing the electrons. Due to the positive potential of the gate electrode 30', a portion of the emitted electrons is accelerated towards the body of the gate electrode 30', e.g. towards the grid rods. As a disadvan-40 tage, the electric current through the gate electrode 30' reduces the generator efficiency. In order to suppress the electron absorption at the grid rods, the conventional thermoelectronic generator 100' is provided with a magnetic field device 40' for creating a magnetic field. Mag-45 netic field lines extend between the emitter 10' and the collector 20' through the holes of the gate electrode 30'. [0006] Advantageously, the generator efficiency can be improved by the effect of the magnetic field. However, the magnetic field device 40' may result in various dis-50 advantages restricting the application of the conventional thermoelectronic generator. The magnetic field has to be generated with permanent magnets or electromagnets, which increase the size and costs of the conventional generators, resulting in limitations with regard to appli-55 cations in mobile systems. Furthermore, a thermal insulation of the magnetic field device relative to the remaining system may be required for improving a long-term

operation stability of the magnetic field device. Finally,

with the use of the magnetic field device, the range of available materials of the remaining generator components is restricted as the remaining components should not include magnetic materials.

[0007] It is generally known that electron tubes, e. g. for controlling electric currents, may have a triode configuration including an electrode which functions as a gate electrode as well. However, due to the specific work functions features of the cathode and anode electrodes and the low operation temperature, electron tubes cannot be used as thermoelectronic generators. Typically, the gate electrode of a conventional electron tube is a grid electrode with filaments, wherein the electrons pass the meshes between the filaments. This type of gate electrode would have the same disadvantages as described above. C. Li et al. have proposed a field emission electron tube with another gate electrode which is made of graphene (see [8]). The gate electrode is subjected to a high voltage for obtaining field strengths in a range above 10⁶ V/m, so that electrons can be created by field emission and pass the electrode. However, this field emission electron tube could not work as a thermoelectronic generator, in particular due to the necessarily lower work function of the field emitter compared with the collector.

[0008] The objective of the present invention is to provide an improved thermoelectronic energy conversion device, which is capable of avoiding disadvantages and limitations of conventional thermoelectronic generators. It is a particular objective of the invention to provide the thermoelectronic energy conversion device having a reduced weight and size, reduced costs, improved operation stability and/or improved variability in terms of materials for manufacturing the energy conversion device. It is a further objective of the invention to provide an improved power source device, which can be manufactured with low cost and which has low size and weight. Furthermore, it is an objective of the invention to provide an improved method of thermoelectronic energy conversion, wherein the thermoelectronic energy conversion device is used.

[0009] The above objectives are solved with a thermoelectronic energy conversion device, a power source device and a method of thermoelectronic energy conversion, comprising the features of the independent claims, respectively. Preferred embodiments and applications of the invention are defined in the dependent claims.

[0010] According to a first general aspect of the invention, a thermoelectronic energy conversion device is provided, which comprises an electron emitter (cathode), an electron collector (anode) and a gate electrode. The electron emitter and the electron collector are arranged with a mutual gap (spacing), wherein emitter and collector surfaces point to the gap, resp.. The electron collector is made of a material having a work function that is lower compared with the work function of the electron emitter material. Accordingly, the electron emitter is adapted for a temperature-dependent release of electrons into the gap, while the electron collector is adapted for a collection of the released electrons. The gate electrode is arranged for creating an electric field, e. g. an electron accelerating electrical potential, an alternating potential and/or a switched potential sequence, in the gap between the electron emitter and the electron collector.

[0011] According to the invention, the gate electrode comprises at least one membrane-shaped, electrically conductive or semi-conductive electrode layer, which is at least partially transparent for the electrons (semi-trans-

¹⁰ parent electrode layer). Advantageously, the inventors have found that the at least one membrane-shaped, partially or completely transparent electrode layer (or: gate electrode layer) is capable of creating the electric field, while reducing the above electron absorption in the gate

¹⁵ electrode material. A freestanding thin membrane of a material with electron transmission (or low electron absorption) can be passed by the electrons with only small or negligible energy loss, so that they can be used as homogeneous, positively charged gate electrodes. The material and/or thickness of the at least one gate electrode layer are selected such that electrons accelerated towards the gate electrode are transmitted through the layer material, i.e. the electrons pass through a continuous section of the material layer. The electrons pass

25 through the layer material as such. [0012] The at least one gate electrode layer is partially transparent, i.e. it has at least 20 %, preferably at least 25 %, particularly preferred at least 50 % electron transmission probability. Preferably, the at least one mem-30 brane-shaped, partially transparent electrode layer consists of a two-dimensional material (graphene-like material). Particularly preferred, the two-dimensional material is at least one atomic monolayer. As an important advantage of the invention, the gate electrode obviates the 35 need for magnetic fields. The inventive thermoelectronic energy conversion device can be provided without a magnetic field device, and it requires at least three electrodes only.

[0013] The electron emitter and collector electrodes
 can be provided as plates or membranes spaced from each other, in particular having a planar shape. The gate electrode may be provided, e. g. manufactured, on the emitter or on the collector electrode, provided it is electrically insulated from the emitter or collector electrode,

45 resp.. The membrane structure of the electrodes allows the construction of the thermoelectronic energy conversion device with a compact structure. As the emitter and collector electrodes also may comprise thin films, foils, or membranes, the weight and/or the material demand 50 of the generator can be further reduced. In particular, the emitter and collector electrodes may comprise two-dimensional, mono- or multilayer materials, in particular graphene-like materials, like the gate electrode. Furthermore, with the gate electrode used according to the in-55 vention, the efficiency of the thermoelectronic energy conversion can be improved. The invention proposes new heat- and/or light-to-current-converters with reduced volume, weight and material requirements. Moving or vibrating mechanical parts are avoided, so that the inventive energy conversion device is capable of noisefree and vibration-free operation. As the energy conversion device does not require external magnetic fields, the creation of magnetic stray fields is avoided.

[0014] Contrary to the conventional technique of C. Li et al. [8], the at least one membrane-shaped, partially or completely transparent electrode layer is provided in a thermoelectronic energy conversion device, but not in a field emission triode. The inventors have found that the membrane-shaped electrode layer is sufficiently stable even with the strong temperature gradient between the emitter and the collector. The inventive thermoelectronic energy conversion device is adapted to apply a voltage to the gate electrode, wherein the gate electrode voltage is adapted for removing space charges. In other words, the gate electrode used with the invention is subjected to an essentially lower voltage compared with a field emission voltage, e. g. according to C. Li et al. [8]. The inventors have found that the membrane-shaped electrode layer is capable to pass the electrons even with the relatively low space charge removing gate electrode voltage.

[0015] According to a second general aspect of the invention, a power source device is provided, which comprises at least one heat source and at least one energy conversion device according to the above first aspect of the invention. The term "heat source" refers to any component, which is capable of creating a temperature gradient, so that the electron emitter has a higher temperature compared with the electron collector. According to preferred applications of the invention, the heat source may comprise an active heat and/or a passive source. The active heat source is configured for heating the electron emitter by a conversion heat of a radioactive decay of a radioactive element or by fuel combustion, or by hot materials generated in manufacturing processes such as hot steel in steel fabrication plants, while the passive heat source is heated by an irradiation, e.g. with light (e.g. solar absorber) and arranged for a heat transfer to the electron emitter.

[0016] Depending on the application of the invention, one single energy conversion device can be thermally coupled with the at least one heat source for heating the electron emitter, or multiple energy conversion devices, e.g. an array of energy conversion devices can be coupled with one single heat source or with a plurality of heat sources.

[0017] Advantageously, the power source device according to the invention is an ultra-light heat-to-currentconverter having an improved power density compared with conventional generators. As an example, a power density of 50 W/g or more can be obtained with the use of an energy conversion device including a graphenebased gate electrode. As a further advantage, the power source device of the invention has a large range of applications, e.g. for providing a source of electric current in vehicles, ships, in particular submarines, airplanes and/or space crafts. Furthermore, current sources for buildings, e.g. as solar power stations or block heating works in buildings, can be provided. As a further range of applications, current sources in portable devices, like

- ⁵ e.g. portable computers, or stationary devices can be provided, wherein gas fuel reservoirs or solar energy converters, optionally using photon-enhanced thermoionic emission [11], can be provided.
- [0018] According to a third general aspect of the invention, a method of converting energy using the thermoelectronic energy converter device of the above first aspect of the invention is provided, wherein the method includes the steps of creating a temperature gradient of the electron emitter relative to the electron connector,

¹⁵ e.g. by coupling the energy converter device with at least one heat source, releasing electrons from the electron emitter, accelerating the electrons towards the electron collector by the effect of an accelerating electric potential applied to the gate electrode, and collecting the electrons

20 with the electron collector, which is connected with a consumer circuit and/or an accumulator device. According to the invention, the accelerated electrons pass the at least one electrode layer of the gate electrode.

[0019] According to a preferred embodiment of the invention, the at least one electrode layer of the gate electrode includes at least one of graphene, silicene, phosphorene, stanene, germanene, MoS₂, C₃N₄ and boron nitride. Advantageously, graphene and the further preferred examples have a high heat conductivity (see e.g.

- ³⁰ [10]), so that these materials are suitable for use with electron emitters at high temperatures, e.g. 2000 °C. Furthermore, these materials have a high transmission probability. As an example, graphene has a transmission probability of 27 % for 66 eV electrons (see [5]).
- ³⁵ [0020] Conductive or semiconductive, two-dimensional materials, like graphene or graphene-like materials, have further advantages as they allow a targeted reduction of electron absorption by changing the Fermi energy of the layer material and/or a reduction of energy losses
- 40 by adjusting a plasmon frequency in the layer material by adding a doping substance to the layer material. Accordingly, with a preferred embodiment of the invention, the at least one electrode layer includes at least one dopant. Advantageously, the doping allows a shifting of the
- ⁴⁵ Fermi energy (see e.g. [6, 7]), so that the absorption of electrons can be reduced, in particular in predetermined electron energy intervals. In case a two-dimensional material is used that conducts electricity only poorly, this conduction can be enhanced by doping the two-dimen-
- sional material or by adding one or more ultrathin conducting layers onto the two-dimensional material. Furthermore, when the electrons pass graphene or similar materials, they can excite plasmons, thus losing energy. The plasmon frequency, e.g. in graphene, can be
 changed by doping, so that energy losses of the electrons are reduced.

[0021] According to a particularly preferred embodiment of the invention, the dopant of the at least one elec-

trode layer comprises at least one of B, N, Bi, Sb, Au, NO_2 , ammonia and polyethyleneimine. Preferred doping concentrations are e.g. 1010 - 1014 cm⁻².

[0022] With a further preferred feature of the invention, the at least one electrode layer of the gate electrode is made of a material, which is insensitive to ionizing radiation. Advantageously, this feature increases the longterm stability of the energy conversion device operation, in particular under the effect of ionizing radiation. This advantage is important in particular for applications of the invention in space crafts, wherein a radioactive heat source is used. As a further advantage, two-dimensional membranes of the above materials are stable under the effect of ionizing radiation. This stability can even be improved if the at least one electrode layer is made of an isotope selected for a higher insensitivity compared with other isotopes. With a preferred example, the at least one electrode layer can consist of graphene, which is completely made of C¹² isotopes.

[0023] Further advantages in terms of an increased conversion efficiency can be obtained if the gate electrode of the inventive energy conversion device has through-holes. The through-holes are openings in the at least one electrode layer. The electrode layer is formed as a grid, e. g. a regular or irregular grid. Preferably, the regular grid is a hexagonal grid. The through-holes may have a circular or non-circular, e. g. elliptic, rectangular or triangular shape.

[0024] Preferably, a cross-sectional dimension, like the hole diameter, of the through-holes is smaller than a fivefold distance between the electron emitter and the electron collector, preferably smaller than twice a distance between the electron emitter and the electron collector, particularly preferred smaller than one single distance or even the smaller than one of the distances emitter - gate or gate - collector. The through-holes have the particular advantage that the electron absorption is further reduced, while the mechanical stability of the gate electrode can be kept. In case the layer material is unpatterned, the electrons pass through a continuous section of the material layer. In case the layer material is manufactured to comprise, e.g., holes, the electrons pass through the layer material as such or through the holes. [0025] The inventors have found that the number of electrons reaching the electron collector continuously increases as a function of decreasing hole diameter with constant gate electrode transparency (area of throughholes / area of the gate electrode) if the diameter of the holes is small compared with the distance between the electron emitter and the electron collector. With reducing the hole diameter, the homogeneity of the electric field is improved as transversal field components are reduced. Accordingly, a transversal deflection of electrons is reduced, thus decreasing the electron absorption at the gate electrode and increasing the electron current to the electron collector. With a diminishing hole diameter down to 0, the transversal components are completely suppressed (see e.g. [4]). Thus, according to particularly preferred features of the invention, the cross-sectional dimension, like the hole diameter, of the through-holes can be selected to be smaller than 500 μ m, in particular smaller than 200 μ m. Furthermore, in particular with an emitter collector distance of e.g. 10 μ m, a hole diameter below 10 μ m, in particular below 5 μ m, e.g. 1 μ m, is preferred. The inventors have found that e.g. a structured graphene

grid with a hole diameter of 1 μm and a lateral width of the layer sections between the holes of 5 nm has an
electron absorption below 1 %. In particular this low electron absorption allows to omit a magnetic field, thus clearly showing the advantage compared with the conventional techniques.

[0026] Advantageously, the through-holes can be created e.g. with electron beam lithography or optical lithography, combined with ion etching or chemical etching. An irregular grid of through-holes can be made e.g. by ion irradiation. The inventors have found that an essential reduction of the electron absorption can be obtained, if
the total area of the through-holes is at least 10 %, preferably at least 20 %, particularly preferred at least 50 %, or even at least 80 %, of the area of the gate electrode exposed to the emitter and collector electrodes.

[0027] According to a further preferred embodiment of
the invention, the at least one electrode layer of the gate electrode is connected with a frame. The frame is arranged between the electron emitter and the electron collector. Preferably, the at least one electrode layer is spanned on the frame, so that a stable mechanical support of the at least one electrode layer is provided. The frame is electrically isolated with respect to the electron emitter and/or the electron collector, e.g. with ceramic spacers. With preferred examples, the spacers comprise aluminium oxide (sapphire, Al₂O₃) or yttrium-stabilized

[0028] According to a further advantageous modification of the invention, the gate electrode further comprises a supporting layer, which is connected with the at least one electrode layer. The supporting layer carries the at
40 least one electrode layer. Advantageously, this increases the mechanical stability of the gate electrode and the positioning of the gate electrode with a distance relative to both of the electron collector and the electron emitter. Preferably, the supporting layer has a thickness in a

⁴⁵ range of 5 μm to 100 μm. With a particularly preferred example, the supporting layer is made of silicon, which has advantages in terms of mechanical stability and heat conductivity. Alternatively, the supporting layer is made of germanium or tungsten. The supporting layer is a grid
⁵⁰ with supporting layer through-holes having diameters in a range of e.g. 1 μm to 100 μm.

[0029] According to a further advantageous embodiment of the invention, the gate electrode may comprise multiple membrane-shaped electrically conductive or semiconductive electrode layers spaced from each other. The gate electrode may include a stack of two-dimensional materials, preferably monolayers, each providing an electrode layer. The material thickness and optional

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through-holes of the electrode layers are selected such that the gate electrode has an electron transparency of at least 20 %, preferably at least 25 %, particularly preferred 50 % or more. Advantageously, multiple electrode layers can be manufactured by a growing process, wherein the electrode layers are deposited with sacrificial layers there between, which are removed subsequently. This allows the adjustment of distances of the electrode layers below 0.1 μ m, in particular below 10 μ m. Preferred examples of materials, which can be used for creating the sacrificial layers comprise Cu, Fe, Al, or oxides, like CaMnO₃, SrMnO₃, La₂CuO₄ or YBa₂C₃O₇, which can be etched with weak acids, or even frozen water, which can be removed after deposition of the electrode layers. [0030] The application of the invention is not restricted to the three electrode embodiment with one electrode emitter, one gate electrode, having one or more electrode layers and being connected with one gate voltage source, and one electrode collector. It is alternatively possible to provide more electrodes, in particular to provide more gate electrodes, each being connected with a specific gate voltage source and including one or more electrode layers. The electrode layers of the gate electrodes may comprise continuous layers or layers having throughholes as described above. The provision of multiple gate electrodes may provide advantages in terms of enhancing the possible spacing between the emitter and collector and reducing heat losses.

[0031] As a further advantage of the invention, the structure of the energy conversion device can be adapted to the particular application thereof. Preferably, the electrodes of the energy conversion device are arranged within an evacuated container, which allows a heating of the electron emitter. Alternatively, the electrodes can be arranged in a container, which includes a working gas. The working gas, like e.g. Cs vapor, Cs-O vapor or ionized Cs-vapor, is capable of reducing space charges in the gap between the electron emitter and the electron collector and/or influencing a work function of the electron emitter, the electron collector and/or the gate electrode. Further examples of working gases are gases based on other alkali metals, like Rb or K, or Ba, optionally mixed with oxygen. Alternatively, the energy conversion device can be provided without a container. In particular, a pressure equilibrium can be provided if the energy conversion device is used on a surface of a space craft in contact with the space.

[0032] Further details and advantages of the invention are described in the following with reference to the attached drawings, which show in:

- Figure 1: a schematic cross-sectional illustration of a thermoelectronic energy conversion device according to a first embodiment of the invention;
- Figure 2: a schematic cross-sectional illustration of a thermoelectronic energy conversion device

according to a further embodiment of the invention;

- Figure 3: schematic illustrations of a frame carrying a gate electrode;
- Figure 4: a microscopy image of a supporting layer carrying a gate electrode;
- ¹⁰ Figure 5: a schematic illustration of a power source device according to an embodiment of the invention; and
- Figure 6: a schematic cross-sectional illustration of a conventional thermoelectronic energy conversion device (prior art).

[0033] Features of preferred embodiments of the invention are described in the following with particular reference to the design of the gate electrode of a thermoelectronic energy conversion device. Exemplary reference is made to graphene-based gate electrodes. The graphene membrane can be made on and/or optionally transferred to a frame or a supporting layer by chemical vapor
 ²⁵ deposition or any other procedure as conventionally

known. The invention is not restricted to the use of graphene. It is emphasized that other two-dimensional materials, e.g. as mentioned above, can be used as alternatives.

30 [0034] Furthermore, exemplary reference is made to a thermoelectronic energy conversion device having one single electron emitter, one single electron collector and one single gate electrode. Alternatively, the thermoelectronic energy conversion device can have multiple gate

- ³⁵ electrodes and/or multiple pairs of electron emitters and collectors, each with a gap accommodating one or more gate electrode(s). Features of thermoelectronic generators, like the function principle thereof, the design of the electron emitter and electron collector, or the adaptation
- 40 of applying thermal energy to the electron emitter are not described as far as they are known from conventional techniques.

[0035] It is emphasized that the drawings are schematic illustrations only, which do not represent scaled ver-

⁴⁵ sions of practical devices. With practical implementations of the invention, the skilled person will be able to select geometrical dimensions, structural properties, materials and the electric circuitry in dependency on the particular application requirements.

50 [0036] According to Figure 1, the thermoelectronic energy conversion device 100 comprises an electron emitter 10, an electron collector 20 and a gate electrode 30. The electron emitter 10 is a planar electrode plate, which is made of e. g. BaO-impregnated W, LaB₆ or lanthanum 55 doped tungsten and electrically connected with ground potential (earth potential). In practice, the electron emitter 10 may be supported by mechanical components (not shown). Furthermore, an energy absorber device and/or

heat source (not shown) may be provided in thermal contact with the electron emitter 10. The electron collector 20 is a planar electrode plate as well, which is made of e. g. of a doped diamond film, a Cs-, BaO- or La-, LaOdoped or impregnated (porous) metal, or an electrically conducting material with a specifically prepared surface, wherein the exposed surface 21 of the electron collector 20 is arranged with a distance D from the exposed surface 11 of the electron emitter 10. The distance D is e. g. 100 $\mu m.$ The area of each of the exposed surfaces 11, 21 is e. g. 1 mm² or 1 cm². The electron collector 20 is connected via a load circuitry 60 with the electron emitter 10 and the ground potential. The load circuitry 60 includes e.g. an accumulator device and/or an electric consumer device and/or a load resistance. It is pointed out that the emitter and collector electrodes may also be realized as thin films, foils, or membranes to reduce the weight and/or the material demand of the generator.

[0037] The gap 2 between the electron emitter 10 and the electron collector 20 is evacuated or filled with a working gas, as it is known from conventional thermoelectronic generators. With the preferred application in a power source device for use in the outer space, the gap 2 is evacuated in accordance with the outer vacuum conditions. In an alternative implementation, the arrangement of the electron emitter 10, the electron collector 20 and the gate electrode 30 is encapsulated by a pressure tight casing (not shown), so that the gap 2 can be evacuated or filled with the working gas.

[0038] The gate electrode 30 comprises at least one membrane-shaped electrode layer 31, having a planar, preferably two-dimensional shape and extending in the gap 2 parallel to the parallel planar exposed surfaces 11, 21 of the electron emitter 10 and the electron collector 20, respectively. A distance d between the electron emitter 10 and the gate electrode 30 is e. g. 50 μ m. The gate electrode 30 is connected with a gate voltage source 32, which is adapted for applying e. g. a positive accelerating voltage or an alternating voltage to the at least one electrode layer 31. The electrode layer 31 is e. g. a graphene mono- or multilayer as described below with reference to Figure 2. It is supported by a frame as described below with reference to Figure 3.

[0039] Figure 1 schematically illustrates a gate heater unit 35, which is arranged for heating the gate electrode 30. The gate heater unit 35 is provided in direct contact with the electrode layer 31, and it contains e. g. a resistor heating for annealing (tempering) the electrode layer 31. Advantageously, this allows a removal of contaminations from the electrode layer 31. The gate heater unit 35 is a switchable component, so that the annealing can be conducted on request or in dependency on predetermined operation conditions of the electron tube device 100.

[0040] In practical use for converting heat into electric current, the electron emitter 10 is thermally coupled with a heat source (see e.g. Figure 5). The temperature of the electron emitter 10 is e.g. 1400 °C, while the temperature of the electron collector 20 is e.g. 400 °C. Due to this

temperature gradient, electrons 1 are released from the exposed surface 11 of the electron emitter 10. The electrons 1 are accelerated by the accelerating electric potential created with the gate voltage source 32, having a voltage of e.g. 3 V. Most of the electrons 1 are transmitted through the electrode layer 31 of the gate electrode 30

and absorbed by the electron collector 20. Accordingly, an electric current flows through the load circuitry 60. **[0041]** A further embodiment of the thermoelectronic

 energy conversion device 100 with the electron emitter
 10, the electron collector 20 and the gate electrode 30 is
 illustrated in Fig-ure 2. This illustration represents a preferred example of a practical application of the invention,
 wherein e. g. a graphene electrode layer 31 is used. How-

¹⁵ ever, the application of the invention is not restricted to the use of graphene as the electrode layer material, but rather possible with the other material examples as cited above or even further two-dimensional materials having electric conductivity or semi-conductivity.

²⁰ **[0042]** The thermoelectronic energy conversion device 100 of Figure 2 comprises a support structure 50, including a base plate 51, gate electrode spacers 52 and electron collector spacers 53. The base plate 51 is made e.g. of Al_2O_3 with a through-hole 54. The electron emitter

²⁵ 10 is supported by the base plate 51, wherein a back side 12 of the electron emitter 10 is exposed at the through-hole 54. With an example, the back side 12 of the electron emitter 10 can be irradiated through the through-hole 54 with solar energy 3.

30 [0043] The gate electrode spacers 52 are supported on an inner side of the base plate 51 facing towards the electron collector 20. The gate electrode spacers 52 are made of e.g. Al₂O₃ with a thickness of e.g. 20 μm. The electron collector spacers 53 have a thickness defining
35 the distance D between the exposed surfaces 11, 21 of the electron emitter 10 and the electron collector 20, respectively. The electron collector spacers 53 are made of e.g. Al₂O₃. The gate electrode 30 comprises the electrode layer 31 made of graphene, which is supported by a frame 33.

[0044] The graphene electrode layer 31 is arranged on the frame 33 in particular by one of the following procedures. Firstly, the graphene electrode layer 31 can be manufactured separately with a conventional method

⁴⁵ and subsequently transferred and fixed to the frame 33.
Alternatively, the graphene electrode layer 31 can be grown on an auxiliary layer, which is connected with the frame 33 and subsequently removed. Furthermore, the graphene electrode layer 31 can be grown on a support⁵⁰ ing layer 34 (see Figure 4).

[0045] Figure 3 schematically shows a top view of the frame 33 having an outer shape, e.g. rectangular shape, which is adapted to the geometry of the support structure 50, and a through-hole with a shape, e.g. circular shape, which is adapted to the shape of the electron emitter 10. The frame 33 has a double function in terms of positioning the electrode layer 31 relative to the electron emitter 10 (see Figure 2) and providing an electrical contact with

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the electrode layer 31. Accordingly, the frame 33 is made of or at least covered with a conductive, e.g. metallic, or semi-conductive material, which is electrically coupled with the gate voltage source (see Figure 1, 32).

[0046] With a preferred example, the electrode layer 31 could be electrically connected as follows. Firstly, the electrode layer 31, e.g. a graphene layer, is connected with an upper surface of the frame 33, wherein the upper surface of the frame 33 is not completely covered by the electrode layer 31. An outer section of the upper surface remains exposed. Subsequently, a thin metallic layer, e.g. a Pt layer, is deposited on the frame 33. The deposition is obtained using e.g. a sputtering or other thin film deposition process. The metallic layer creates the electric contact with the electrode layer 31, and the electrode layer 31 is fixed on the frame 33 by the metallic layer. Finally, the metallic layer is connected with the gate voltage source 32.

[0047] For increasing the mechanical stability, the electrode layer 31 can be grown on a supporting layer 34. An example of a supporting layer is shown with an REM image in Figure 4. The supporting layer 34 is made of e.g. Si with a hexagonal structure having a mesh diameter of some 10 μ m. It is noted that the provision of the supporting layer 34 is not strictly necessary. Due to the tear strength of two-dimensional materials, e.g. graphene, the electrode layer 31 can be created with an area of some cm² without an additional supporting layer. Those skilled in the art will appreciate that also stacks of several supporting layers with different hole diameters may be used advantageously.

[0048] Figure 5 schematically illustrates a power source device 200 according to an embodiment of the invention, comprising a heat source 210 and a thermoelectronic energy conversion device 100 according to the invention. The heat source 210 comprises e.g. a cell including a radioactive substance, wherein heat is generated during the radioactive decay of the radioactive substance. The electron emitter 10 of the energy conversion device 100 is directly connected with the heat source 210. With an alternative embodiment of the invention, a plurality of energy conversion devices 100 can be fixed in thermal contact with the heat source 210, each being electrically connected with a common load circuitry or separate load circuitries (see Figure 1, 60).

[0049] The features of the invention in the above description, the drawings and the claims can be of significance both individually as well in combination or subcombination for the realization of the invention in its various embodiments.

Claims

- Thermoelectronic energy conversion device (100), ⁵⁵ comprising:
 - an electron emitter (10), which is adapted for

a temperature-dependent release of electrons (1),

- an electron collector (20), which is adapted for a collection of the electrons (1), wherein the electron collector (20) and the electron emitter (10) are spaced from each other by a gap (2), and

- a gate electrode (30), which is arranged between the electron emitter (10) and the electron collector (20), wherein the gate electrode (30) is adapted for subjecting the electrons (1) in the gap (2) to an electrical potential,

characterized in that

- the gate electrode (30) comprises at least one membrane-shaped, electrically conductive or semiconductive electrode layer (31), which is at least partially transparent for the electrons (1).

2. Energy conversion device according to claim 1, having at least one of the features

- the at least one electrode layer (31) includes monolayer or multilayer graphene, silicene, phosphorene, stanene, germanene, MoS_2 , C_3N_4 or boron nitride, and

- the at least one electrode layer (31) includes at least one dopant, in particular B, N, Bi, Sb, Au, NO₂, ammonia and/or polyethyleneimine.

3. Energy conversion device according to one of the foregoing claims, having at least one of the features

- the gate electrode (30) is in thermal contact with a gate heater unit (35),

 the at least one electrode layer (31) is made of a material which is insensitive to ionizing radiation, and

- the at least one electrode layer (31) is an atomic monolayer.

4. Energy conversion device according to one of the foregoing claims, wherein

- the at least one electrode layer (31) has through-holes, wherein a hole diameter of the through-holes is smaller than the fivefold distance between the electron emitter (10) and the electron collector (20).

50 **5.** Energy conversion device according to claim 4, wherein the through-holes have at least one of the features:

- the cross-sectional dimension of the throughholes is smaller than 500 $\mu m,$ in particular smaller than 200 μm

- the area of the through-holes is at least 10 % of the area of the gate electrode exposed to the

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emitter and collector electrodes, and - the through-holes are created by electron beam lithography or by optical lithography, combined with ion etching, reactive etching, or chemical etching, and/or by ion irradiation.

6. Energy conversion device according to one of the foregoing claims, wherein

- the at least one electrode layer (31) is spanned on a frame (33), which is arranged between the electron emitter (10) and the electron collector (20).

7. Energy conversion device according to claim 6, wherein

- the frame (33) is electrically isolated with respect to at least one of the electron emitter (10) and the electron collector (20) by gate electrode ²⁰ spacers (52).

8. Energy conversion device according to one of the foregoing claims, wherein

- the gate electrode (30) further comprises a supporting layer (34), which carries the at least one electrode layer (31).

9. Energy conversion device according to claim 8, 30 wherein

- the supporting layer is made of silicon, germanium or tungsten.

10. Energy conversion device according to one of the foregoing claims, wherein

- the gate electrode (30) comprises multiple membrane-shaped electrically conductive or 40 semi-conductive electrode layers.

11. Energy conversion device according to one of the foregoing claims, comprising

- at least one further gate electrode which includes at least one of a monolayer- or multilayershaped electrode layer and an electrode grid.

12. Energy conversion device according to one of the ⁵⁰ foregoing claims, having at least one of the features:

- the electron emitter (10), the electron collector (20) and the gate electrode (30) are arranged in an evacuated container,

- the electron emitter (10), the electron collector (20) and the gate electrode (30) are arranged in a container including a working gas reducing space charges in the gap (2) and/or influencing a work function of at least one of the electron emitter (10), the electron collector (20) and the gate electrode (30),

- the energy conversion device (100) does not include a magnetic field device.
- **13.** Power source device (200), comprising
 - at least one heat source, and
 at least one energy conversion device according to one of the foregoing claims.
- 14. Power source device according to claim 13, wherein

- the at least one heat source is adapted for providing heat by a radioactive decay of a radioactive element, by photon irradiation or by fuel combustion.

15. Method of converting energy using the thermoelectronic energy converter device (100) according to one of the foregoing claims, comprising the steps of:

- releasing electrons (1) from the electron emitter (10),

- accelerating the electrons (1) released from the electron emitter (10) by the accelerating electric potential in the gap (2) through the gate electrode (30) toward the electron collector (20), and

- collecting the electrons (1) with the electron collector (20).

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FIG. 2



FIG. 3



FIG. 4



FIG. 5



FIG. 6 (Prior Art)



EUROPEAN SEARCH REPORT

Application Number EP 14 00 3488

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