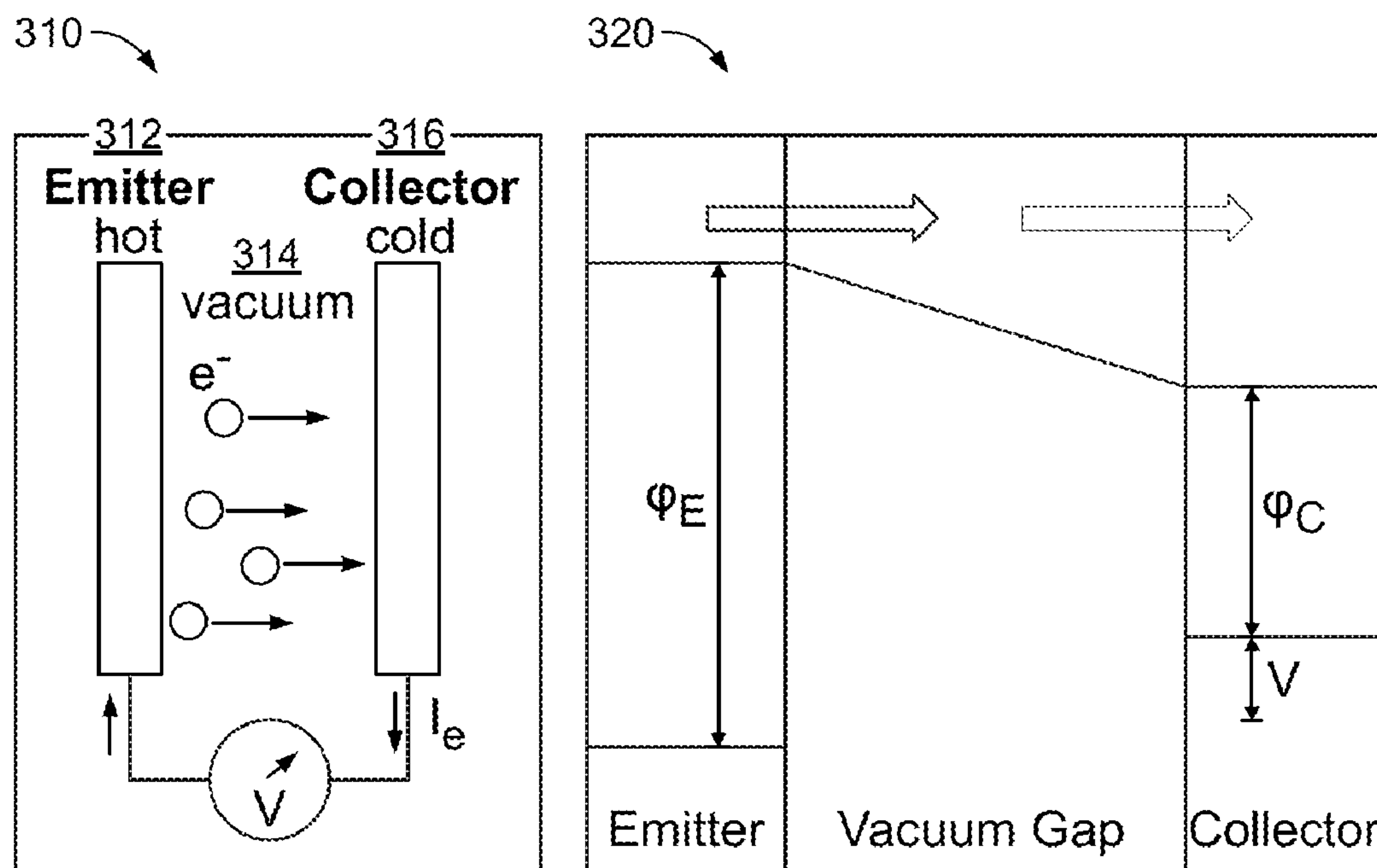




US 20180204702A1

(19) **United States**(12) **Patent Application Publication**
Koeck et al.(10) **Pub. No.: US 2018/0204702 A1**(43) **Pub. Date: Jul. 19, 2018**(54) **PHOSPHORUS DOPED DIAMOND
ELECTRODE WITH TUNABLE LOW WORK
FUNCTION FOR EMITTER AND
COLLECTOR APPLICATIONS**(71) Applicant: **Arizona Board of Regents on Behalf
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(US)(21) Appl. No.: **15/921,225**(22) Filed: **Mar. 14, 2018****Related U.S. Application Data**(62) Division of application No. 15/588,362, filed on May
5, 2017, now Pat. No. 9,922,791.(60) Provisional application No. 62/332,338, filed on May
5, 2016.**Publication Classification**(51) **Int. Cl.****H01J 19/30** (2006.01)**C30B 29/04** (2006.01)**C30B 25/16** (2006.01)**C30B 25/18** (2006.01)**C30B 25/20** (2006.01)**H01J 9/04** (2006.01)**H01J 9/14** (2006.01)**H01J 19/06** (2006.01)**H01J 45/00** (2006.01)(52) **U.S. Cl.**CPC **H01J 19/30** (2013.01); **C30B 29/04**
(2013.01); **C30B 25/16** (2013.01); **C30B**
25/186 (2013.01); **C30B 25/20** (2013.01);
H01J 45/00 (2013.01); **H01J 9/04** (2013.01);
H01J 9/14 (2013.01); **H01J 19/06** (2013.01)**ABSTRACT**(57) An apparatus includes an emitter electrode including a
phosphorus doped diamond layer with low work function.
The apparatus further includes a collector electrode and a
vacuum gap disposed between the emitter and the collector.
The collector has a work function of 0.84 eV or less.

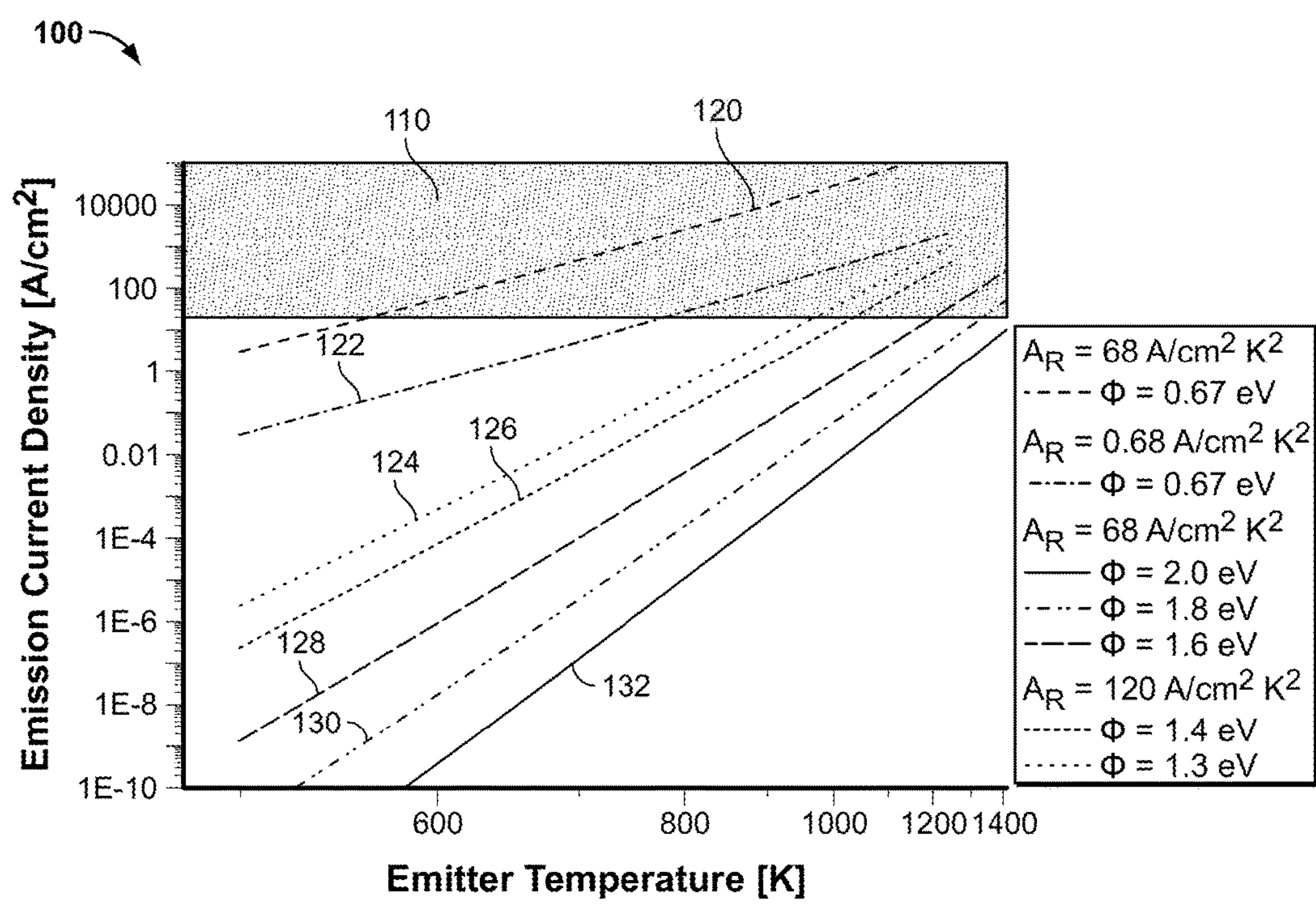


FIG. 1

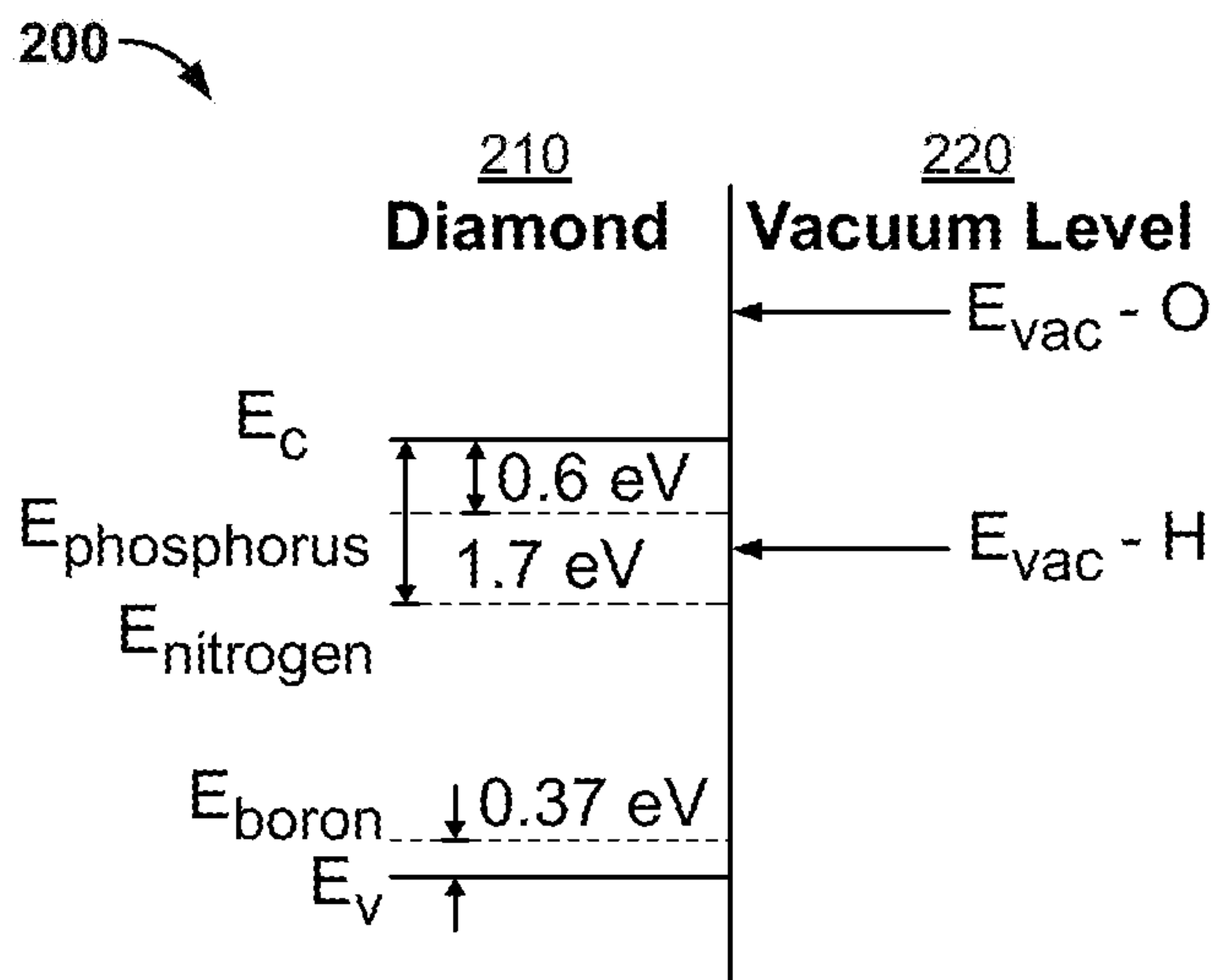


FIG. 2

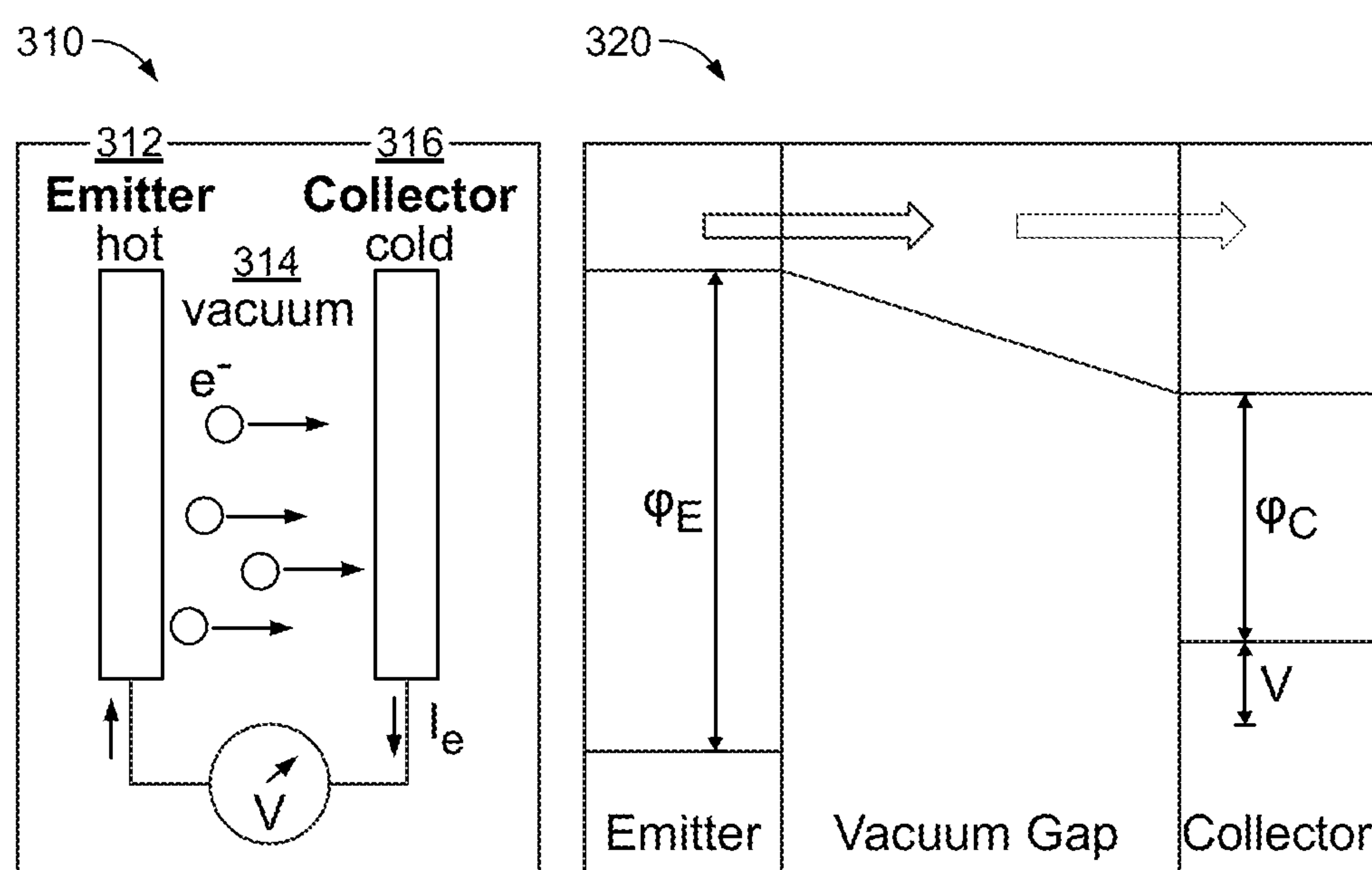


FIG. 3

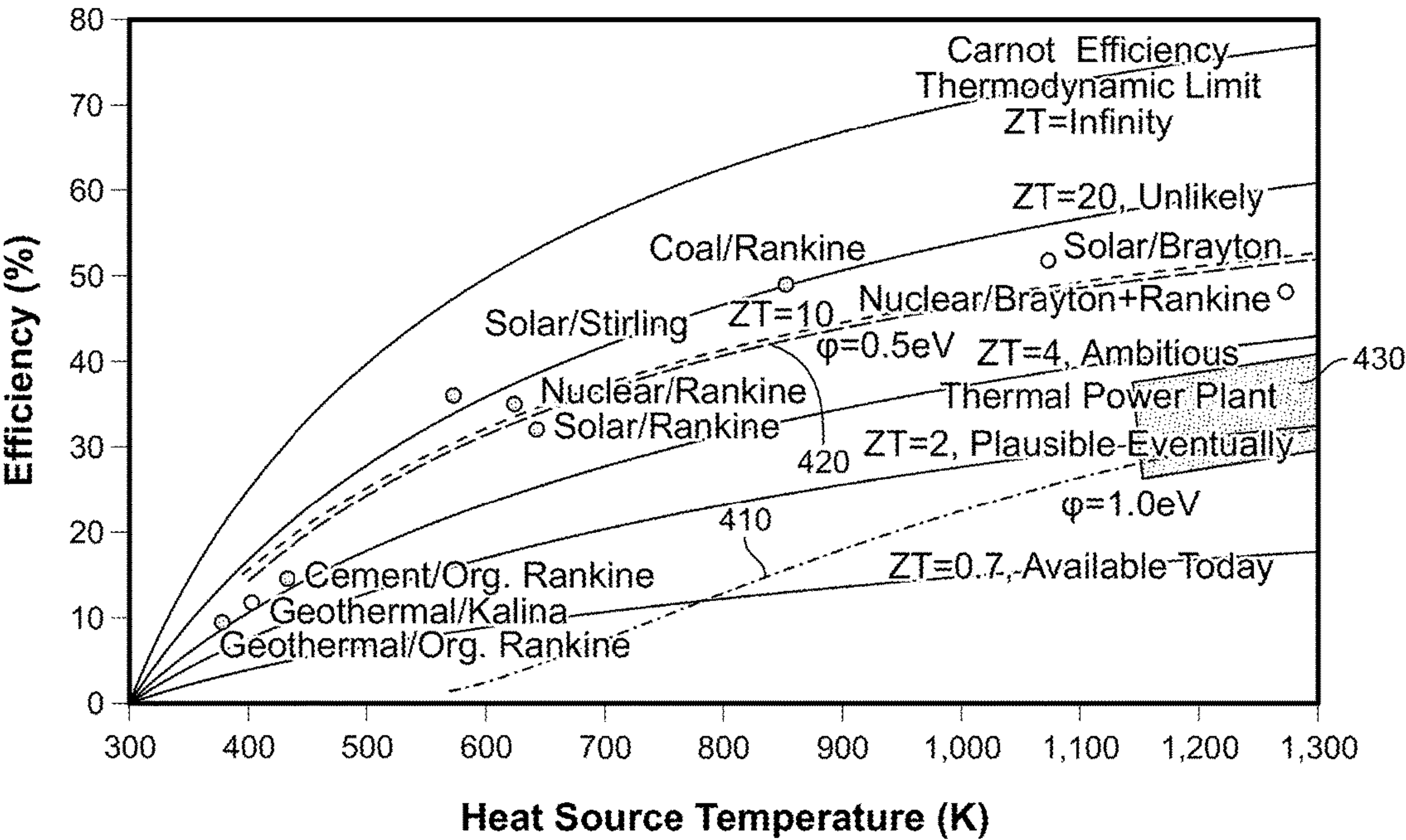


FIG. 4

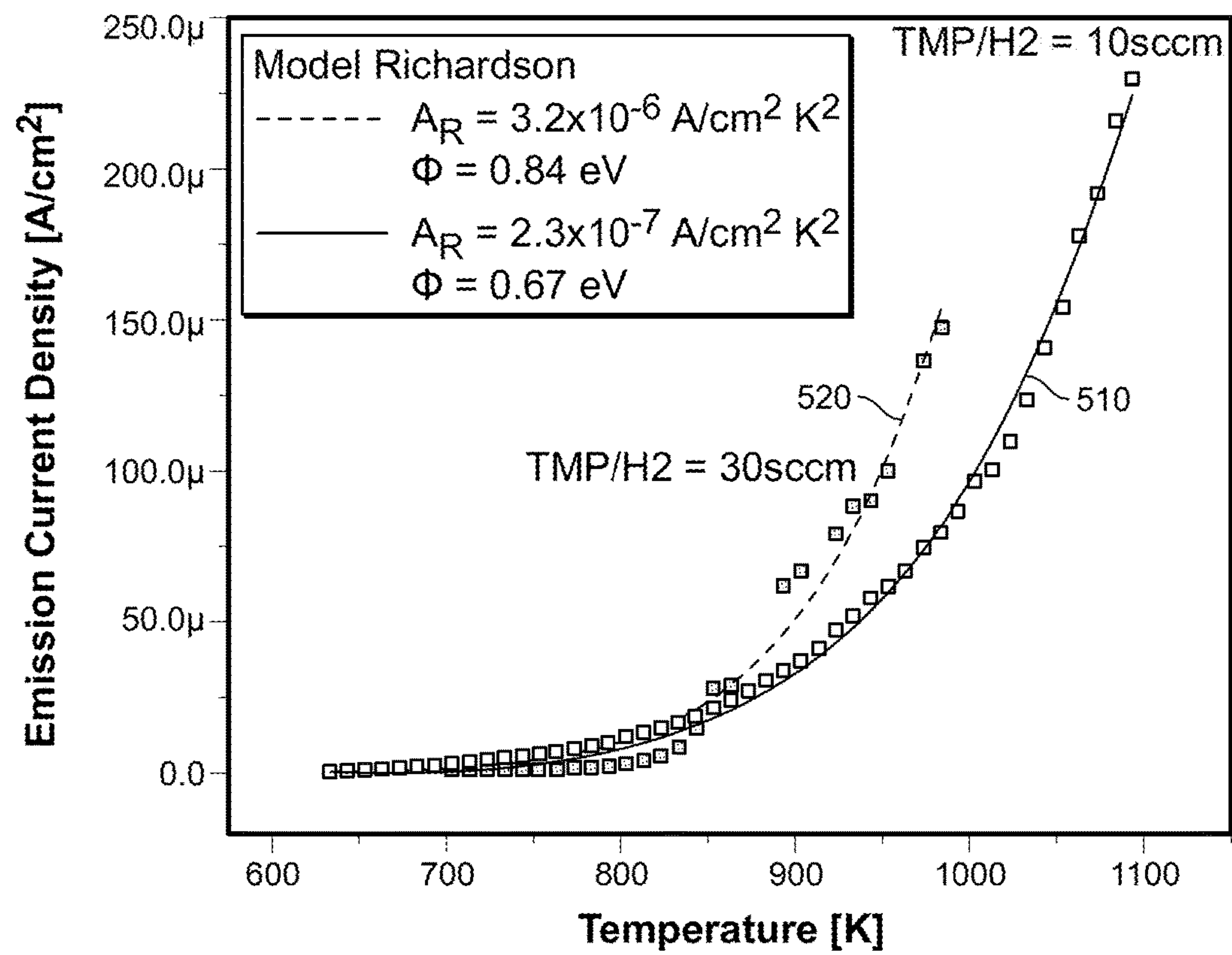


FIG. 5

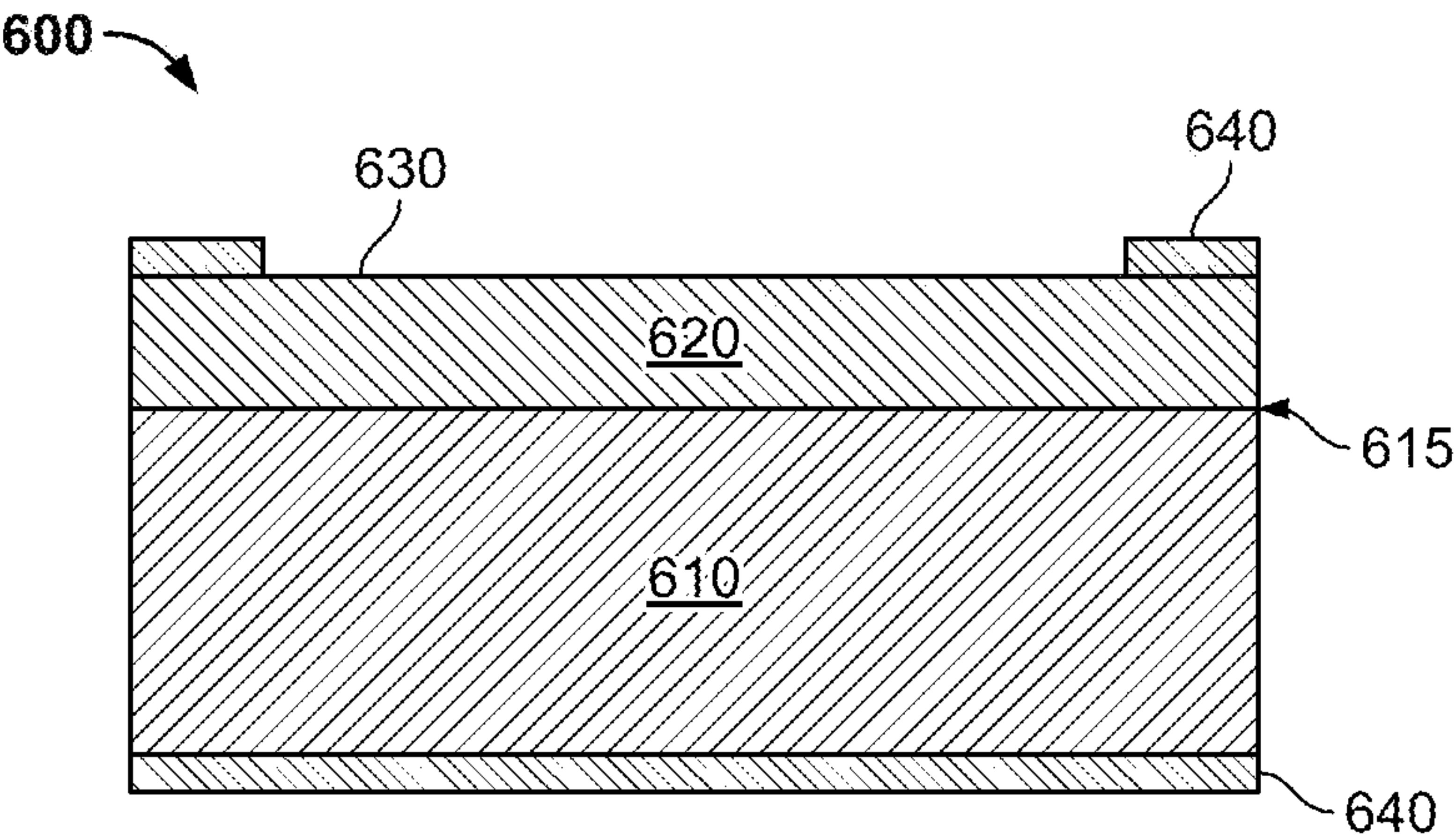


FIG. 6

PHOSPHORUS DOPED DIAMOND ELECTRODE WITH TUNABLE LOW WORK FUNCTION FOR EMITTER AND COLLECTOR APPLICATIONS

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application is a divisional application of U.S. patent application Ser. No. 15/588,362, filed on May 5, 2017, which claims the benefit of U.S. Provisional Application Ser. No. 62/332,338, filed May 5, 2016, and entitled, “Phosphorus doped diamond electrode with tunable low work function for emitter and collector applications,” both of which are incorporated herein by reference in their entireties.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This disclosure was made with government support under N00014-10-1-0540 awarded by the Office of Naval Research. The government has certain rights in the disclosure.

BACKGROUND

[0003] Low work function electrodes are highly sought after as they can significantly advance and enable technologies that rely on electron transfer in devices such as electron sources for communications and in particular direct energy converters that transform heat into electricity without mechanically moving components. Electron sources utilizing thermionic electron emitters are widely deployed in high power/high frequency communications (travelling wave tubes, TWT's), radar, free electron lasers, directed energy weapons, X-ray sources and space propulsion. Conventional electron sources based on metallic cathodes operate at temperatures exceeding 1000° C. Lowering the operating temperature would lead to a less involved design, a reduced power demand, and a lighter and smaller payload for operation in mobile terrestrial and satellite applications.

[0004] Thermionic energy converters operate through the generation of an electron emission current from a thermionic electron emitter or cathode which is held at a temperature optimized for its emission barrier or work function, typically in excess of 1000° C. for refractory metal based emitters. A second lower work function electrode is coupled to the thermionic emitter, through a small vacuum gap, which establishes a configuration that can generate electrical power. The efficiency can then directly be related to the work function of the counter-electrode, the collector, where an ideal value of 0.5 eV was reported. This ultra-low work function would enable predicted efficiencies greater than 50%. To achieve a similar efficiency with solid-state thermo-electric conversion would require a material with ZT~10. However, the current best materials exhibit ZT~2. It is notable that traditional thermal power plants can be characterized as operating with ZT~3. Additionally, establishing a means to control the electrode work function would enable devices to operate with optimum performance at the desired temperature.

SUMMARY

[0005] According to a first aspect, an apparatus is provided. The apparatus includes a collector including a phos-

phorus doped diamond layer. The apparatus further includes a thermionic emitter and a vacuum gap disposed between the emitter and the collector. The collector has a work function of 0.84 eV or less.

[0006] According to a second aspect, a method is provided for making an apparatus. The method may include one or more of the following acts: preparing a substrate using a wet-chemical cleaning procedure; loading the substrate into a plasma enhanced chemical vapor deposition (PECVD) reactor and prepare a surface of the substrate for doped diamond growth; exposing the substrate to a pure hydrogen plasma for a preset duration; and depositing a phosphorus doped diamond layer on the substrate.

[0007] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 illustrates simulation results of the electron emission current using the Richardson-Dushman expression for various work functions ϕ according to an aspect of the disclosure.

[0009] FIG. 2 illustrates a band diagram according to an aspect of the disclosure.

[0010] FIG. 3 illustrates an example vacuum thermionic energy converter device according to an aspect of the disclosure.

[0011] FIG. 4 illustrates conversion efficiency for various power generators in comparison with the thermo-electric ZT figure of merit and the corresponding efficiency of a vacuum-thermionic converter with collector work function ϕ of 1 eV and 0.5 eV.

[0012] FIG. 5 illustrates thermionic emission vs temperature for samples with an epitaxial phosphorus doped diamond layer on nitrogen doped single crystal diamond (100) substrates according to an aspect of the disclosure and the work function (ϕ) extracted from a fit to the Richardson formalism.

[0013] FIG. 6 illustrates a schematic of the doped diamond electrode device according to an aspect of the disclosure.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0014] Before the present disclosure is described in further detail, it is to be understood that the disclosure is not limited to the particular embodiments described. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. The scope of the present disclosure will be limited only by the claims.

[0015] As used herein, the singular forms “a”, “an”, and “the” include plural embodiments unless the context clearly dictates otherwise.

[0016] Specific structures, devices, and methods relating to thermionic and solar energy conversion have been disclosed. It should be apparent to those skilled in the art that many additional modifications beside those already described are possible without departing from the inventive concepts. In interpreting this disclosure, all terms should be interpreted in the broadest possible manner consistent with the context. Variations of the term “comprising” should be interpreted as referring to elements, components, or steps in a non-exclusive manner, so the referenced elements, com-

ponents, or steps may be combined with other elements, components, or steps that are not expressly referenced. Embodiments referenced as “comprising” certain elements are also contemplated as “consisting essentially of” and “consisting of” those elements. If a series of numerical ranges are recited, this disclosure contemplates combinations of the lower and upper bounds of those ranges that are not explicitly recited. For example, if a range between 1 and 10 or between 2 and 9 is recited, this disclosure also contemplates a range between 1 and 9 or between 2 and 10.

[0017] Diamond based electrodes are a preferred material for electron sources in general and energy conversion in particular as the material exhibits excellent high temperature stability, mechanical properties exceeding that of the hardest metals and exceptional resistance to radiation. Additionally, with its high thermal conductivity and electron mobility and the ability to accept shallow donors in its lattice, a diamond based electrode may overcome limits seen with conventional materials.

[0018] Low and ultra-low work function doped diamond electrodes were prepared by deposition of a thin phosphorus doped diamond layer on single crystal nitrogen doped, high-pressure, high-temperature (HPHT) substrates through epitaxial layer growth using plasma enhanced chemical vapor deposition (PECVD). The nitrogen doped single crystal substrate allows electrical conduction that improves with temperature suitable for electron sources operating at elevated temperatures. Prior to diamond deposition the surface is cleaned by a wet-chemical procedure including H₂SO₄, H₂O₂, NH₄OH and HF followed by exposure to a pure hydrogen plasma at a higher temperature to prepare a clean surface. Utilizing hydrogen (H₂) as carrier gas, methane (CH₄) as carbon source and a phosphorus source, here a 200 ppm trimethylphosphine/hydrogen (TMP/H₂) gas mixture, a thin phosphorus doped layer is deposited by establishing a short growth period typically timed for 7 minutes. Optionally, a finishing step in a pure hydrogen plasma establishes a hydrogen passivated surface that induces a negative electron affinity (NEA) characteristic and allows further lowering of the work function or emission barrier.

[0019] The devices characterized with respect to the thermionic emission law of Richardson-Dushman indicated an ultra-low work function of 0.67 eV. This is the one of the lowest work functions reported and the lowest work function material operating at temperatures exceeding 800° C. Adjustment of growth conditions enabled tuning of the work function value where a readily achieved alternate deposition regime achieved a work function of 0.84 eV.

[0020] FIG. 1 illustrates simulation of the electron emission current using the Richardson-Dushman expression for various work functions ϕ . The results are presented for three different values of the Richardson constant, the theoretical value for metals ($A_R=120$ A/cm²K²), the theoretical value for diamond ($A_R=68$ A/cm²K²) and the diamond value reduced by a factor of 100 that reflects the range of anticipated experimental values. The upper region **110** presents an emission current density >20 A/cm² that would compete with or surpass the present emitter technology. Moderate work function metals of 1.3-1.4 eV with the theoretical Richardson constant of 120 A/cm²K² may provide higher current densities at higher temperatures. Here, line **120** illustrates the change of emission current density values as the emitter temperature increases when the A_R is the theo-

retical value (68 A/cm²K²) for diamond and the work function is 0.67 eV. Line **122** illustrates the change of emission current density values as the emitter temperature increases when the work function is 0.67 eV and the A_R is one hundredth the theoretical value (0.68 A/cm²K²) for diamond as an example when A_R deviates to lower values.

[0021] In FIG. 1, line **124** illustrates the change of emission current density values as the emitter temperature increases when the A_R is the theoretical value for metals and the work function is 1.3 eV. Line **126** illustrates the change of emission current density values as the emitter temperature increases when the A_R is the theoretical value for metals and the work function is 1.4 eV. Line **128** illustrates the change of emission current density values as the emitter temperature increases when the A_R is the theoretical value for diamond and the work function is 1.6 eV. Line **130** illustrates the change of emission current density values as the emitter temperature increases when the A_R is the theoretical value for diamond and the work function is 1.8 eV. Line **132** illustrates the change of emission current density values as the emitter temperature increases when the A_R is the theoretical value for diamond and the work function is 2.0 eV.

[0022] FIG. 2 illustrates a band diagram **200** in a flat band configuration for diamond **210** indicating the donor states for nitrogen, and phosphorus and the acceptor states for boron which reside between the valence, EV, and conduction band, EC. The vacuum level **220** for a hydrogen terminated and oxygen terminated surface is marked, which corresponds to a negative electron affinity (NEA) and a positive electron affinity (PEA), respectively.

[0023] FIG. 3 illustrates a vacuum thermionic energy converter device **310** comprised of a thermionic electron emitter **312**, a vacuum gap **314**, and a collector **316** (left image). The corresponding band schematic **320** indicates emitter and collector work function, ϕ_E and ϕ_C , respectively, and the self-generated voltage, V, due to the work function difference. The thermionic electron emitter **312** may include a N-doped single crystal diamond. The collector **316** may include a phosphorus doped diamond layer. The phosphorus doped diamond layer may be a P-doped homoepitaxial diamond layer.

[0024] FIG. 4 illustrates conversion efficiencies for various power generators in comparison with the thermo-electric ZT figure of merit and the corresponding efficiency of a vacuum-thermionic converter with collector work function ϕ of 1 eV (line **410**) and 0.5 eV (line **420**). The feasibility of higher ZT values is indicated. The ZT value for different power conversion processes are indicated as is the operation of thermal power plants (yellow region **430**).

[0025] FIG. 5 illustrates thermionic emission vs. temperature for samples with an epitaxial phosphorus doped diamond layer on nitrogen doped single crystal diamond (100) substrates. The phosphorus doped diamond films were grown with 10 sccm TMP/H₂ (curve **510**) and 30 sccm TMP/H₂ (curve **520**). An ultra-low work function of 0.67 eV was deduced from the Richardson relation for the film grown with 10 sccm TMP/H₂. An increase of the work function to 0.84 eV was observed for the film grown with a 30 sccm TMP/H₂ flow rate. (The solid lines present a fit to the Richardson-Dushman expression.)

[0026] FIG. 6 illustrates a schematic of the low work function doped diamond electrode device **600** according to an aspect of the disclosure. In FIG. 6, the electrode device **600** may include the conducting (doped) single crystal

diamond substrate **610** with (100) or similar orientation (nitrogen doped single crystal, high-pressure, high-temperature (HPHT) or CVD diamond) with a prepared surface (the controlled interface **615**); the thin (5 nm-100 nm) phosphorus doped diamond layer **620** with varying and controlled doping concentration and with diamond surface **630** generated by optional surface treatment to induce negative electron affinity properties (hydrogen passivation). Electrical contacts **640** are prepared using metallic(gold) or conducting, doped nano-structured diamond conductors

[0027] Electron Sources—Introduction:

[0028] Thermionic electron sources are an integral part in today's advanced terrestrial and space based telecommunications through travelling wavetubes (TWT's), space exploration through propulsion and energy generators, national security through radar and directed energy weapons, science, health care and industry through electron microscopy, free electron lasers, X-ray sources, electron beam lithography and microwave generators. While each application group requires specifics for operation a common criterion is the power requirement to establish necessary output levels. As the power requirements are directly related to the device (cathode) operating temperature, establishing efficient emission at a lower temperature would translate into a refined system design and reduced power consumption. This becomes more critical for mobile or space applications where part of the payload needs to address power generation. To account for the increased power requirements in satellites which range from 1 kW to 25 kW, silicon based solar panels are being replaced by triple-junction InGaP/InGaAs/Ge solar cells with a conversion efficiency of about 30%. As satellites present relay stations for terrestrial communications via travelling wave tubes, the impact of improved electron sources may be significant. Likewise, it is apparent that more efficient power sources are necessary for space communications and exploration. In fact, electrical power for the Mars Curiosity rover is supplied by a multi-mission radioisotope thermo-electric generator (MMRTG) utilizing a 2000 W thermal power heat source that is converted by thermo-electrics to about 120 W electrical power in a bulky configuration measuring 25 in. in diameter (fin tip to fin tip), 26 in. in length and weighing about 94 lbs.

[0029] Increasing demand for high power/high frequency communications (THz) can be achieved by novel cathodes capable of delivering high current densities. For current TWTs the cathodes are typically heated to 1100° C. and electrons are extracted via thermionic emission and the application of a high voltage. The cathode voltage can range from thousands to hundreds of thousands of volts and establish cathode currents greater than 10 A which requires a cathode material capable of the high emission current densities.

[0030] Physics of Thermionic Electron Emission:

[0031] Vacuum thermionic electron emission, first formulated by Richardson-Dushman, relates the emission current density $J(T)$ to the emission barrier or work function ϕ and the Richardson or emission constant A_R through the expression

$$J(T)=A_R T^2 e^{(-\phi/(k_B T))} \quad (1)$$

where

$$A_R=(4\pi m_0 k_B^2 e^2)/h, \quad (2)$$

[0032] with Boltzmann's constant, k_B , electron effective mass, m_0 , electronic charge, e , and Planck's constant h . For diamond a value for A_R of 68 A/cm²K² was reported. A simulation of (1) is shown in FIG. 1) for various work function values. The plot shows the expected current density that may be obtained from a low work function of 0.6 eV emitter where A_R ranges from 68–0.68 A/cm²K². With $\phi=0.6$ eV and $A_R=0.68$ A/cm²K² the cathode is able to provide a current density of ~20 A/cm² at around 500° C. surpassing any present emitter technology. Some of the lowest work functions have been reported for Ba—Ca—Al oxides. One report of 12-CaO 7-Al₂O₃ (C12A7) indicates a work function of 0.6 eV. However, thermionic applications are apparently limited to temperatures less than 500° C. More importantly, for single crystal C12A7, a shift in the work function to 2.1 eV was observed at a higher temperature regime up to 950° C. which limits use for most energy conversion and communication applications.

[0033] Diamond as Electron Emitter:

[0034] Considering diamond for electron emitter applications requires evaluation of its band structure that is schematically drawn in FIG. 2. Here, the doping levels are indicated for a flat band configuration, for donor levels of nitrogen at 1.7 eV below the conduction band minimum (CBM) and phosphorus at 0.6 eV below the CBM. A unique band configuration arises when the diamond surface is terminated by hydrogen. In this case the vacuum level is shifted below the CBM eliminating a surface barrier for electron emission. Thermal promotion of electrons from shallow states into the CBM would then allow their unhindered release into vacuum. For clean and oxygen terminated surfaces the vacuum level is positioned above the CBM establishing a positive electron affinity (PEA) surface. Oxygenated and clean diamond surfaces with various orientations were reported with PEA values ranging from 0.6 eV to 1.45 eV. In conjunction with shallow donors, PEA doped diamond surfaces can provide work functions less than 2 eV suitable for emitter applications.

[0035] Ultra-low work function diamond as collector electrode for direct energy conversion: The direct conversion of heat into electricity by means of vacuum thermionic energy conversion presents an approach for electrical power generation where high conversion efficiencies are feasible as hot and cold side of the generator is separated by a vacuum gap (see FIG. 3). A vacuum thermionic converter is comprised of a hot side, a thermionic electron emitter and a vacuum gap providing a thermal barrier to the counter-electrode, the collector. This is contrasted by solid-state thermo-electric conversion techniques that rely on materials with low thermal conductivity to establish a sufficiently large thermal gradient between the hot and cold side. The conversion efficiency is typically described by the ZT value where the best current materials exhibit a ZT of about 2 which is reduced to about 1.5 for operating temperatures greater than about 700K. As a comparison, the efficiency of today's thermal power plants would correspond to a ZT value of about 3 and is shown in a comprehensive plot for various heat engines (see FIG. 4). For vacuum thermionic energy conversion a similar figure of merit can be related to the collector work function, and its relation to thermo-electric ZT values is displayed in the efficiency plot in FIG. 4.

[0036] Engineering of Low Work Function Doped Diamond Cathodes:

[0037] One of the focus of this disclosure is on the preparation of an ultra-low work function collector that can also act as a thermionic emitter or cathode. As electron emitters have to support the electron current across the device an electrically conducting diamond substrate, here, a nitrogen doped, single crystal, high-pressure, high-temperature substrate with (100) surface orientation was selected. These substrates were characterized at elevated temperatures where a Richardson constant A_R of 62 A/cm²K² was observed, a value approaching the theoretical value for diamond of 68 A/cm²K². This established the capability of doped diamond to enable high values for the emission or Richardson constant crucial for efficient thermionic emitters. Preparation of the low work function collector and emitter device commenced with a wet-chemical cleaning procedure that consisted of:

[0038] Boil in H₂SO₄/H₂O₂/H₂O, 3:1:1 at 220° C. for 15 min

[0039] HF treatment for 5 min

[0040] Boil in NH₄OH/H₂O₂/H₂O, 1:1:5 at 75° C. for 15 min

[0041] rinse with DI water after each step

[0042] The thus prepared substrate was then loaded into the PECVD reactor and exposed to a pure hydrogen plasma at 800° C.-900° C. for 15 min. This process prepares the surface for the doped diamond growth. A thin phosphorus doped diamond layer was then deposited using a methane flow rate of typically 2 sccm (0.5% of the total gas flow) and a 200 ppm trimethylphosphine/hydrogen (the phosphorus source) flow rate between 10 sccm and 30 sccm with hydrogen as carrier gas with a total gas flow rate of 400 sccm. The phosphorus doped layer is deposited at around 900° C.-1000° C. using a microwave power of 2500 W and a chamber pressure of 75-85 Torr. With these growth conditions and by utilization of plasma focusing geometry of the sample holder, heating of the substrate is achieved by the plasma discharge. Furthermore, a water-cooled sample stage and PECVD reactor reduce incorporation of impurities during deposition. The growth period is timed for about 7 minutes after which methane and TMP/H₂ flow is terminated and the sample cooled under hydrogen plasma exposure which induces a negative electron affinity surface. Results from two devices are presented here, where the TMP/H₂ flow rate was established at 10 sccm and 30 sccm. The average thicknesses of the films are estimated to be between 5 nm and 100 nm, and the layer thickness can be further optimized to achieve a low resistivity and work function.

[0043] Thermionic Emitter Characterization:

[0044] To prepare the collector and thermionic cathode, electrical contacts are prepared using a thin gold layer on the top surface as well as the backside of the substrate (see FIG. 6). In an emission characterization chamber, a bias voltage is applied to the device to overcome space charge effects, and the emission current is recorded as a function of temperature as shown in FIG. 5. For the sample prepared with 10 sccm of TMP/H₂ an ultra-low work function of 0.67 eV was extracted from a fit to the Richardson expression. As the TMP/H₂ flow rate is increased to 30 sccm, the work function was observed to increase to 0.84 eV. The devices were operated at temperatures up to 950° C. indicating high temperature stability of the device.

[0045] A novel device structure based on doped diamond has been developed where a donor state establishes a surface

with a low work function that can be further reduced through suitable surface terminations. This device can provide a work function as low as 0.67 eV where the operating temperature exceeds 800° C. The cathodes are readily prepared on (100) oriented single crystal diamond substrates a preferred crystallographic orientation for device manufacturing. Tuning the value of the work function was achieved by adjusting the growth parameters. With a modified growth regime a cathode with a work function of 0.84 eV was engineered. These low work function thermionic electron emitters may advance high power/high frequency telecommunications, as well as applications where electron sources may be a key component. Secondly, in direct energy conversion application of the low work function electrode as collector conversion efficiencies approaching 50% may be realized.

[0046] Thin layers of phosphorus doped diamond with controlled doping concentration on (100) single crystal nitrogen doped diamond that allow preparation of ultra-low work function collectors and thermionic emitters with tunable work function.

[0047] The phosphorus doped diamond collector/emitter with a work function of 0.67 eV presents the only known material that can maintain this low emission barrier across a wide temperature regime which has been measured up to 950° C. Additionally, we have established a means to control the work function by adjusting the phosphorus doping, where a variation of the work function to 0.84 eV was demonstrated. The low work function is achieved without adsorbates or coatings.

[0048] Diamond based electrodes are a preferred material for electron sources in general and energy conversion in particular as the material exhibits excellent high temperature stability, mechanical properties exceeding that of the hardest metals and exceptional resistance to radiation. Additionally, with its high thermal conductivity and electron mobility and the ability to accept shallow donors in its lattice, a diamond based electrode may overcome limits obtainable by conventional materials.

[0049] Low and ultra-low work function doped diamond electrodes were prepared by deposition of a thin phosphorus doped diamond layer on single crystal nitrogen doped, high-pressure, high-temperature (HPHT) substrates through epitaxial layer growth using plasma enhanced chemical vapor deposition (PECVD). The nitrogen doped single crystal substrate allows electrical conduction that improves with temperature suitable for electron sources operating at elevated temperatures. Prior to diamond deposition the surface is cleaned by a wet-chemical procedure including H₂SO₄, H₂O₂, NH₄OH and HF followed by exposure to a pure hydrogen plasma at a higher temperature to prepare a clean surface. Utilizing hydrogen (H₂) as carrier gas, methane (CH₄) as carbon source and a phosphorus source, here a 200 ppm trimethylphosphine/hydrogen (TMP/H₂) gas mixture, a thin phosphorus doped layer is deposited by establishing a short growth period typically timed for no more than 7 minutes. Optionally, a finishing step in a pure hydrogen plasma establishes a hydrogen passivated surface that induces a negative electron affinity (NEA) characteristic and allows further lowering of the work function or emission barrier.

[0050] The disclosed devices may be characterized with respect to the thermionic emission law of Richardson-Dushman and indicated an ultra-low work function of 0.67

eV. This is one of the lowest work functions reported and the lowest work function material operating at temperatures exceeding 800° C. Adjustment of growth conditions may be enabled by tuning of the work function value where a readily achieved alternate deposition regime achieved a work function of 0.84 eV.

[0051] The disclosure also provides a low work function electrode as a thermionic electrode emitter that utilizes shallow diamond donors such as phosphorus. The disclosed devices may include thermionic cathodes and may be employed in a wide variety of applications. The low work function electrode may include a negative electron affinity surface for ultra-low work function electrodes, a positive or zero electron affinity for a low work function where the ultra-low work function of the negative electron affinity surface is increased by the value of the electron affinity (typically 1 eV). The low work function electrode has a reduced upward band bending and a thin 5-100 nm thin phosphorus doped diamond layer. The low work function electrode can enable efficient energy conversion devices.

[0052] Although the invention has been described in considerable detail with reference to certain embodiments, one skilled in the art will appreciate that the present invention may be practiced by other than the described embodiments, which have been presented for purposes of illustration and not of limitation. Therefore, the scope of the appended claims should not be limited to the above description contained herein.

What is claimed is:

1. A method for forming an electrode, comprising:
loading a substrate into a plasma enhanced chemical vapor deposition (PECVD) reactor and preparing a surface of the substrate for doped diamond growth;
exposing the substrate to a pure hydrogen plasma for a preset duration; and
depositing a phosphorus doped diamond layer on the substrate to form the electrode,
wherein the electrode comprises a collector that has a work function of 0.84 eV or less.
2. The method of claim 1, wherein the wet-chemical cleaning procedure comprises:
boiling the substrate in H₂SO₄/H₂O₂/H₂O at 220° C. for at least fifteen minutes;

treating the substrate for at least five minutes using a solution comprising hydrofluoric acid; and
boiling the substrate in NH₄OH/H₂O₂/H₂O at 75° C. for at least fifteen minutes.

3. The method of claim 2, wherein the wet-chemical cleaning procedure further comprises:

rinsing the substrate with deionized water after each step.

4. The method of claim 1, wherein exposing the substrate to the pure hydrogen plasma for the preset duration comprises:

exposing the substrate to the pure hydrogen plasma at a preset temperature range for at least fifteen minutes.

5. The method of claim 4, wherein the preset temperature range comprises a low temperature not greater than 800° C. and a high temperature of at least 900° C.

6. The method of claim 1, wherein depositing the phosphorus doped diamond layer on the substrate comprises:

depositing the phosphorus doped diamond layer using a methane flow rate of 2 sccm and a 200 ppm trimethylphosphine/hydrogen (the phosphorus source) flow rate between 10 sccm and 30 sccm with hydrogen as carrier gas.

7. The method of claim 6, wherein the methane flow rate is 0.5% of a total gas flow rate of 400 sccm.

8. The method of claim 1, wherein depositing the phosphorus doped diamond layer on the substrate comprises:

depositing the phosphorus doped layer at around 900° C.-1200° C. using a microwave power of at least 2500 W and a preset chamber pressure range.

9. The method of claim 17, wherein the preset chamber pressure range comprises a range of 75 to 85 Torr.

10. The method of claim 1, further comprising:

controlling impurities during layer deposition by using a water-cooled sample stage in the PECVD reactor.

11. The method of claim 10, further comprising:

timing a growth period of the doped diamond growth for less than or equal to seven minutes;

terminating methane and TMP/H₂ flow after the growth period; and

inducing a negative electron affinity to the surface of the substrate using hydrogen plasma exposure.

* * * * *