(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 March 2003 (06.03.2003)

PCT

(10) International Publication Number
WO 03/019597 A1

(51) International Patent Classification[7]: H01J 1/312, 9/02

(21) International Application Number: PCT/IB02/03482

(22) International Filing Date: 28 August 2002 (28.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2001/7240 31 August 2001 (31.08.2001) ZA

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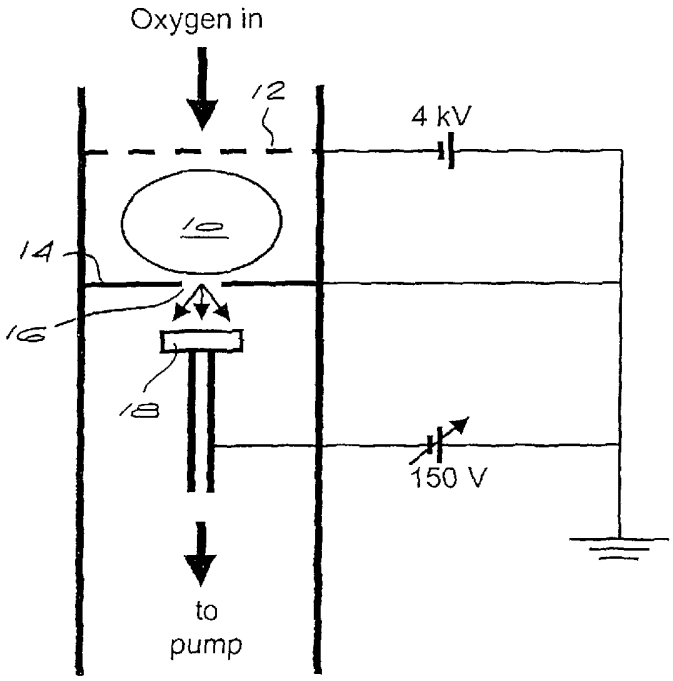
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

[Continued on next page]

(54) Title: CATHODIC DEVICE



(57) Abstract: A cathodic device having "cold cathode" properties is created by providing a substrate of diamond material having negative electron affinity characteristics, and implanting low energy oxygen or nitrogen ions to create a depletion layer at or near the surface of the substrate. The depletion layer acts as an "ohmic"-tunneling region through which conducting electrons in the substrate can tunnel and be emitted from the surface of the substrate into an adjacent vacuum. Preferably, the dopant ions are implanted at low energies, less than 1 keV.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

CATHODIC DEVICE

BACKGROUND OF THE INVENTION

THIS invention relates to a method of creating a cathodic device and to a device formed by the method.

In general, the term cathode refers to a negatively charged piece of conducting material (metal or semiconductor) that serves as an "electrode" from which electrons can be extracted for useful purposes. These electrons may, for example, be picked up by positive ions in electrolytic baths to generate chemical reactions, or be emitted into gaseous environments to assist with the generation of plasmas, or into a vacuum without any plasma generation. In the field of electronics, cathodes are usually devices, or material-vacuum interfaces, from which electrons can be extracted, or emitted, from the material into the vacuum. These electrons, once present in the vacuum, can then be manipulated, by suitably applied electric fields, to form an array of useful devices. Typical examples are thermo-ionic valves (vacuum tubes) and cathode ray tubes such as those used in televisions and computer monitors.

In order to exit a cathode and enter the surrounding vacuum, electrons usually need to scale an energy barrier. If the cathode is a metal, this barrier is roughly the same as the work function of this metal. There exist different methods to extract electrons, over such an energy barrier into the vacuum. One can apply

a very large field to the cathode surface by a suitably placed anode (field emission). Usually the latter mechanism involves some form of dielectric breakdown of the cathode material, which is accompanied by damage creation. In order to limit the latter, sharp points are usually employed to enhance the electric field that extracts the electrons. One can also excite electrons from the material by using light (photons) of the appropriate wavelength (photo-electric emission). To obtain a large enough electron current, a high intensity of light is needed, and such devices are usually bulky and inefficient for the majority of applications. It is also possible to use electron or ion irradiation of the cathode material (secondary emission). However, this is even more impractical than using photon irradiation.

Since the birth of electronics, the preferred method to extract electrons from a cathode has been to heat the latter (thermo-ionic emission). In such a conventional cathode, a suitable conductive material, such as a tungsten wire, is heated by passing a current through it. At a high enough temperature electrons "boil" out of the material, forming a cloud of electrons in the vacuum at the cathode-vacuum interface. Large electric fields, with their concomitant adverse effects on the cathode material, are then not needed to extract the electrons. The application of suitable electric fields, to this "cloud" of electrons, is then used to generate the myriad of "vacuum-electronic" devices that are known today. For example, high voltage acceleration of these electrons could be used to generate an "electron gun", which directs a beam of electrons at a phosphor-coated surface.

Thermo-ionic electronic devices have certain advantages above present day solid-state electronic devices: For example, they can handle much higher power levels. However, they are bulky, expensive and power-hungry (heating of the cathodes consumes high levels of electric power). To overcome these drawbacks, one would, ideally, prefer a cathode material that, without heating, emits electrons into the vacuum (surrounding it) at room, or even lower,

temperatures. Hypothetically, one would like an electron-conducting material, in which the latter electrons are at a higher energy than they would be at in the surrounding vacuum; i.e. the lowest energy they can be at in the vacuum (the so-called vacuum level) must be lower. It is said that such a material has negative electron affinity (NEA), and it is generally accepted in the scientific literature that, if such a material could be found or generated, one should be able to extract electrons from it into the vacuum without encountering an energy barrier. One can then use such a material to manufacture so-called cold cathodes. Such a cold cathode would require no heating to liberate electrons into the vacuum, and should, thus, provide "field emission" of electrons from its surface, without suffering any damage (even if the emitting surface is flat and smooth), when applying an electric field. Furthermore, the latter field can be low and moderate and need not be as high as required for normal field emission.

There are indications that large band gap semiconductors like, for example, diamond, cubic boron nitride, and aluminium nitride may be NEA materials, in which those electrons that are present in their conduction bands, are at higher energies than the vacuum level. For example, in a famous experiment by Himpsel et al (1979), on p-type semiconducting diamond, it was found that, when the dangling bonds on the diamond's surface are terminated by hydrogen atoms, electrons, excited by optical means into the conduction band, could be extracted into the vacuum without encountering any energy barrier. From this result, it was reasoned that n-type doped diamond, which, contrary to p-type doped diamond, has electrons in its conduction band, should be able to act as an ideal cold cathode. Much research and experimentation has been carried out in attempts to dope diamond n-type, and thus to create so-called cold cathodes.

At present, it is possible to incorporate phosphorous atoms during growth to generate n-type diamond. Many attempts have been made to manufacture

cold cathodes from the latter material. However, even when terminating the surface bonds with hydrogen atoms, the results achieved to date are dubious. In all cases, electrons could only be extracted over energy barriers, and similar physics applies as in the case of normal field emission. Even in the cases where electron emission occur when using relatively low electric fields, the processes involved could be modeled in terms of defects or graphitic patches on the surface. At best, the electron emission obtained so far, has been erratic and non-uniform over the emitting surface. A consensus seems to be emerging that the NEA effect measured on p-type diamonds, when optically exciting electrons into the conduction band, is a surface effect caused by the dipolar nature of the hydrogen-carbon bonds on the diamond's surface, and that diamond, or for that matter any other material, may not be truly NEA in nature.

However, the surface of a material is a massive defect that can change the physical properties to be different, on, at, or near, the surface from what they would be in the bulk if no surface were present. The electron energy levels can be severely affected by the surface. For example, a well known mechanism that can operate is the so-called "pinning" of the Fermi-level at the surface. Suffice to say that surfaces can be extremely complicated, and it is theoretically possible that if no surface exists, the conduction band may be situated at a higher energy than the vacuum level, but that this advantage is destroyed by the necessity to have a surface through which the electrons have to move into the vacuum.

In this respect, it is worthwhile to consider another type of interface that is generated when manufacturing an electrical contact by depositing a metal onto the surface of a semiconductor. The metal is a conductor, and this interface is thus totally different from the one to the vacuum, where the latter is an insulator. However, also in the case of the electrical contact, the surface of the semiconductor is important. Consider, for example, an n-type semiconductor with a metal contact. Even though both materials are conducting, an energy

barrier (for example, a Schottky barrier) may form that inhibits the free flow of electrons from the semiconductor into the metal when applying an electric field over the interface. To remove such a barrier the contact has to be made "ohmic". The generation of ohmic contacts on semiconductors is more of an art than a science. Many processes involving different approaches like chemical interactions between the metal and the surface, mechanical treatment of the surface before metal deposition, suitable, high density, doping near the surface, etc., are employed. The result of many of these treatments is to create a thin region at the interface through which the electrons, owing to their wave nature, can tunnel from the semiconductor to the metal and vice versa.

It is an object of the invention to provide a method of creating a cathodic device which exhibits at least some of the properties of a "cold cathode" device as discussed.

SUMMARY OF THE INVENTION

According to the invention there is provided a method of creating a cathodic device, the method comprising:

providing a substrate of a material having negative electron affinity characteristics; and

generating a layer within the substrate at, on, or adjacent to the surface thereof that will act as an "ohmic" - tunneling region through which the conducting electrons in the substrate can tunnel and be emitted from the surface of the substrate into an adjacent vacuum.

The extracted electrons can be increased and contained within the vacuum between the diamond and an extracting electrode or anode to form a long

living, stable electron-gas of very high conductivity. This gas is maintained by its ability to screen electric fields, and, in this respect, it acts as a superconductor.

The substrate may comprise diamond, cubic boron nitride, or aluminium nitride, for example. Other materials having negative electron affinity characteristics (i.e. a conduction band above the vacuum level) may also be utilised.

The "ohmic"-tunneling contact is preferably manufactured by generating a sufficient density of donor states near, and at, the surface of the NEA semiconductor, to form a depletion layer sufficiently narrow for electrons in the conduction band to tunnel through it and to be emitted into the vacuum.

The substrate is preferably doped with a large dose of suitable low energy ions in order to create the donor states needed to form a shallow depletion layer at the surface thereof.

Preferably, the dopant ions should form shallow donor states, and therefore oxygen and nitrogen ions, as discussed in International patent application no. PCT/IB00/00870, could be used when the substrate comprises diamond. It is preferable that such ions should be implanted at low energies, typically in the 1 keV range and lower.

In a preferred method, the dopant ions were implanted at energies of approximately 150 eV, and were oxygen ions extracted from an oxygen DC-plasma and directed onto the surface of the substrate by a negative bias voltage selected according to the desired electron energy, to give an implanted ion dose of approximately 2×10^{17} cm^{-2}.

The density of donor states in the depletion region should preferably exceed 1×10^{17} cm^{-3}.

The invention extends to a cathodic device formed by the above-defined method.

The invention further extends to a cathodic device comprising:

a substrate of a diamond material having negative electron affinity characteristics; and

a depletion layer at, on or adjacent to a surface of the substrate formed by doping of the substrate with oxygen or nitrogen ions at an energy of less than 1 keV, the depletion layer acting as an "ohmic" - tunneling region through which conducting electrons in the substrate can tunnel and be emitted from the surface of the substrate into an adjacent vacuum.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a simplified schematic diagram of apparatus for implanting low energy ions into a diamond substrate, used in the method of the invention;

Figure 2 is a set of graphs showing the characteristics of a diamond substrate treated by the method of the invention;

Figure 3 is a simplified schematic diagram of apparatus used to measure the electrical characteristics of the treated substrate;

Figure 4 is a set of graphs showing the relationship between current and distance between a probe of the measurement apparatus and the treated substrate; and

Figure 5 is a graph showing the relationship between current and probe potential for a given probe distance.

DESCRIPTION OF AN EMBODIMENT

A prototype cathodic device according to the present invention was created utilising a substrate material believed to have negative electron affinity (NEA) characteristics, and doping the surface and near-surface region of the substrate to a very high density with the intention of creating a narrow depletion layer near the surface which is narrow enough to allow electrons to tunnel through it and to be emitted from the surface of the substrate to form a "cloud" or "gas" of electrons adjacent the surface in a vacuum.

In the prototype method of the invention, oxygen-ion implantation was used to create the highly doped layer in diamond. As described in International patent application no. PCT/IB00/00870 it is possible to generate shallow, metastable, oxygen-related donor states by oxygen-ion implantation. All the results are consistent with oxygen atoms interacting, in some way, with vacant lattice sites in the diamond to generate these donor states. In order to test whether it is possible to generate a highly over-doped near-surface layer in diamond, which will be n-type and allow tunneling of the electrons to an adjacent vacuum, it was decided to use very low energy (150 eV) oxygen ions. With this energy, the ions will be deposited near to the surface (over the first 15 Angstrom) with

little damage to the diamond substrate (about one vacancy per ion). It is also known that a polished diamond surface already has vacancies below its surface and that the doped layer achieved should thus be deeper than 15 Angstrom, because some of the implanted oxygen-interstitials can diffuse to deeper lying vacancies to form donor levels (as described in the abovementioned patent application).

It is difficult to generate such low energy ions on a standard ion implanter. Ion implanters usually extract ions from the source with a minimum energy of about 25 keV. To obtain 150 eV ions these higher energy ions need to be slowed down. This requires sophisticated lenses and electronics. Thus, it was decided rather to extract the oxygen ions directly from an oxygen DC-plasma onto the diamond. The equipment used is illustrated schematically in Figure 1. The oxygen plasma 10 was generated between a grid 12 and a plate 14 with a hole 16 in it. The ions were then extracted out of the hole, by applying a 150 Volt negative bias, and directed onto the surface of the substrate.

A natural, high purity, type IIa diamond 18, as polished, was treated in this equipment, such that according to the current measured on the diamond, the implanted ion dose came to $\approx 2 \times 10^{17} cm^{-2}$. The resistance of the diamond was then measured with increasing temperature up to 350°C and during subsequent cooling back to room temperature. As can be seen in Figure 2 (open squares), the resistance during cooling was far lower. This can be ascribed to annealing of the radiation damage and the formation of more oxygen-related donor states. To test whether further annealing could lead to a further decrease in resistance, the diamond was annealed for another 4 hours at 400°C in a high purity Argon atmosphere. Instead of decreasing, the resistance increased, as can be seen in Figure 2. Nonetheless, the layer was still conducting, and behaved in the manner expected from O^+-ion-doped diamond when using keV-energy ions that generate donor states lying far deeper than 15 Angstrom below the surface.

To test whether this decrease could be ascribed to contaminants on the surface, the diamond was boiled in an oxidising acid solution containing sulphuric, nitric and perchloric acids. As can be seen in Figure 2, the resistance and its behaviour stayed basically the same. Thus it seems more probable that during the subsequent 400°C anneal, some of the implanted oxygen donors may have become deactivated. As already mentioned, these oxygen donors are metastable: they anneal out at higher temperatures. The surface affects defects, and it is thus quite possible that those nearer the surface could be more unstable than those situated deeper, which were created by in-diffusion of the oxygen ions. Accordingly, the plasma treatment was repeated, and the same measurements done (filled squares in Figure 2), but this time the diamond was maintained, while allowing an electric current to flow through it, above 350°C for 24 hours before cooling it.

The diamond was then mounted in a high vacuum system (vacuum better than 10^{-6} mbar), which contained a probe, schematically shown in Figure 3, to detect any cold cathode action. This is a typical experimental arrangement that has been employed in different laboratories to test for possible cold cathode action. The probe used, and shown schematically in Figure 3, has been designed to facilitate accurate measurement of the gap distance between the diamond and the probe point. It comprises a cylindrical plunger-like body 20 formed from insulating material and moveable axially within an open-ended tubular housing 22. A micrometer movement (not shown) was used to move the whole assembly towards or away from the treated diamond. The probe point 26 is gold plated and has a radius of 0.5mm. When it is moved onto the surface of the diamond substrate 18, the cylindrical plunger 20 presses upwards against the spring 24, a switch consisting of two metal pins opens, and the ohmmeter measures an open circuit. By pulling the point away from the surface the metal pins make contact and the ohmmeter measures a closed

circuit. This gives a calibration point, which can be used to determine when the probe breaks contact with the surface.

The probe was pushed against the diamond substrate surface and a positive potential of 1000 Volt was applied to the probe point. A current of just over 0.5 mA flowed: i.e. the resistance of the diamond between the contact and the probe was just under 2 MΩ. The probe was then moved to a position 1 micrometer away from the diamond's surface. The current dropped, but did not go to zero. It, at first, decreased to about 0.29 mA, and then increased again to the same value it had when the probe made contact to the surface. The probe was then pulled back to increase the gap to 2 μm. Again, the current at first decreased, this time to about 0.12 mA, but it recovered, again, with time. This kept on occurring as the gap was increased. The results can be seen in Figure 4.

After the measurements at 4 μm, the system was allowed to stabilize for a far longer time than before. When moving to 5 μm, the drop in current was less. After that, the time for stabilization, after each 1 μm increase in the gap, was made even longer, and the probe could be moved right out to 16 μm before the current dropped away. It was then found that by moving the probe back towards the surface, one could again pick up the current of ≈ 0.5 mA before reaching the surface, and again increase the gap slowly without losing it. However, if one increased the gap too fast, the current fell away very quickly. The slight increase in current with increasing gap indicated in Figure 4 is probably a result of the diamond heating up owing to the current flowing through it. It is thus clear that the current (electrons) that exits the diamond into the vacuum, is after its stabilization, the same as when the probe is touching the diamond's surface. In a follow up experiment on another diamond, the gap could be increased to 100 μm, before the current fell away to zero.

After the measurements with the positive potential, shown in Figure 4, were completed, the probe was again moved onto the surface and the voltage switched to negative, before pulling it away from the surface. The fascinating result ensued that the current did not drop away after moving the probe to leave a gap of 1 μm. This result is also shown in Figure 4. However, as can also be seen in Figure 4, further increases in the gap between the probe and surface caused a decrease in the current, which now did not recover to the higher value at zero gap distance, until at 7 μm it became zero.

The positive voltage was again used, and after the current stabilized at a gap distance of 10 μm, the potential was changed from +1000 Volt in steps down to -1000 Volt, while monitoring the current. The result can be seen in Figure 5. For the same magnitude of the potential, current flow occurred in both directions with the same magnitude when the polarity was changed from positive to negative. Furthermore, when pushing the probe against the surface, exactly the same curve is measured; i.e. the current is the same, whether there is a gap or not. This means that the voltage drop over the gap is negligibly small compared to the voltage drop over the diamond itself. Current flow through the gap, when a negative potential is applied to the probe, requires electrons to be emitted from the probe point and then enter the surface of the diamond. It is understandable that electrons in the gap can be pushed back into the diamond, because this proves that the objective of creating an "ohmic"- tunneling contact between the diamond and the vacuum has been achieved. However, the probe point consists of metal, and it is thus not an NEA material. It's Fermi level should be situated below the vacuum level. Emission of electrons from the probe point into the gap, without encountering a barrier, can only occur if the metal's Fermi level is at the same energy as the vacuum level. The fact that the current is actually measured, means that the latter must have actually occurred: the Fermi level of the metal probe must have equilibrated with the vacuum level.

In the derivation of the Child-Langmuir equation for electron transport between a cathode and electrode in a hot filament vacuum diode, the current density J as a function of average electron density at an applied potential V, can be written as:

$$J = -ne\left[\frac{2eV}{m}\right]^{1/2}$$

where n is the average density of electrons, m an electron's mass and e an electron's charge. If n increases, the current will increase. As seen in Figure 4, the current at first fell when the probe (with a positive potential on it) was pulled away from the surface of the diamond. However by leaving it for a while the current increased. This could only happen if more electrons entered the gap.

Obviously, the more electrons there are, the easier conduction will be: i.e. the resistance of the gap decreases. This decrease means that less voltage V is required to sustain the same current. Thus the voltage drop over the gap decreases, and appears over the diamond. The current through the diamond increases, and more electrons enter the gap. This keeps on occurring until most, and most probably all, the voltage drop is over the diamond. The current cannot increase anymore because there is no more voltage available, and it thus stabilises at the same value one would measure if there were no gap at all.

It is now simple to deduce why, under these circumstances, current can also flow in the reverse direction. The gap is not a pure vacuum gap anymore. It contains a high density of electrons and is highly conducting. In other words, it acts as a metal with its Fermi level at the vacuum level. Another metal making contact with it, has no choice but to align its Fermi level with the vacuum level: i.e. an ohmic contact to the electron cloud within the gap ensues. Because

there are now effectively ohmic contacts at the diamond surface as well as the probe surface, the current can flow with ease (encountering no barriers at all) either way through the gap.

Although the term “ohmic” is a misnomer for an interface between a semiconductor and an insulator, by lateral thinking, the present invention extends this concept to the case where one has an interface between an NEA material and the vacuum. The invention shows that in order to extract electrons from the conduction band of an NEA material (so that they can reside outside the material in the adjacent vacuum) without having to scale an energy barrier, one has to construct a thin “ohmic” tunneling barrier at the surface of the NEA material through which the electrons can be extracted into the vacuum.

Once formed, this "vacuum-electron-gas" or "cloud" is remarkably stable. One can switch off the potential, and leave it off for days before switching on again, and the conduction will be there immediately. One can change the voltage instantaneously from one value to another, and the current will adjust to the corresponding value shown in Figure 5. Thus, the electron cloud within the gap forms a stable (or a long-lived metastable) material phase that consists entirely of electrons trapped within the vacuum region between the diamond and the metal probe.

The current flowing through it stabilises when it reaches the same value as the maximum current that can flow through the diamond when applying the same voltage directly to the diamond. This implies that the current flows through the gap with zero, or very near to zero, voltage over the gap.

In a follow-up experiment, nitrogen ions were used to generate the donor states needed in the depletion region. The same results were obtained as described above for the oxygen ions.

CLAIMS

1. A method of creating a cathodic device, the method comprising:

providing a substrate of a material having negative electron affinity characteristics; and

generating a layer within the substrate at, on, or adjacent to the surface thereof that will act as an "ohmic" - tunneling region through which conducting electrons in the substrate can tunnel and be emitted from the surface of the substrate into an adjacent vacuum.

2. A method according to claim 1 wherein the substrate comprises diamond, cubic boron nitride, or aluminium nitride.

3. A method according to claim 2 wherein the substrate comprises a type IIa diamond.

4. A method according to claim 2 or claim 3 wherein the substrate has a polished surface.

5. A method according to any one of claims 1 to 4 wherein the "ohmic"-tunneling region is manufactured by generating a sufficient density of donor states near, and at, the surface of the substrate, to form a depletion layer sufficiently narrow for electrons in the conduction band to tunnel through it and to be emitted into the vacuum.

6. A method according to claim 5 wherein the substrate is doped with a large dose of suitable dopant ions in order to create the donor states

needed to form a shallow depletion layer at the surface of the substrate.

7. A method according to claim 6 wherein the dopant ions are oxygen or nitrogen ions.

8. A method according to claim 6 or claim 7 wherein the dopant ions are implanted at low energies.

9. A method according to claim 8 wherein the dopant ions are implanted at energies of less than 1keV.

10. A method according to claim 9 wherein the dopant ions are implanted at energies of approximately 150 eV.

11. A method according to any one of claims 7 to 10 wherein the dopant ions are oxygen ions extracted from an oxygen DC-plasma and directed onto the surface of the substrate by a negative bias voltage selected according to a desired electron energy.

12. A method according to any one of claims 6 to 11 wherein the implanted ion dose is approximately 2×10^{17} cm^{-2}.

13. A method according to any one of claims 6 to 12 wherein the density of donor states in the depletion region exceeds 1×10^{17} cm^{-3}

14. A cathodic device comprising:

a substrate of a diamond material having negative electron affinity characteristics; and

a depletion layer at, on or adjacent to a surface of the substrate formed by doping of the substrate with oxygen or nitrogen ions at an energy of less than 1 keV, the depletion layer acting as an "ohmic" - tunneling region through which conducting electrons in the substrate can tunnel and be emitted from the surface of the substrate into an adjacent vacuum.

Figure 1

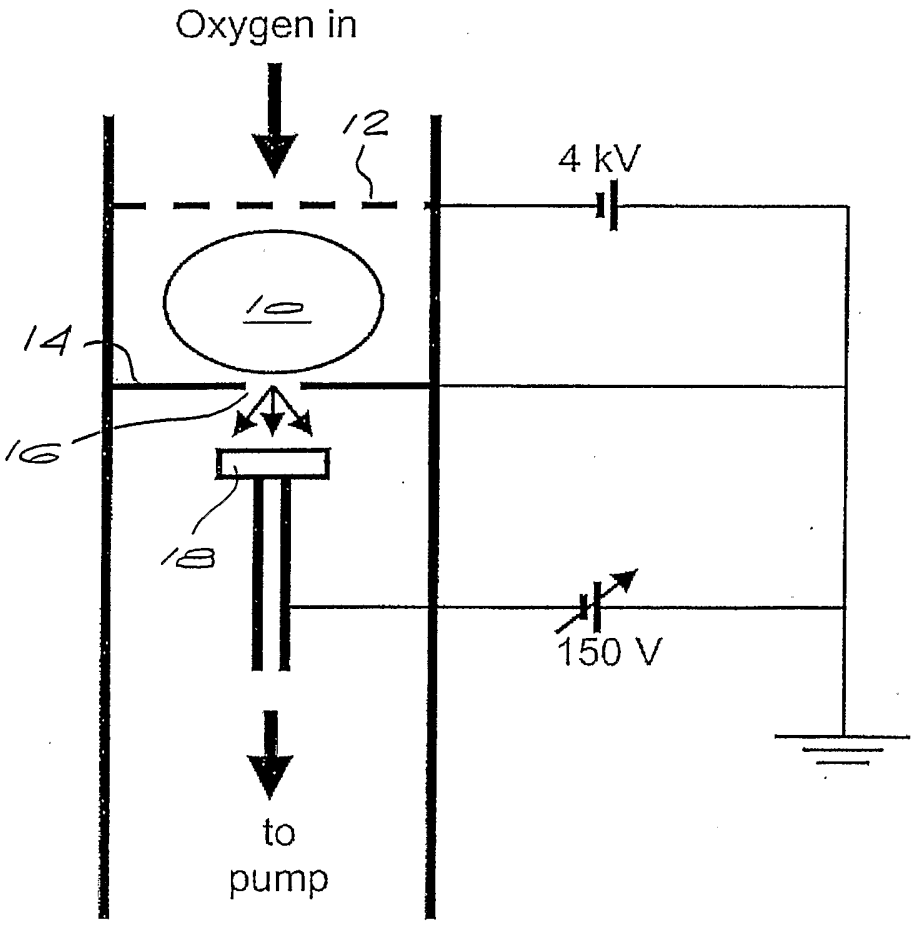
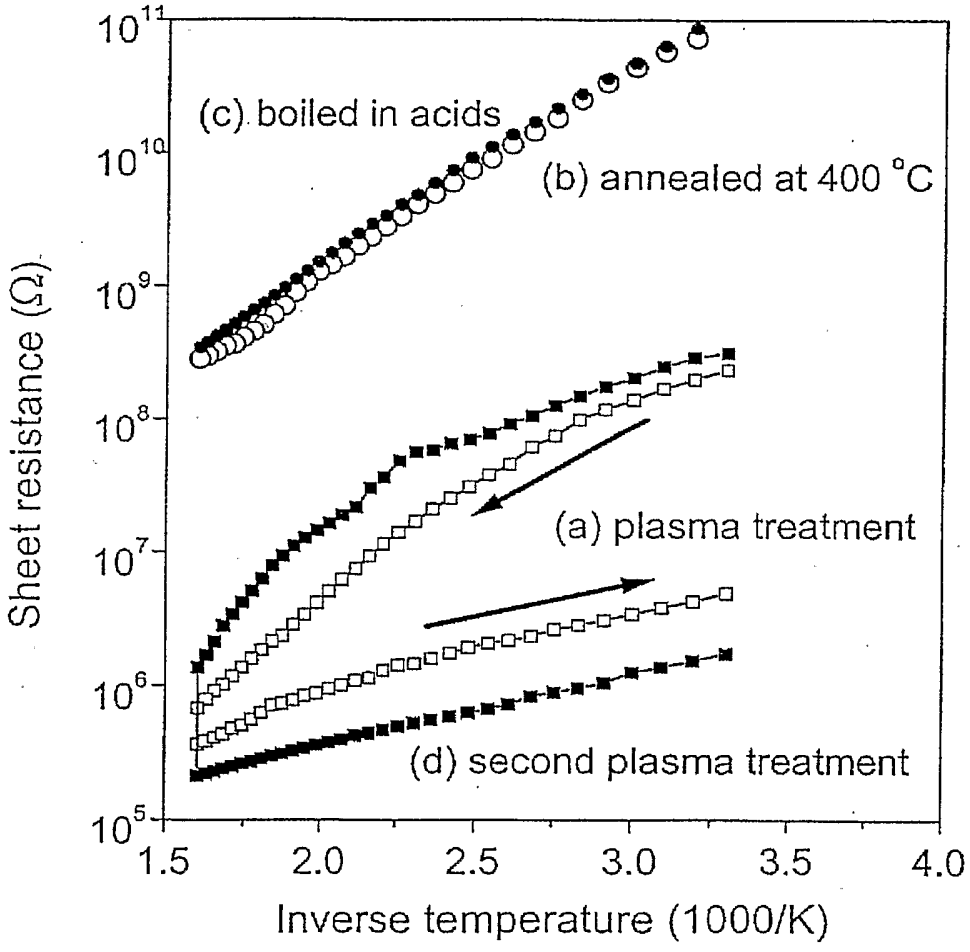


Figure 2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10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
(c) boiled in acids
(b) annealed at 400 °C
(a) plasma treatment
(d) second plasma treatment
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2.0
2.5
3.0
3.5
4.0
Inverse temperature (1000/K)

Figure 3

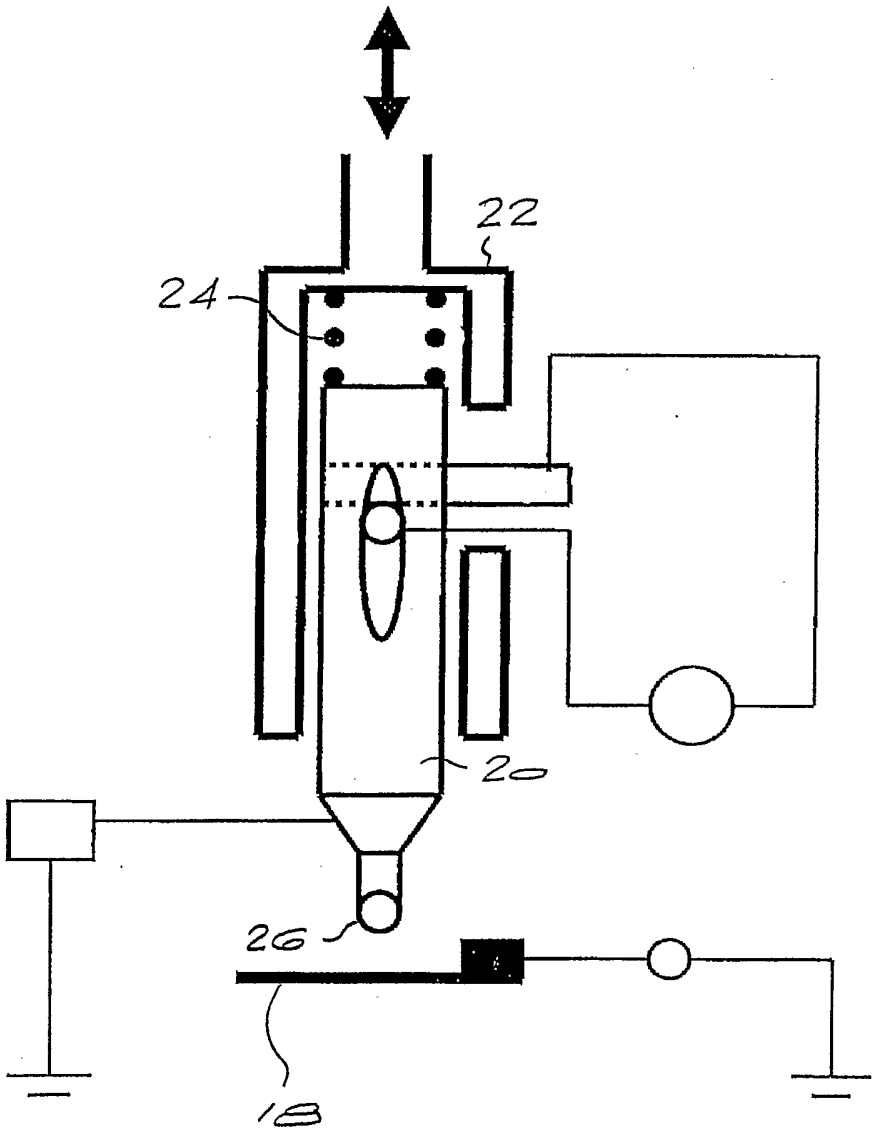
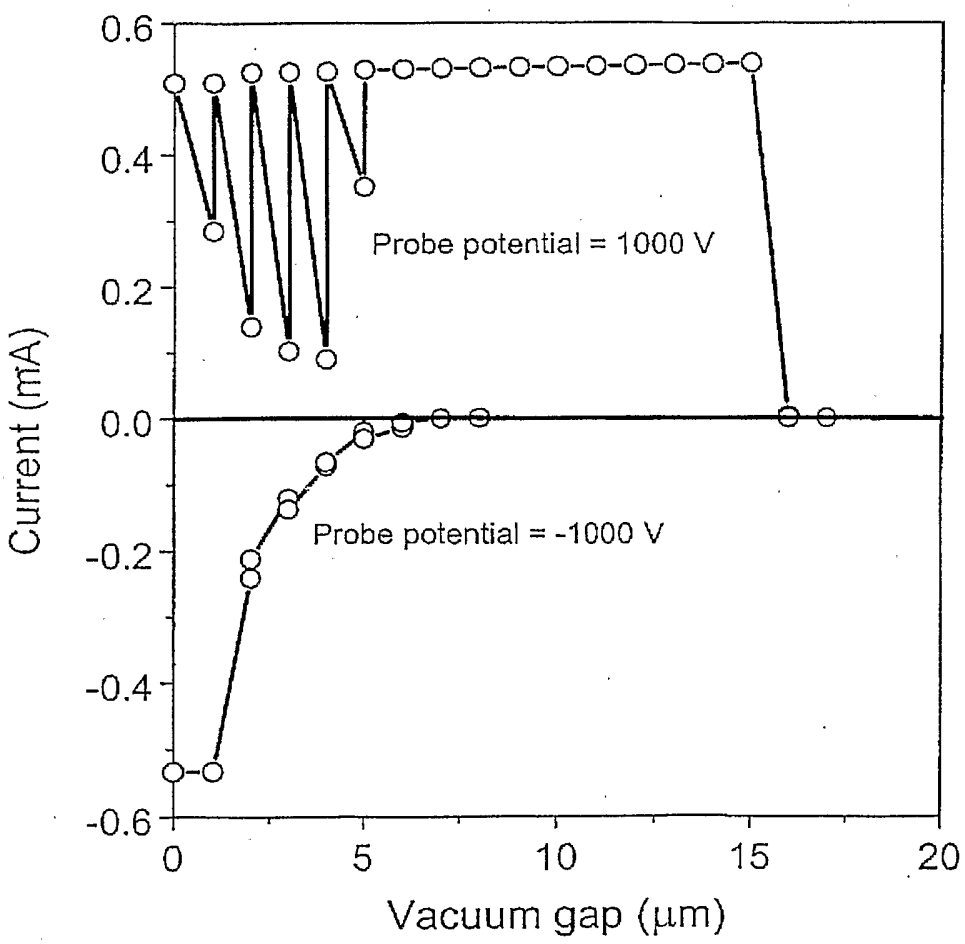


Figure 4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0.2
0.0
-0.2
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Probe potential = 1000 V
Probe potential = -1000 V
0
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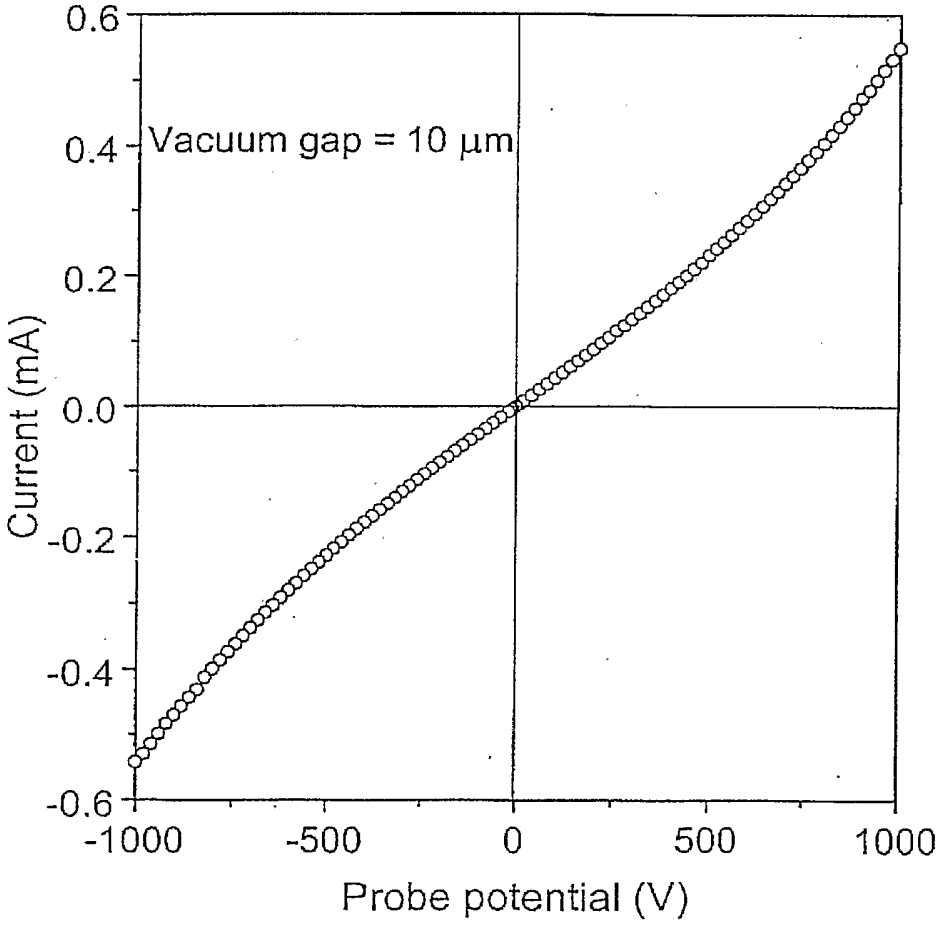
10
15
20
Vacuum gap (μm)

Figure 5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Current (mA)
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500
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Probe potential (V)

INTERNATIONAL SEARCH REPORT

Internati Application No
PCT/IB 02/03482

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01J1/312 H01J9/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01J

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

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

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y		13
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[X] Further documents are listed in the continuation of box C.

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3 February 2003	13/02/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Weisser, W

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Internat Application No
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