THIS INVENTION relates to an electrical flow path, a conductor, an electronic component and an electronic device.

The Applicant has shown that low-energy ion-implantation of diamond using an oxygen-plasma, can produce a high density of electron donor-sites very near to and below the surface of the diamond so that electrons can be extracted from such a diamond by an electric-field between the surface of the diamond and an anode (PCT/IB02/03482). The experimental arrangement is shown schematically in Figure 1. The Applicant found that, above a critical voltage, a black rod, which connected the diamond-surface to the anode, formed and an equilibrium-current then flowed through the circuit. Without being bound by theory, the Applicant believes that, when electrons are extracted perpendicularly from the diamond surface, a dipole layer consisting of positive donor charges just below the surface and external electrons tightly bonded to the surface by these positive charges, forms across the surface. By applying a voltage by means of the anode, the dipole layer grows in width until the externally bonded electrons make contact with the anode. An electron-current can then flow perpendicularly to the diamond's surface from the diamond through the externally-bonded electrons into the anode.

Without being bound by theory, but based on the physics-models of solid state electronic interfaces, the Applicant believes that there is no electric-field present along the rod even though it transfers a current from the diamond to the anode. Since this is the defining behaviour that

Kamerlingh-Onnes discovered for superconduction in 1911, it appeared that the rod is a superconducting phase.

The possible electronic applications of the phase that forms in this manner are at present limited. It would be preferable if lateral flow, low resistance regions could be produced on, for example, an electronic chip. It is thus an object of the invention to produce a low resistance electrical flow path in which external electrons can move freely along the surface of a substrate such as oxygen-doped diamond. Ideally such regions should be superconducting, but even if they only have a much lower resistance than the connecting materials used at present, their generation would have a substantial impact on the speed and size of electronic chips incorporating such a doped substrate.

It is well known in the scientific literature on diamond that low energy oxygen-ion treatment of a diamond substrate totally quenches all lateral conduction along the surface of such a diamond. Only when using hydrogen has lateral conduction been observed, but this occurs below the surface of the diamond. In fact, if such a hydrogen-treated diamond is subsequently subjected to oxygen-ion treatment, even this conduction is quenched and thus disappears: The surface then becomes insulating along the lateral direction.

The Applicant has now found that by increasing the density of implanted oxygen ions (below and near to the surface) to very high values while, during the latter treatment, annealing the diamond to prevent the diamond surface from becoming graphitic, then, in contradiction to what has been reported in the scientific literature, lateral conduction does eventually initiate. It thus appears that, at these ion densities, the oxygen-plasma treatment no longer quenches lateral conduction, but actually causes conduction to occur. Subsequent experiments have shown that this lateral conduction occurs on the surface of, and externally to the diamond. This implies that some of the electrons which are bonded to the surface (to in this manner form a dipole layer across the surface) become free to transport a current laterally on the surface, and externally to the diamond. This produces an extremely low-resistance and hence an extremely low resistivity, pure-electron, conducting-phase external to the surface. This phase can be employed in the design and manufacture of novel electronic devices. The resistivity of these phases is far lower than that of the known metals and materials normally used to make connections on electronic chips.

It was subsequently found that the same conduction can also be generated when using nitrogen ions; and even hydrogen ions, provided that in the latter case the subsurface of the diamond is first pre-treated by low-energy carbon-ion implantation to generate a high density of vacant lattice sites. Any other ion (and even electrons) can also be used for the latter purpose, provided that a layer with vacancies forms near and below the surface. After subsequent hydrogen-plasma treatment, the conduction obtained is then not subsurface anymore, but also in this case occurs by free electrons which can move laterally and externally to the diamond.

Thus according to a first aspect of the invention, there is provided an electrical flow path, at least part of which is formed by a body of a substrate material at least part of which is a doped part having a surface and implanted atoms at or below the surface, at least part of the surface defining a low resistance section of the electrical flow path.

The electrical flow path may be part of a circuit which may include a voltage source. The body of substrate material may form part of an electronic component and the circuit and the electronic component may be part of an electronic device.

The electronic component may be connected to the flow path by connectors. The resistivity of the low resistance section of the electrical flow path may be less than about $2X10^{-8}$ Ω-m and will probably be less than about $5X10^{-13}$ Ω-m.

The substrate material may be selected from materials which have low electron-affinities, like for example, diamond, carbon-based materials like graphene or graphene-dominated materials, polymers, cubic boron nitride, aluminium-nitride, gallium-nitride, ß-alumina and the like.

The implanted atoms may be selected from oxygen, hydrogen, lithium, nitrogen, fluorine, chlorine, sulphur, phosphorus, arsenic and the like.

The connectors may be gold connectors, but should preferably have even lower electronic work-functions.

At least some of the implanted atoms may be at depths of between about 0,1 Å and 5000 Å below the surface of the substrate. The density of the implanted atoms may be between about 10^{17} cm^{-3} and 10^{23} cm^{-3}.

According to another aspect of the invention, there is provided a conductor which includes an elongate substrate having a longitudinal surface which defines a current flow path extending along the length thereof, wherein at least part of the surface is a doped part.

According to another aspect of the invention, there is provided a conductor which is circular around a hole which defines a current flow path around the hole.

According to another aspect of the invention, there is provided an electronic device which includes an electrical flow path, at least part of which is formed by a body of a substrate material at least part of which is a doped part having a surface and implanted atoms at or below the surface, at least part of the surface defining a low resistance section of the electrical flow path.

In a series of experiments, two gold-plated metal contacts were brought into contact with the surface of a diamond substrate which had been plasma-doped with oxygen atoms. The resistance between the contacts along the surface of the diamond was measured. Since the diamond was subjected to consecutive plasma-treatments in order to measure the resistance as a function of the ion density, the resistance measurements required that the two contacts must be mechanically pressed onto the diamond surface. This introduced a measure of irreproducibility in the results. However, the latter process allowed the measurement of the resistance as a function of ion-dose. To minimise the irreproducibility, a measuring-apparatus was eventually constructed as shown schematically in Fig. 2. In this case the treated diamond surface was lowered onto two gold-plated glass slides by a spring-loaded micrometer. The distance L between the contacts could be changed so the resistance could also be measured as a function of L.

An example of the change in resistance with implanted oxygen-ion dose is shown in Figure 3. These measurements were all made for the same distance L between the contacts. At first nothing could be measured, just as expected for the oxygen-ion plasma-treatments which have been reported in the literature. But after an incubation ion-dose, measurable conduction appeared. As the ion dose increased further, the resistance decreased and then saturated at an average value of about 200 kΩ. This suggests that the density of donors nearest to the surface cannot increase indefinitely and reaches a saturated maximum value. This result was consistently produced in a number of diamonds and the scatter in the results could in all cases be solely ascribed to the irreproducibility in the contact resistances.

When the distance between the contacts was increased the resistance, within experimental error, did not change. This indicates that the measured resistance was dominated by the resistances of the contacts and that the diamond substrate had a near zero resistivity. Figure 4 shows the current as a function of the distance L between the two contacts for the same voltage at six different distances L between the contacts. The data points fall well within the normal scatter obtained for all these experiments, indicating that the current is the same for any distance L.

Without being bound by theory, if the near-surface donors emit enough electrons for some of them to accumulate on the surface as free electrons which can then transport a current laterally with low resistivity, the contacts will encounter such electrons as soon as they are pressed against the surface. Therefore those electrons, which are present on and around the contact areas before pushing the contacts onto the surface, should under these conditions flow into the metal-contacts. This will in turn generate a dipole over the diamond-metal interface and each metal-contact will then become negatively-charged. Such a contact will then push surrounding free electrons (if they are present on the surface) away. This is schematically illustrated in Figure 5 which shows high resistance gaps of lengths ΔL which form at the contacts. The circles represent the electrons schematically.

In a number of experiments, using different diamonds, the same results were obtained within experimental error. When a longer type Ib diamond was used the voltage over two points between, and spaced far away from the two contacts, was measured but the voltage was so low that it was not possible to make a reliable measurement. This suggested that the resistivity between the contacts was far lower than the resistance of the contacts. Again without being bound by theory, these results suggested that the current is transported by free electrons on the surface but do not prove this conclusively since the current might be transferred below the surface.

However, the following analysis is completely commensurate with conduction on and external to the surface:

If it is assumed that, for a distance L, the material between the contacts has a resistance R_P and each contact has a resistance R_C. The total resistance R_Ω is then given by:

$$R_\Omega = R_P + 2R_C$$

(1)

Assuming the diamond to have a width w, the apparent sheet resistivity can then be written as R_{AS} where:

$$R_{AS} = \frac{wR_\Omega}{L} = \frac{wR_P}{L} + \frac{2wR_C}{L}$$

(2)

Assuming conduction on and external to the surface, the resistance caused by the gaps ΔL shown in Figure 5 must be subtracted so that the actual sheet resistivity R_S of the electron-phase in the gap L between the contacts will then be:

$$R_S = \frac{wR_P}{(L - 2\Delta L)}$$

(3)

Eq. 2 can thus be written as:

$$R_{AS} = R_S\left(\frac{L - 2\Delta L}{L}\right) + \frac{2wR_C}{L}$$

(4)

For L very large, one will have that $R_{AS} \rightarrow R_S$. However, if the external electron phase has zero-resistivity, then R_S will be negligible for any value of $L \geq 2\Delta L$ right up to infinity. The second term will then completely determine the apparent sheet resistivity R_{AS}: When extrapolated to infinite values for L, R_{AS} must then decay inversely with L towards zero. A plot of R_{AS} as a function of inverse length 1/L must then give a linear relationship with a slope equal to ($2wR_C$) which extrapolates to zero for R_{AS} when 1/L goes to zero on the graph.

The apparent sheet resistivity R_{AS} is plotted in Figure 6 as a function of inverse L used in a single set of measurements on one of the diamonds. The data-point for very small L is shown in the bottom inset. A linear least squares fit was carried out using all the points. This resulted in the solid line and a value for R_S=-28 Ω (see top inset in Figure 6). Since the smallest distance could be affected by serrations at the edges of the glass slides, a least square fit was also carried out by neglecting this point. This resulted in the dashed line in Figure 7 which gives an even lower sheet resistivity when L^{-1}=0. A sheet resistivity can never be negative so that these results are consistent with a very small resistivity, and strongly indicate zero resistivity. If a constant value for the contact resistances is not used but the assumption is made that they, in addition, decrease with increasing contact area, as they should when the conduction occurs below the surface, the sheet resistivity extrapolates to even larger negative values for "infinite" L. This is further evidence that the conduction is not occurring below the surface.

Subsequent measurements using more data points were all consistent with the conclusion that the sheet resistivity extrapolates to be near, if not exactly, zero when L becomes infinitely long.

The invention is now described, by way of example with reference to the following Examples and Figures, in which:

Figure 1 is a schematic illustration of the experimental arrangement used in PCT/IB02/03482 to extract electrons from a highly-doped n-type diamond into the vacuum;

Figure 2 schematically shows the experimental set-up used to lower an implanted diamond-surface onto two contacts that can be adjusted to have different distances L between them: The arm which lowered the diamond was spring loaded and had a micro-switch which opened as soon as the spring reached a certain compression;

Figure 3 is a typical plot (not the best one) showing the change in resistance as a function of implanted oxygen-ion dose;

Figure 4 is a magnified plot showing current as a function of the distance L between two contacts for the same voltage at six different distances L between the contacts on the surface of an oxygen-doped diamond;

Figure 5 schematically shows how gold-contacts become negatively charged and generate regions around them of length ΔL which have a high resistance, thus causing the contacts to dominate the resistance measurements when a current flows on, and external to the surface from one contact to the other;

Figure 6 shows the apparent sheet resistivity as a function of the inverse of the distance L between the contacts; a least squares fit through the data points, extrapolates to a negative resistivity for $L^{-1}=0$ (i.e. for L equal to infinity);

Figure 7 shows current measured through a doped type Ib diamond as a function of the vertical distance d of the contacts from the surface; data for the minimum and maximum distances between the contacts are shown.

Figure 8 shows a circular ring of diamond which has been treated by an oxygen-ion plasma so that it can conduct by external electrons on the surface; a circular current could be induced around the hole by applying an increasing magnetic-field; after switching off the magnetic field, the ring trapped magnetic flux within the hole; and

Figure 9 is a schematic illustration of a conducting device having a pure-electron channel capped with a gold metal foil generated on a diamond substrate by means of oxygen-ion implantation; the resistivity was lower than for the metal layer without an electron-channel and was in fact too low to be measured.

Example 1

To generate free electrons externally to the surface of a diamond, so that lateral charge transfer could take place along the surface, the surface of a natural type IIa (high purity) diamond with a surface area of 3.6x3.6 mm^2 was cleaned by boiling in a solution of hydrochloric, perchloric and sulphuric acids and then rinsed in distilled water. The cleaned diamond was heated and doped with oxygen by ion implantation with oxygen ions using a plasma implantation-apparatus. The diamond was biased at 150 volt in order to generate implanted atoms near to the surface and a number of implantations were carried out. Each implantation was conducted for a short period of about 60 seconds. Each implantation was carried out after the table on which the diamond was mounted had been heated to a temperature of 400°C. After each implantation step, the diamond was cooled to room temperature and removed from the vacuum system. The electrical resistance between two gold-plated metal contacts, spaced a distance L apart, was then measured by pushing the contacts onto the doped diamond-surface and recording the current as a function of the applied voltage. The results are shown in Figure 3.

As the ion dosage increased (shown as implantation time on the x-axis in Figure 3), an incubation ion-dose was reached beyond which conduction could be measured. With increasing ion-dose, the resistance dropped and, at higher doses saturated to the same value, within experimental error.

This process was repeated using different diamonds. Although there was a degree of scattering in the values of the measured resistance, the resistance in each case settled within experimental error at the same value when the same ion-energy was used.

Example 2

The process of Example 1 was repeated but the distance L between the contacts was changed. Again, the resistance in each case settled within experimental error at the same value as that obtained in Example 1 when the same ion-energy was used.

Example 3

In a variation of the process of Example 1, a relatively long diamond was used. The two contacts were displaced to be at various distances L of between 0.01 mm and 3.1 mm. The experimental set-up is schematically illustrated in Figure 2. The resistances for different distances L between the contacts were measured and the results are shown in Figure 4. From the figure it can be seen that, for distances L from 0,01 mm to 3,1 mm, the average value of the current was slightly above 0.35mA. The current for L=0.01 mm was lower than that for L=3.1 mm even though the latter distance is 310 times longer. This suggests that, within experimental error, the current is the same for all values of L.

Example 4

The process of Example 3 was repeated using a relatively long synthetic type Ib diamond. When moving the diamond vertically relative to the contacts, the total resistance was measured as a function of the micrometer-movement. The accuracy was ±0.2 μm. Special care was taken to ensure that the diamond's surface was parallel to the surfaces of the contacts. The currents measured between the contacts for smallest and largest distances between the contacts given by L=0.01 mm and L=3.1 mm, as a function of vertical micrometer movement, are shown in Figure 7.

From the position at which the micro-switch acts, up to a micrometer-movement of 22.5 μm, the diamond was still touching the contacts although with decreasing pressure. The vertical bar in Figure 7 shows the distance at which the diamond clears the contacts. At that point the vertical distance d between the surface of the diamond and the contact-surfaces is zero. In both cases a current flows when the gap distance d is larger than zero. This shows that an external electron-phase is present between the diamond-surface and the contacts.

For the distance L=0.1 mm between the contacts, the current stabilised at about 0.15 mA. Current-flow at this value could be measured up to a value of d≅82.5 μm. For the large gap between the contacts L=3.1 mm, the current started to stabilise but collapsed to zero at a distance d≅10 μm. In the latter case the contacts covered a far smaller surface area of the diamond than in the case where L is very small.

Example 5

In order to totally exclude any metal-contacts to the conducting material, a diamond substrate was laser-machined to form a ring as shown in Fig. 8. The ring was then plasma-treated with oxygen-ions so that its external surface became conductive. A circular current was induced around the hole of the ring by increasing a magnetic-field perpendicular to the conducting surface of the ring and thus also through the hole. After the magnetic-field reached its maximum value, it was switched off. A magnetometer was used to confirm that a magnetic-field remained trapped within the hole of the ring. This can only occur when the current decays very slowly, or does not decay at all; thus proving that the phase on the surface of the diamond has a very low resistance; which might even be zero.

Example 6

In order to produce a device for which there is no gap **L**, i.e. to generate a phase between the diamond and a single metal contact-layer on top of the external electron-layer a channel was generated within a diamond by a series of high-energy carbon-ion implantations to a very high dose, followed by annealing and etching away the graphitised material in a boiling solution of hydrochloric, sulphuric and perchloric acids. The channel depth was estimated to be $d \sim 1$ μm or more. The bottom of the channel was then rendered n-type conducting by implanting suitable shallow oxygen-donors within the channel to a very high dose. A gold foil was placed on top of the channel and secured in place with an adhesive along its edges. The device is schematically illustrated in Figure 9. The distance between the base of the channel and the surface of the metal was, in different embodiments, between about 3-5 Å and 100 μm. The resistance inside the channel was measured and compared to the resistance inside the channel of a similar device in which the ion implantation step had been omitted. The resistance was found to be far lower for the device that had been implanted and was, within the accuracy of the measuring equipment, essentially zero.

All the measured results show that conduction occurs by means of free charge-carriers outside the diamond surface.

DATED THIS 14th DAY OF APRIL 2011

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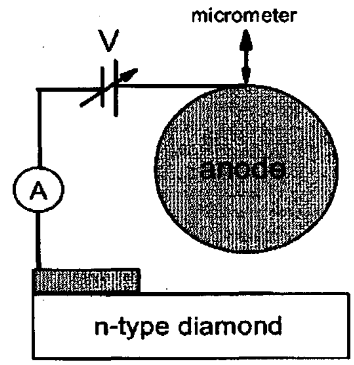

FIG 1

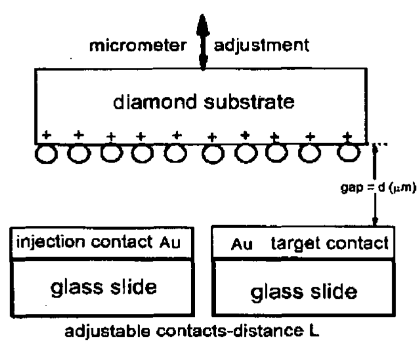

FIG 2

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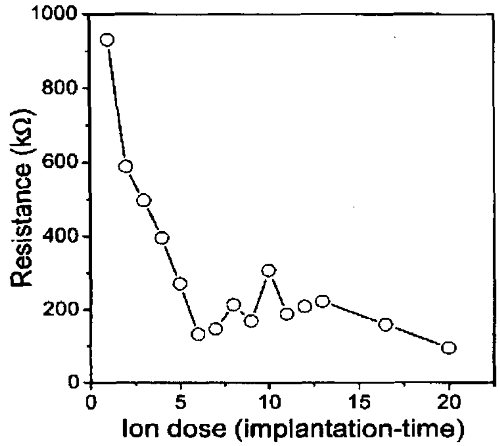

FIG 3

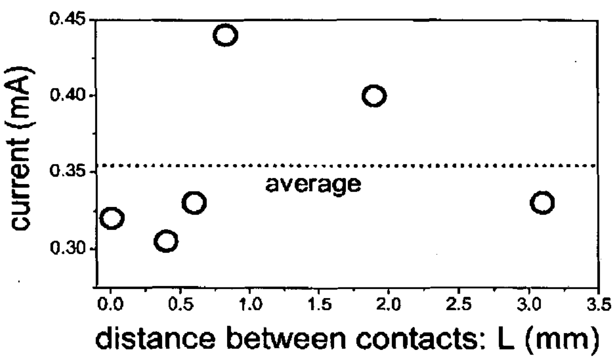

FIG 4

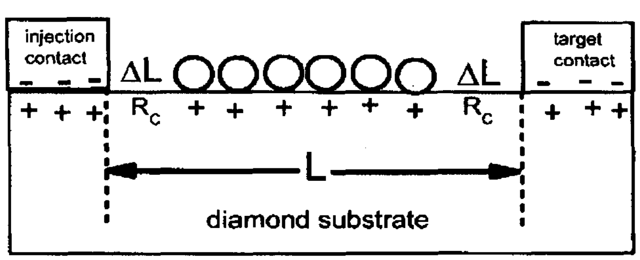

FIG 5

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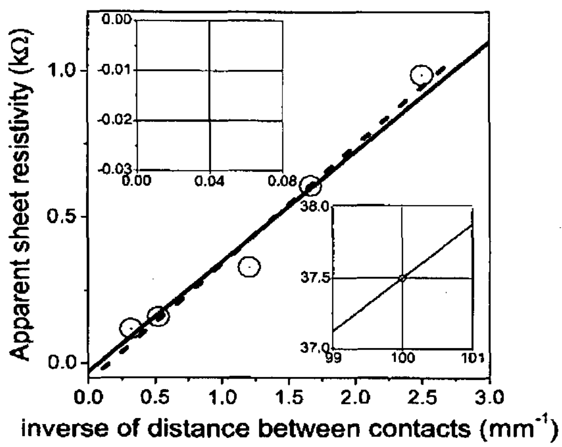

FIG 6

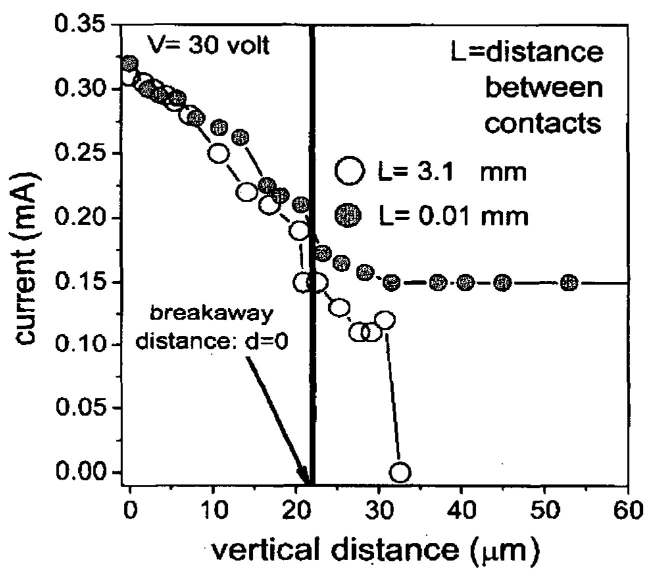

FIG 7

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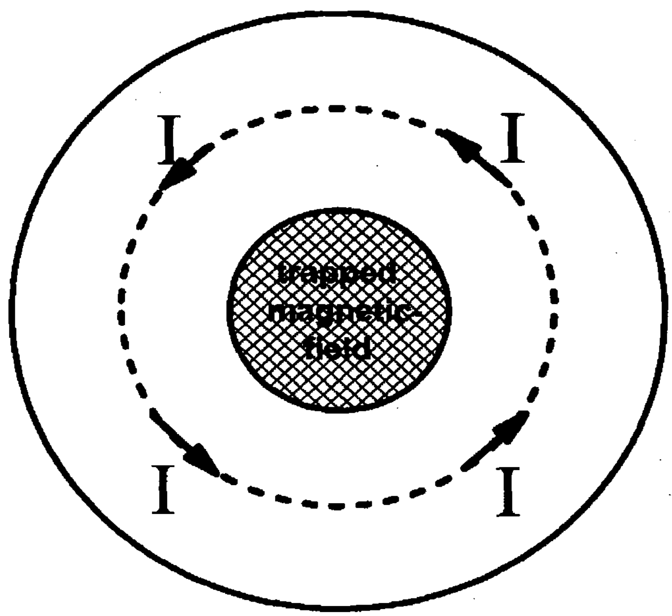

FIG 8

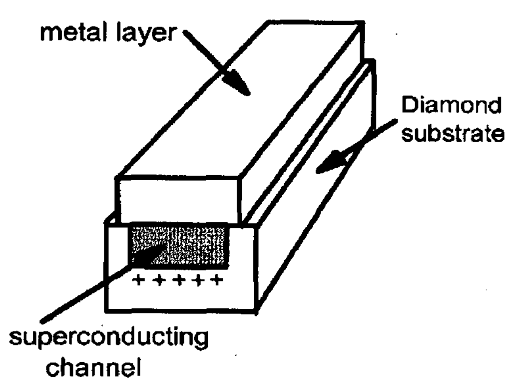

FIG 9

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