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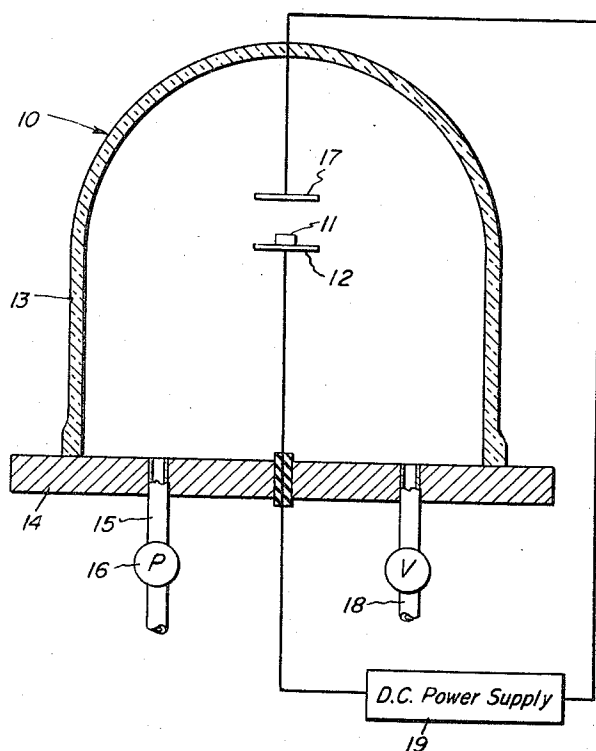
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PROCESS FOR DOPING A DIAMOND IN A GASEOUS ELECTRICAL DISCHARGE

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2 Sheets-Sheet 1

Fig. 1.



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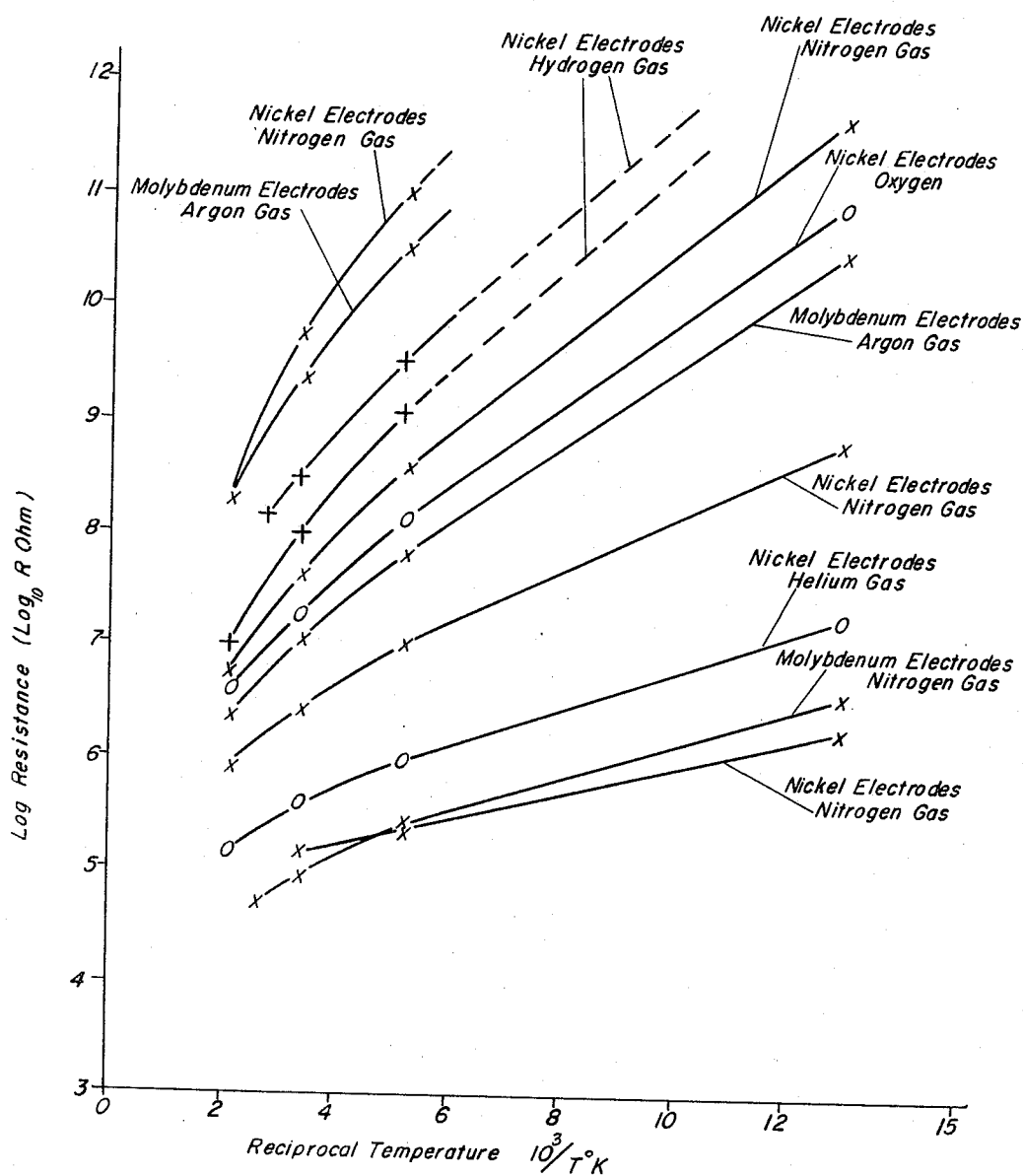
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2 Sheets-Sheet 2

Fig. 2.



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1

3,317,354

## PROCESS FOR DOPING A DIAMOND IN A GASEOUS ELECTRICAL DISCHARGE

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4 Claims. (Cl. 148—1.5)

This invention relates to the transformation of diamond, which is ordinarily a very good insulator, into an electronic semiconductor and more particularly to the introduction of additional energy levels in the surface region of a diamond crystal by bombarding the surface area thereof with gas ions by means of a glow discharge.

According to the atomic theory of matter, when atoms are packed tightly together in a solid, the energy levels of the individual atoms forming the solid expand into "energy bands." Between the several bands of energy levels are bands of forbidden energy levels in which electrons may not locate themselves. The valence electrons of the individual atoms are located in the filled band of highest energy level, and above and below the band occupied by the valence electrons are regions having forbidden energy levels within which electrons cannot remain.

In the case of insulator materials, a relatively wide region of forbidden energy level separates the filled band corresponding to the valence electrons from the next higher permissible (usually entirely empty) band of energy levels in which the valence electrons can conceivably exist. Unless some means is provided for escape of a valence electron into a permitted level in an unfilled band, electronic conduction cannot take place. This escape may be temporarily effected by applying a large increase in temperature to the material, or the escape may be permanently effected by the addition of permissible energy levels into the otherwise forbidden gap.

When the latter process is employed, the resulting structure is an electronic semiconductor (an electronic conductor whose resistivity at room temperature is in the range of  $10^{-2}$  to  $10^{-9}$  ohm-cm.) because impurities will have been introduced into the erstwhile insulator crystal, or else imperfections will have been impressed upon the crystal lattice of the pure substance. In connection with the former mechanism for altering the energy-level distribution, two types of semiconductors may be produced; the n-type (donor) extrinsic semiconductor and the p-type (acceptor) extrinsic semiconductor. These two types of semiconductors are distinguished from each other in that the sign of the Hall effect for the n-type is opposite to that for the p-type. More detailed information on the general theory of semiconduction and the manner for the preparation of semiconductors is set forth in the textbook, "Applied Electronics," by T. S. Gray (2nd Edition, 1954, Technology Press-John Wiley and Sons, Inc.) on pages 67 et seq. and on pages 778 et seq.

It is, therefore, among the objects of this invention to provide a method for introducing additional energy levels into the crystal lattice of diamond to render the diamond electronically semiconductive.

It is another object of this invention to provide a method for selectively introducing p- or n-type semiconducting qualities into diamond crystals.

It is a further object of this invention to produce n-type semiconducting diamond crystals.

These and other objects may be secured by subjecting diamond crystals to glow discharge ion bombardment under a voltage potential of at least 1.5 kilovolts for a period of time sufficient to modify the crystallinity of the outer surface of the diamond, so as to change the crys-

2

talline nature thereof with respect to the diamond substrate.

The exact nature of this invention as well as other objects and advantages thereof will be readily apparent from consideration of the following specification relating to the annexed drawing in which:

FIG. 1 schematically represents a gas discharge apparatus suitable for the conduct of glow discharge ion bombardment in the practice of this invention; and

FIG. 2 is a graphic representation of the effect of temperature on the resistance of diamonds rendered semiconductive by the process of this invention.

In the practice of this invention one or more diamonds are placed within the gas discharge apparatus 10, shown in FIG. 1, within container 11 placed upon the metal receiver cathode 12, which is connected into the circuitry shown. It is preferable to clean the diamonds before placing them in apparatus 10, although small amounts of surface contamination may later be removed while the diamonds are inside apparatus 10 by evacuation heating, an ion bombardment. Bell jar 13, after being placed in sealing engagement with the surface of support 14, is evacuated by pipe 15 by means of a vacuum pump 16 to a pressure of about at least  $10^{-5}$  mm. Hg. Receiver cathode 12 is usually of nickel or molybdenum metal, and anode 17, made of the same metal as cathode 12, is located about 1-inch thereabove.

Experiments performed with different gases and different electrode materials in connection with the gas ion bombardment of both natural and man-produced diamonds have established that in practice of this invention the kind of gas employed with bell jar 13 is a significantly more important parameter than the composition of the electrodes. Gases which may be employed in the practice of this invention include, for example, nitrogen, hydrogen, oxygen, the noble gases and mixtures thereof.

After evacuation of bell jar 13, a gas able to sustain a glow discharge is introduced into the bell jar through pipe 18 to a concentration providing a pressure ranging from about 10 to about 200 mm. Hg. At this pressure, a voltage differential in excess of about 1500 volts is impressed between anode 17 and cathode 12 by means of D.C. power supply 19. At this potential gas-discharge currents of at least 20 milliamperes are produced whereby receiver cathode 12 is bombarded by ions of the gaseous environment, which bombarding ions have very high kinetic energies, i.e., in the order of about several hundred volts.

These high velocity ions strike the diamond material in container 11 resting upon cathode 12 as these ions are directed toward the surface of cathode 12 covered by the diamond material. Thus, in spite of the fact that the diamonds are originally excellent electrical insulators, the bombarding gas ions can initially be directed against the surface thereof as a result of the orientation of electrodes 12 and 17. Later the factor of electrode orientation is augmented by the very changes produced by the ion bombardment.

During the process of gas ion bombardment by glow discharge, it may be of advantage to cause agitation of the cathode 12 to cause reorientation of the diamond material in container 11 to insure exposure of the entire surface of diamond material for a sufficiently long period of time to effect the desired surface modification. In general, exposure to glow discharge for a period between about  $1\frac{1}{2}$  and about 2 hours is preferred. Longer exposure is unnecessary in that the expense of the process is increased, but longer exposure is none the less operable. Also, if the current and voltage are increased, a shorter period of exposure may be successfully employed. Agitation of the diamond material is not to be employed, of course, when only a selected portion of a crystal is to be transformed into a particular type of semiconductor.

This type of semiconductor construction will be described in greater detail below.

After the appropriate exposure to gas ion bombardment, the diamond material was usually found to be coated with a thin film of metal sputtered from receiver cathode 12 during this bombardment. Electron diffraction studies of the surfaces of the bombarded diamond crystals, after first cleaning with aqua regia and distilled water to remove the foreign matter, indicate that the outermost layer of each diamond crystal is transformed to a quasi-amorphous state, which is at most only slightly crystalline. The electrical behavior of diamond crystals so modified discloses that the electrical conductivity of these modified diamond crystals cannot be dependent upon the presence of any film of graphite or metal but must be true electronic conduction.

#### Example 1

Employing the apparatus disclosed and described herein in the conduct of this invention, nitrogen was employed as the gas within the bell jar at a pressure of 50 microns Hg at 30° C. Natural octahedral diamond crystals about 1 millimeter in size having electrical resistance of about  $10^{11}$  ohms or greater at 25° C. (before treatment) were placed upon the receiver cathode and exposed to a glow discharge ion bombardment for a period of about 2 hours. The electrical resistance was measured in every instance by placing each crystal between massive silver electrodes and readings were taken with a sensitive electrometer. The crystals when removed from the glow discharge apparatus had a thin metallic film thereover, which film was removed when the crystals were cleaned with aqua regia and then with distilled water. These crystals after bombardment and cleaning had a light gray-brown surface coloration and electrical resistances of from about  $10^4$  to about  $10^8$  ohms at 25° C. as measured by the above-described method. When measured at about 60° C., the electrical resistance of the crystals was reduced to about one half the value given for 25° C. Measurements of the thermoelectric powers of the diamond crystals established that these crystals were n-type semiconductors having thermoelectric powers of the order of 10 microvolts per degree centigrade. Electron diffraction studies of the surfaces of these crystals indicated that these surfaces were decrystallized to a considerable extent, compared to the crystallinity of the original diamond material, to depths below the surface in the order of about 100 angstroms.

#### Example 2

Crystals of man-produced diamond were also subjected to substantially the same conditions as recited in Example 1. Comparable results were obtained.

#### Example 3

Crystals of cubic boron nitride produced in accordance with the teachings of U.S. 2,947,617 were subjected to substantially the same conditions as recited in Example 1 and contrary to the experience with diamond, the resistance of the cubic boron nitride crystals was increased slightly.

#### Example 4

The procedure set forth in Example 1 was repeated starting with p-type semiconducting diamonds as, for example, may be prepared by another process. It was found that p-type semiconducting diamonds heavily doped with boron remained p-type semiconductors after exposure to glow discharge ion bombardment, but some aluminum-doped crystals were converted by ion bombardment with nitrogen from p-type to n-type semiconductors in their surface regions. This latter behavior suggests the possibility of making semiconducting devices, such as diodes or transistors, by preparing semiconducting diamond crystals by the high pressure methods disclosed in S.N. 130,439 (filed Aug. 9, 1961—Wentorf, Jr., et al.) or S.N. 135,273 (filed Aug. 17, 1961—Cannon) and later to the ion-bombardment method disclosed herein.

#### Example 5

The general process described in Example 1 was repeated with argon substituted for nitrogen (analysis established that the argon contained in the order of 0.1 percent of nitrogen and 0.1 percent oxygen). After bombardment and cleaning with aqua regia and then distilled water, the diamond crystals were found to be n-type semiconductors with resistances of the magnitude recited in Example 1.

#### Example 6

Repetition of the process described in Example 1 employing hydrogen as the gaseous environment was found to produce p-type semiconductors with other electrical characteristics substantially as described in Example 1.

#### Example 7

Repetition of the process described in Example 1 employing helium as the gaseous environment was found to produce semiconducting crystals having room temperature resistances of about  $10^5$ – $10^6$  ohm but whose thermoelectric powers were too small to be detected.

A graphic summary of the resistance behavior as a function of temperature for various semiconducting diamonds prepared by the method of this invention is shown in FIG. 2. Each line with (+) designations thereon indicates the formation of a p-type semiconductor with the particular gas; each line with (x) designations there along indicates an n-type semiconductor, and each line with (o) designations there along indicates formation of a semiconductor in terms of resistance qualities, but one having thermoelectric powers too small to measure, indicating that both positive and negative carriers contribute about equally to the conductivity of these crystals.

It is known that the mere presence of hydrogen or nitrogen atoms in diamond crystals does not of itself render these crystals semiconductive. Diamonds containing as much as  $10^{18}$  atoms per cubic centimeter of each of hydrogen and nitrogen have been produced by graphite-to-diamond conversion in the presence of known catalyst metals. These diamonds have been tested for their electrical properties and were found to be effective electrical insulators.

It is believed that in the practice of this invention gas ions are actually driven into the surface of the diamond and are responsible for the contribution of a particular character to the semiconductor as being a p-type or an n-type semiconductor. The reason for the difference in electrical behavior between a diamond crystal containing atoms as, for example hydrogen atoms, wherein the atoms were introduced during the creation of the crystal, and a diamond crystal wherein gas ions have been deliberately introduced by the practice of this invention is not known, but this difference in electrical behavior is manifest. Possibly of equal or of greater import as an explanation of this extraordinary behavior is the clear evidence of substantial physical disturbance to the diamond crystal in the surface regions thereof. This physical disturbance indicates the possibility of the rearrangement of the carbon atoms under the impact of the gas ions thereby rendering the surface less crystalline than it was in its original state.

An n-type semiconducting diamond crystal prepared by the method of Example 1 was embedded in spectroscopic graphite in the reaction chamber of a high pressure apparatus such as is described in Hall—U.S. 2,941,248 and exposed for a period of about 12 minutes to the simultaneous application of about 63 kilobars of pressure and a temperature of about 1700° C. After this high pressure, high temperature exposure, the crystal was removed, cleaned in a hot mixture of sulfuric and nitric acids, then in distilled water, and then tested and was found to have lost its semiconducting properties.

For comparison, similar semiconducting diamond crystals prepared by the method of Example 1 were treated for a few minutes in a hot mixture of sulfuric acid and

potassium nitrate which treatment was employed to remove any graphite, amorphous carbon, or other non-diamond impurities from the diamond surfaces. After these diamond crystals prepared as in Example 1 had been cleaned in distilled water, the electrical resistances of the diamond crystals were tested and found to have increased by factors of from 10 to 1,000, but the crystals still remained n-type semiconductors. Electron diffraction studies of the crystals after this treatment showed that the exposed surface of the diamond had increased its crystallinity to approach that of ordinary diamond.

It has also been found that n-type semiconducting diamond crystals prepared by the method of Example 1 are altered by exposure to temperature in the range of 300–400° C. for periods of an hour or more in air. The gray-brown surface coloration of the crystals becomes less intense and their electrical resistances increase by factors of 10 to 1000. It is likely that this high temperature treatment improves the crystallinity of the surfaces and permits some of the trapped impurity atoms to leave the crystal.

The aforementioned observed effects (loss of semiconduction by exposure to high temperatures in air, or to high-temperature, high-pressure conditions in the diamond-stable region, and by treatment with sulfuric acid-potassium nitrate) indicate that the enhanced electrical conductivity of the gas ion bombarded diamond crystals is limited primarily to, and perhaps entirely, to the outermost surface layers of the diamond crystals. In further support of this conclusion it would seem that by employing accelerating potentials imparted to the gas ions of the magnitude practiced in this invention, it is not expected that bombarding gas ions are able to penetrate a distance greater than about a few thousand Angstroms into the diamond crystals. Limitation of the semiconducting activity of the diamond to a thin outer layer of the crystal is of particular advantage for yielding better high frequency response in certain semiconducting devices.

Thus, by the discovery of this novel method it is possible to selectively and predictably convert nominal electrical insulator diamonds into semiconductors of selected types.

Obviously modifications and variations of this invention, as for example changing the gas environment, changing the electrode disposition, the time of exposure or varying the potential, are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A method for introducing additional allowed energy levels for electron occupancy into a material to selectively product semiconductor behavior by said material comprising the steps of:

(a) placing diamond material on a cathode within a closed chamber,

(1) said diamond material being disposed between said cathode and an anode spaced therefrom within said chamber,

(b) evacuating said chamber,

(c) introducing a gas capable of supporting a glow discharge into said chamber,

(1) said gas being selected from the group consisting of nitrogen, hydrogen, oxygen, the noble gases and mixtures thereof, and being at a total internal gas pressure ranging between about 10 and about 200 microns of mercury,

(d) impressing a voltage potential between said anode and said cathode to create glow discharge current within said chamber,

(1) said voltage differential amounting to a potential of at least about 1.5 kilovolts, and

(e) exposing said diamond material to the glow discharge during which exposure ions leave the vicinity of said anode and travel toward said cathode impinging upon said diamond material.

2. The method substantially as recited in claim 1 wherein the gas is selected from the group consisting of nitrogen and argon whereby an n-type semiconducting material is produced and the period of exposure as at least about 1½ hours.

3. The method substantially as recited in claim 1 wherein the gas is hydrogen whereby a p-type semiconducting material is produced.

4. A method for converting at least a portion of the surface of a p-type semiconductor diamond to function as an n-type semiconductor diamond comprising the steps of:

(a) placing a p-type semiconductor diamond on a cathode within a closed chamber,

(1) said diamond being disposed between said cathode and an anode spaced therefrom within said chamber,

(b) evacuating said chamber,

(c) introducing a gas chosen from the group consisting of nitrogen and argon to provide a total internal gas pressure ranging between about 10 and about 200 microns of mercury,

(d) impressing a voltage potential between said anode and said cathode to create glow discharge current within said chamber,

(1) said voltage differential amounting to a potential of at least about 1.5 kilovolts, and

(e) exposing a selected extent of the surface of said diamond to the glow discharge.

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