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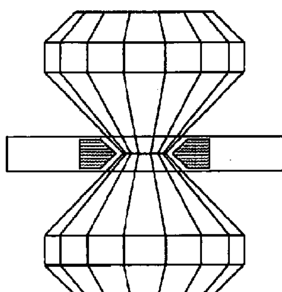

(57) Abstract: The present invention is directed to new uses and applications for colorless, single- crystal diamonds produced at a rapid growth rate. The present invention is also directed to methods for producing single crystal diamonds of varying color at a rapid growth rate and new uses and applications for such single-crystal, colored diamonds.

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NEW DIAMOND USES/APPLICATIONS BASED ON SINGLE-CRYSTAL CVD DIAMOND PRODUCED AT RAPID GROWTH RATE

1. Field of the Invention

5 **[0004]** The present invention relates to uses and applications for diamond. More particularly, the present invention relates to applications and uses of single-crystal diamond produced at a high growth rate using Microwave Plasma Chemical Vapor Deposition (MPCVD) within a deposition chamber.

10 2. Description of Related Art

[0005] Large-scale production of synthetic diamond has long been an objective of both research and industry. Diamond, in addition to its gem properties, is the hardest known material, has the highest known thermal conductivity, and is transparent to a wide variety of electromagnetic radiation. Monocrystalline diamond in particular possesses a wide 15 range of important properties, including a low coefficient of thermal

expansion, the highest known thermal conductivity, chemical inertness, wear resistance, low friction, and optical transparency from the ultra-violet (UV) to the far infrared (IR). Therefore, it is valuable because of its wide range of applications in a number of industries and research applications, in addition to its value as a gemstone.

[0006] For at least the last twenty years, a process of producing small quantities of diamond by chemical vapor deposition (CVD) has been available. As reported by B. V. Spitsyn *et al.* in "Vapor Growth of Diamond on Diamond and Other Surfaces," Journal of Crystal Growth, vol. 52, pp. 219-226, the process involves CVD of diamond on a substrate by using a combination of methane, or another simple hydrocarbon gas, and hydrogen gas at reduced pressures and temperatures of 800-1200° C. The inclusion of hydrogen gas prevents the formation of graphite as the diamond nucleates and grows. Growth rates of up to 1 μm/hour have been reported with this technique.

[0007] Subsequent work, for example, that of Kamo *et al.* as reported in "Diamond Synthesis from Gas Phase in Microwave Plasma," Journal of Crystal Growth, vol. 62, pp. 642-644, demonstrated the use of Microwave Plasma Chemical Vapor Deposition (MPCVD) to produce diamond at pressures of 1-8 kPa at temperatures of 800-1000° C with microwave power of 300-700 W at a frequency of 2.45 GHz. A concentration of 1-3 % methane gas was used in the process of Kamo *et al.* Maximum growth rates of 3 μm/hour have been reported using this MPCVD process. In the above-described processes, and in a number of other reported processes, the growth rates are limited to only a few micrometers per hour.

[0008] Methods of improving the growth rates of single-crystal chemical vapor deposition (SC-CVD) diamonds have recently been reported [1, 2, 3, 4, 5]. SC-CVD diamonds reported so far, however, are relatively small, are discolored, and/or are flawed. Large (*e.g.*, over three carats, as commercially available high pressure, high temperature (HPHT) synthetic Ib yellow diamond), colorless, flawless synthetic diamonds remain a challenge due to slow growth and other technical difficulties [7, 8, 9]. The color of SC-CVD diamonds in the absence of HPHT annealing can range from light brown to dark brown, thus limiting their applicability as gems, in optics, in scientific research, and in diamond-based electronics [6, 7, 8]. SC-CVD diamonds

have been characterized as type IIa, *i.e.*, possessing less than 10 ppm nitrogen, and have coloration and other optical properties arising from various defects and/or impurities.

[0009] A diamond crystal of 10 carats is approximately five times that of commercially available HPHT diamond and the SC-CVD diamond reported in References [7, 8, 9, 10]. Single-crystal diamonds with larger mass (greater than 100 carats) are needed as anvils for high-pressure research, and crystals with large lateral dimensions (greater than 2.5 cm) are required for applications such as laser windows and substrates for diamond-based electronic devices. High optical quality (UV-visible-IR transmission) and chemical purity are required for all of the above applications. The large SC-CVD diamonds produced so far present problems because of the brownish color.

[0010] Attempts have been made to add oxygen in the growth of polycrystalline CVD diamond. These effects include extending the region of diamond formation [12], reducing silicon and hydrogen impurity levels [13], preferentially etching the non-diamond carbon [11, 14], and attempting to prevent diamond cracks due to an absence of impurities [13]. These attempts were directed primarily to the etching and synthesis of polycrystalline diamonds but not to the production of SC-CVD diamond.

[0011] Attempts have also been made to intentionally vary the color of the single-crystal diamond formed. Yellow diamonds, for instance, have been produced that are similar to HPHT synthetic Ia or Ib diamond in appearance [6].

[0012] U.S. Patent No. 6,858,078 to Hemley *et al.* is directed to an apparatus and method for diamond production. The disclosed apparatus and method can lead to the production of diamonds with a light brown color.

[0013] U.S. Provisional Application No. 60/684,168, filed May 25, 2005, which is hereby incorporated in its entirety by reference, is directed to producing colorless, single-crystal diamonds at rapid growth rate using Microwave Plasma Chemical Vapor Deposition (MPCVD) within a deposition chamber.

[0014] Until now, few attempts have been made to develop products which use single-crystal diamonds produced by MPCVD. Moreover, few attempts have been

made to develop uses and applications for single-crystal diamonds that are not doped with impurities.

[0015] Thus, there remains a need to develop new uses and applications for colorless, single-crystal diamonds produced at a rapid growth rate. There also remains a need to develop new uses and applications for single-crystal diamonds of varying color grown at a rapid growth rate.

SUMMARY

[0016] Accordingly, the present invention is directed to new uses and applications for colorless, single-crystal diamonds produced at a rapid growth rate. The present invention is also directed to methods for producing single crystal diamonds of varying color at a rapid growth rate and new uses and applications for such single-crystal, colored diamonds.

[0017] Additional features and advantages of the invention will be set forth in the description which follows, and will be apparent, in part, from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the structure particularly pointed out in the written description and claims hereof, as well as the appended drawings.

[0018] To achieve these and other advantages and in accordance with the purpose of the present invention, as embodied and broadly described, an embodiment of the invention includes a nozzle, such as that used for high-pressure water jet machining, comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2. In one embodiment, the heat sink holder used to produce the diamond comprises

molybdenum. In another embodiment, all temperature gradients across the growth surface of the diamond are less than about 30 °C. In another embodiment, all temperature gradients across the growth surface of the diamond are less than about 20 °C. In another embodiment, the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

[0019] The single-crystal diamonds that have the characteristics described in the preceding paragraph have additional uses, which include, but are not limited to the following:

a.) wear resistant material—including, but not limited to, water/fluid jet nozzles, cutting instruments (*e.g.*, razors, knives), surgical instruments (*e.g.*, surgical blades, cutting blades for surgical instruments), microtone, hardness indentor, graphical tools, stichels, instruments used in the repair of lithographic pieces, missile radomes, bearings, including those used in ultra-high speed machines, diamond-biomolecule devices, microtomes, and hardness indentors;

b.) optical parts—including, but not limited to, optical windows, reflectors, refractors, lenses, gratings, etalons, alpha particle detectors, and prims;

c.) electronics—including, but not limited to, microchannel cooling assemblies; high purity SC-CVD diamonds for semiconductor components, SC-CVD doped with impurities for semiconductor components

d.) anvils in high pressure apparatuses—including, but not limited to, the "Khvostantsev" or "Paris-Edinburgh" toroid shaped anvils that can be used with multiple optical, electrical, magnetic, and acoustic sensors; Bridgman anvils that are relatively large, have variable heights, and include major angles [15]; Multianviles, Drickamer cells, belt apparatus, piston-cylinder apparatus; precompressing samples for laser or magnetic shock wave studies;

colorless, smooth coating for hydrogen and other applications, apparatus for pre-compressing samples for lasers or magnetic shock;

e.) containers—including, but not limited to, 6 edge {100} plated diamonds can be connected to each other to form a container, CVD diamond coating can be further employed to form a vacuum tight container;

f.) laser source-including, but not limited to, annealing SC-CVD diamond to form a stable H3 center (nitrogen aggregate, N-V center, Si center, or other dopants;

g.) superconductor and conducting diamond—including, but not limited to, HPHT annealing with SC-CVD diamond grown with an impurity such as H, Li, N, Mg, or another low atomic weight element with a size approaching that of carbon;

h.) substrate for other CVD diamond growth—using CVD plates as substrates for CVD growth has the advantage over natural or HPT substrates in large size and toughness (to avoid cracking during growth).

[0020] In one embodiment, for example, the invention is directed to a cutting blade for a surgical instrument comprising a cutting edge comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0021] In another embodiment, the invention is directed to a cutting instrument comprising a cutting edge comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0022] In another embodiment, the invention is directed to a wire drawing die comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0023] In another embodiment, the invention is directed to a bearing comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0024] In another embodiment, the invention is directed to a diamond anvil comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150

torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0025] In another embodiment, the invention is directed to an etalon comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0026] In another embodiment, the invention is directed to an optical window comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0027] In another embodiment, the invention is directed to an alpha particle detector comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising controlling temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals in the range of 900-1400 °C, the diamond is mounted in a heat sink holder made of a material, including, but not limited to, molybdenum to minimize temperature gradients across the growth surface of the diamond (*e.g.*, to less than about 20 °C), growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth

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surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

[0028] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

[0028a] Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

[0028b] Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this specification.

[0028c] In order that the present invention may be more clearly understood, preferred embodiments will be described with reference to the following drawings and examples.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and together with the description serve to explain the principles of the invention.

[0029] FIG. 1 is a diagram of a diamond production apparatus according to an embodiment of the present invention in which a cross-section of deposition apparatus with a specimen holder assembly for holding the diamond stationary during a diamond growth process is depicted.

[0030] FIG. 2a is a perspective view of the deposition apparatus shown in FIG. 1.

[0031] FIG. 2b is a perspective view of the diamond and sheath shown in FIG. 1.

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[0032] FIG. 3 is a diagram of a diamond production apparatus according to an embodiment of the present invention in which a cross-section of a deposition apparatus with a specimen holder assembly for moving the diamond during the diamond growth process is depicted.

5 [0033] FIGS. 4a-4c depict cross-sectional views of holders or thermal masses that can be used in accordance with the present invention.

[0034] FIG. 5 is a diagram of a diamond production apparatus according to another embodiment of the present invention in which a cross-section of a deposition apparatus with a specimen holder assembly for moving the diamond during the diamond growth
10 process is depicted.

[0035] FIG. 6 is a flow diagram illustrating a process 600 in accordance with embodiments of the present invention that can be used with the specimen holder assembly shown in FIG. 1.

[0036] FIG. 7 is a flow diagram illustrating a process 700 in accordance with embodiments of the present invention that can be used with the specimen holder assembly shown in FIG. 3 or with the specimen holder assembly shown in FIG. 5.

[0037] FIG. 8 is a UV-VIS spectrum for an HPHT IIa diamond; an SC-CVD diamond produced according to the method of the invention, *e.g.*., with a deposition chamber atmosphere comprising from about 5 % to about 25 % O_2 per unit of CH_4; and an SC-CVD diamond produced with N_2 gas present as a component of the deposition chamber atmosphere.

[0038] FIG. 9 is photograph of a substantially colorless SC-CVD crystal grown according to the method of the invention, *e.g.*, with a deposition chamber atmosphere comprising from about 5 % to about 25 % O_2 per unit of CH_4, and an SC-CVD crystal grown with N_2 gas present as a component of the deposition chamber atmosphere.

[0039] FIG. 10 is an SC-CVD diamond block formed by deposition on six {100} faces of an HPHT Ib substrate.

[0040] FIG. 11 is an IR absorption spectrum (2500-8000 cm^{-1}) for an SC-CVD diamond produced according to the method of the invention, *e.g.*., with a deposition chamber atmosphere comprising from about 5 % to about 25 % O_2 per unit of CH_4, and an SC-CVD diamond produced with N_2 gas present as a component of the deposition chamber atmosphere.

[0041] FIG. 12 shows a cross-section of a water jet cutting apparatus.

[0042] FIG. 13 shows a cubic container configuration comprised of CVD diamond.

[0043] FIG. 14 shows CVD diamond grown on two plates placed together in step configuration.

[0044] FIG. 15a) shows a diamond anvil cell and gasket supported with a binding ring

[0045] FIG. 15b) shows a beveled diamond anvil.

DETAILED DESCRIPTION

[0046] Reference will now be made in detail to methods of producing diamond used in the applications of the invention. FIG. 1 is a diagram of a diamond production system 100 according to an embodiment of the present invention, in which a

deposition apparatus 102 is depicted in cross-section. The diamond production system 100 includes a Microwave Plasma Chemical Vapor Deposition (MPCVD) system 104 that contains a deposition apparatus 102 as well as reactant and plasma controls 106. For example, the MPCVD system 104 can be a SEKI AX6550 made by Seki Technotron Corp. Tokyo, Japan. This system is capable of producing 6 kilowatts of power output at a frequency of 2.45 GHz. As another example, the MPCVD system 104 can be a SEKI AX5250 made by Seki Technotron Corp. This system is capable of producing 5 kilowatts of power output at a frequency of 2.45 GHz. As another example, the MPCVD system 104 can be a WAVEMAT MPDR 330 313 EHP made by Wavemat, Inc. Such a MPCVD system is capable of producing a 6-kilowatt power output at a frequency of 2.45 GHz, and has a chamber volume of approximately 5,000 cubic centimeters. However, the MPCVD system specifications can vary with the scale of a deposition process in terms of size of the deposition area and/or rate of deposition.

[0047] The MPCVD system 104 includes a chamber within the deposition apparatus 102 that is at least in part defined by a bell jar 108, which is used in sealing the chamber. Prior to MPCVD operations, the air within the chamber is withdrawn. For example, a first mechanical type of vacuum pump is used to draw down the chamber and then a second high vacuum type of vacuum pump, such as a turbopump or cryopump, further draws out the air inside the chamber. Plasma is generated within the chamber by a set of plasma electrodes spaced apart within the chamber. Neither the pumps nor the plasma electrodes are illustrated in FIG. 1.

[0048] The deposition apparatus 102 also includes a specimen holder assembly 120 installed within the chamber of the MPCVD system 104. Typically, a specimen holder assembly is positioned in the center of the deposition chamber floor 122 of the deposition apparatus 102, as shown in FIG. 1. The specimen holder assembly 120 shown in FIG. 1 is illustrated in cross-section. The specimen holder assembly 120 can include a stage 124 installed in the floor of the deposition apparatus 102.

[0049] As shown in FIG. 1, the stage 120 can be attached to the deposition chamber floor 122 using bolts 126a and 126c. The stage 124 can be molybdenum or any other type of material having a high thermal conductivity and high melting point. In

addition, the stage 124 can be cooled during the process of growing diamond by a coolant passing through a coolant pipe 128 within the stage 124. The coolant can be water, a refrigerant or other types of fluid with sufficient heat carrying capacity to cool the stage. Although the coolant pipe is shown as having a U-shaped path through the stage 124 in FIG. 1, the coolant pipe 128 can have a helically shaped path or other types of paths within the stage 124 to more efficiently cool the stage 124.

[0050] Positioned on the stage 124 of the specimen holder assembly 120, as shown in FIG. 1, is a set ring 130 having set screws, such as screws 131a and 131c, for tightening collets 132a and 132b around a sheath 134 that holds diamond 136. The sheath 134 is a holder, which makes a thermal contact with a side surface of the diamond 136 adjacent to an edge of a top surface of the diamond 136. Because collets 132a and 132b are tightened onto the sheath 134 by screws 131, the sheath 134 holds the diamond 136 in a stationary position and acts as a heat-sink to prevent the formation of twins or polycrystalline diamond along the edges of the growth surface of the diamond 136.

[0051] The diamond 136 can include a diamond seed portion 138 and a grown diamond portion 140. The diamond seed portion 138 can be a manufactured diamond or a natural diamond. In one embodiment, the seed is a member of a group consisting of a natural, colorless Ia diamond; a colorless IIa diamond; an HPHT synthetic yellow Ib diamond; and an SC-CVD diamond. In another embodiment, the seed is an SC-CVD diamond. In another embodiment, the seed is an SC-CVD diamond that has {100} faces. In another embodiment, the seed is an SC-CVD diamond that has six {100} faces. In another embodiment, all top {100} surfaces of the seed have areas from about 1 to about 100 mm^2.

[0052] As shown in FIG. 1, the top surface or growth surface of the diamond 136 is positioned within a region of the plasma 141 having a resonant power at a height H above the deposition chamber floor 122. The resonant power can be the maximum resonant power within the plasma 141 or a degree thereof. The top surface or growth surface of the diamond 136 is initially the diamond seed portion 138 and is then the grown diamond portion 140 as the diamond grows.

[0053] As shown in FIG. 1, the top edge of the sheath 134 is at a distance D just below the top surface or top edges of the diamond 136. The distance D should be sufficiently large enough to expose the edges of the growth surface of the diamond 136 to the plasma 141. However, the distance D can not be so large as to prevent the heat-sinking effect of the sheath 134 that prevents the formation of twins or polycrystalline diamond along the edges of the growth surface of the diamond 136. Thus, D should be within a specified distance range, such as 0-1.5 mm. The distance D and the height H, as shown in FIG. 1, are manually set using the screws 131 of the set ring 130 by positioning the diamond 136 in the sheath, positioning the sheath in the collets 132a and 132b, and then tightening the screws 131.

[0054] FIG. 2 is a perspective view of the deposition apparatus shown in FIG. 1. In the center of the deposition chamber floor 122 of FIG. 2 is a circular stage 124 with a central recess 125. As shown in FIG. 2, the stage 124 is held in position by bolts 126a-126d. The stage 124 can be formed of molybdenum or other materials having a high thermal conductivity and high melting point. A set ring 130 with four screws 131a-131b is positioned within the recess 125 of the stage 124 along with collets 132a-132b. In the alternative, the set ring 130 can be bolted to the stage 124 to increase thermal conductance between the stage and the set ring.

[0055] As shown in FIG. 2a, a rectangular sheath 134, which can either be a short length of rectangular tubing or a sheet folded into a rectangle, is positioned in the collets 132a and 132b with a diamond 136 therein. The sheath 124 can be molybdenum or any other type of material having a high thermal conductivity and high melting point. The screws 131a-131d are tightened on the collets 132a-132b such that the sheath 134 is tightened onto the diamond 136 such that the sheath 134 acts as a heat sink on the four side surfaces of the diamond 136. As shown in FIG. 1, the sheath 134 also makes thermal contact to the stage 124. The collets 132a-132b make thermal contact with the stage 124 and serve as thermal masses for transferring heat from the sheath 134 into the stage 124. The tightening of the sheath 134 onto the diamond 136 increases the quality of the thermal contact between the diamond and the sheath. As shown in FIG. 1, the sheath 134 can also make thermal contact to the stage 124. Although a rectangular shape is shown in FIG. 2a for both the sheath and the

diamond, the sheath and the diamond can have any geometric shape such as elliptical, circular or polygonal. The shape of the sheath or holder should be substantially the same as the diamond.

[0056] In the exemplary embodiment of the invention shown in FIGS. 1 and 2a, the stage 124 can have a diameter of approximately 10.1 cm. and the sheath 134 can be approximately 2.5 cm wide. Regardless of the dimensions selected for the stage and the sheath 134, the thermal mass of the stage 122, sheath 124, and collets 132 can be adjusted to provide an optimal heat sink for the diamond 136. Additionally, the path and extent of the coolant pipes 128 can be modified for greater cooling effect, especially if a particularly large diamond is to be produced. Further, a refrigerant or other low temperature fluids can be used as a coolant.

[0057] Molybdenum is only one potential high thermal conductivity, high melting point material used in the stage 124, set ring 130, collets 132, sheath 134 and other components. Molybdenum is suitable for these components because it has a high melting point, which is 2617° C., and a high thermal conductivity, which is 1.38 W/cm K at 298.2 K. In addition, a large graphite build-up does not tend to form on molybdenum. Other materials, such as molybdenum-tungsten alloys or engineered ceramics, having high melting points above the process temperature and a thermal conductivity comparable to that of molybdenum, can alternatively be used instead of molybdenum. Additional materials which have the aforementioned high melting point and high thermal conductivities and can be used in the methods and apparatuses of the invention include, but are not limited to, chromium, iridium, niobium, platinum, rhenium, rhodium, ruthenium, silicon, tantalum, tungsten, and mixtures thereof.

[0058] Returning to FIG. 1, another component of the diamond production system 100 is an noncontact measurement device, such as an infrared pyrometer 142, which is used to monitor the temperature of the diamond seed 138 and later the grown diamond 140 during the growth process without contacting the diamond 136. The infrared pyrometer 142 can be, for example, a MMRON M77/78 two color infrared pyrometer from Mikron Instruments, Inc. of Oakland, N.J. The infrared pyrometer 142 is focused on the diamond seed 138 or later on the grown diamond 140 with a target area

measure of 2 mm. By using the infrared pyrometer 142, the temperature of the growth surface of the diamond 136 is measured to within 1° C.

[0059] The diamond production system 100 of FIG. 1 also includes an MPCVD process controller 144. The MPCVD process controller 144 is typically provided as a component of the MPCVD system 104. As is well-known in the art, the MPCVD process controller 144 exercises feedback control over a number of MPCVD parameters, including, but not limited to, the process temperature, gas mass flow, plasma parameters, and reactant flow rates by using the reactant and plasma controls 106. The MPCVD process controller 144 operates in cooperation with a main process controller 146. The main process controller 146 takes input from the MPCVD controller 144, the infrared pyrometer 142, and from other measuring devices of other components in the diamond production system 100 and carries out executive-level control over the process. For example, the main process controller 146 can measure and control coolant temperatures and/or flow rates of the coolant in the stage using a coolant controller 148.

[0060] The main process controller 146 can be a general purpose computer, a special purpose computing system, such as an ASIC, or any other known type of computing system for controlling MPCVD processes. Depending on the type of main process controller 146, the MPCVD process controller 144 can be integrated into the main process controller so as to consolidate the functions of the two components. For example, the main process controller 146 can be a general purpose computer equipped with the LabVIEW programming language from National Instruments, Inc. of Austin, Tex. and the LabVIEW program such that the general purpose computer is equipped to control, record, and report all of the process parameters.

[0061] The main process controller 146 in FIG. 1 controls the temperatures of the growth surface such that all the temperature gradients across the growth surface of the diamond are less than or equal to 20° C. Precise control over growth surface temperatures and growth surface temperature gradients prevents the formation of polycrystalline diamond or twins such that a large single-crystal diamond can be grown. The ability to control all of the temperature gradients across the growth surface of the diamond 136 is influenced by several factors, including the heat sinking

capability of the stage 124, the positioning of the top surface of the diamond in the plasma 141, the uniformity of the plasma 141 that the growth surface of the diamond is subjected to, the quality of thermal transfer from edges of the diamond via the holder or sheath 134 to the stage 124, the controllability of the microwave power, coolant flow rate, coolant temperature, gas flow rates, reactant flow rate and the detection capabilities of the infrared pyrometer 142. Based upon temperature measurements from the pyrometer 142, the main process controller 146 controls the temperature of the growth surface such that all temperature gradients across the growth surface are less than 20° C by adjusting at least one of microwave power to the plasma 141, the coolant flow rate, coolant temperature, gas flow rates and reactant flow rate.

[0062] FIG. 2b is a perspective view of the diamond 136 shown in FIG. 1 depicting exemplary points P1, P2, P3 and P4 along the growth surface 137 of the diamond 136. FIG. 2b also depicts the distance D between the growth surface 137 or top edges 139 of the diamond 136 and an edge 135 of the sheath 134. Typically, large temperature variations, in terms of temperature differences across the growth surface, occur between the edges and the middle of the growth surface of the diamond. For example, larger temperature gradients occur between the points P1 and P2 than occur between the points P1 and P3. In another example, larger temperature gradients occur between the points P4 and P2 than occur between the points P4 and P3. Thus, controlling temperature of the growth surface of the diamond such that all temperature gradients across the growth surface are less than 20° C should at least take into account a temperature measurement between the middle and an edge 139 of the growth surface 137. For example, the main controller 146 may control the temperature of the growth surface such that the temperature gradient between points P1 and P2 is less than 20° C.

[0063] The spot size of the infrared pyrometer can affect the ability to monitor temperature gradients across the top surface of the diamond and thus the growth rate of the diamond. For example, if the size of the diamond is large in comparison to the spot size of the infrared pyrometer, the temperature at each of the edges of the growth surface of the diamond can be outside of the field of view of the infrared pyrometer. Thus, multiple infrared pyrometers should be used for a diamond with a large growing

area. Each of the multiple pyrometers should be focused on different edges about the surface of the diamond and preferably near the corners, if any. Thus, the main process controller 146, as shown in FIG. 1, should be programmed to integrate overlapping fields of view from the multiple pyrometers to produce a contiguous "map" of the temperatures across the diamond's surface or interpolate between non-overlapping fields of view to a produce an interpreted "map" of the temperatures across the diamond's growth surface. In the alternative, the temperature gradient between a single edge or corner point with respect to the middle of the growth surface can be monitored as indicative of the maximum temperature gradient that exists across the growth surface of the diamond.

[0064] In addition to the infrared pyrometer 142 for temperature control, other process control instrumentation may be included in the diamond production system 100. Additional process control instrumentation can include equipment for determining the type and quality of the diamond 136 while the growth process is underway. Examples of such equipment include visible, infrared, and Raman spectrometers, which are optical in nature and can be focused on the same point as the infrared pyrometer 142 to obtain data on the structure and quality of the diamond while growth is underway. If additional equipment is provided, it can be connected to the main process controller 146 such that the main process controller 146 controls the instrumentation and presents the results of the analytical methods along with other status information. Additional process control instrumentation may be particularly useful in experimental settings, in "scaling up" a process to produce larger diamonds, and in quality control efforts for an existing diamond production system 100 and corresponding process.

[0065] As the diamond 136 grows, both the distance D and the height H increase. As the distance D increases, the heat-sinking capacity of the sheath 134 for the top edges 139 of the growth surface of the diamond 136 reduces. In addition, characteristics of the plasma, such as temperature and/or consistency, change as the growth surface of the diamond 136 extends into the plasma 141. In the diamond production system 100, the growth process is periodically halted so that the position of the diamond 136 can be adjusted downward with respect to the sheath 134 to reduce

the distance D, and both the diamond 136 and the sheath 134 can be adjusted downward with respect to the deposition chamber floor 122 to reduce the height H. This repositioning allows the diamond growth on the growth surface of the diamond 136 to occur within a desired region of resonant power within the plasma 141, allows the infrared pyrometer 142 and any additional instruments to remain focused on the growth surface of the diamond 136, and has the effect of maintaining an efficient thermal contact for sinking heat from the edges of the growth surface of the diamond 136.

[0066] FIG. 3 is a diagram of a diamond production apparatus 300 according to an embodiment of the present invention in which a cross-section of deposition apparatus 304 with a specimen holder assembly 320 for moving the diamond 136 during the diamond growth process is depicted. Some of the components of diamond production apparatus 300 are substantially the same as those of diamond production system 100, and thus the discussion above with regard to FIG. 1 will suffice to describe those components likewise numbered in FIG. 3. For example, the pyrometer 142, deposition chamber floor 122, coolant pipe 128 and bell jar 108 in FIG. 3 are substantially the same as those described in FIG. 1.

[0067] As shown in FIG. 3, the diamond 136 is mounted on a diamond actuator member 360 within the sheath 134 of the specimen holder assembly 320. The diamond 136 is slidably mounted within the sheath 134 on a diamond actuator member 360 that translates along an axis substantially perpendicular to the growth surface. The diamond actuator member 360 protrudes through a stage 324 and is controlled from underneath the stage 324 with a diamond control, which is shown as a part of the coolant and diamond/holder controls 329 in FIG. 3. The diamond actuator member 360 is for setting the height H between the growth surface of the diamond 136 and the deposition chamber floor 122. Although the diamond actuator member 360 in FIG. 3 is shown as a threaded rod, the diamond actuator member can be of any geometric shape that enables positioning of the diamond 136 at height or position above the deposition chamber floor. Those skilled in the art will realize that components placed within the bell jar, such as the diamond actuator member 360,

should be vacuum compatible so as to avoid problems in maintaining the desired atmosphere.

[0068] The actuator (not shown) for the diamond actuator member 360 is a motor (not shown). However, the actuator can be any one of a number of known types of actuator, depending on the size of diamond that is to be grown, the growth rate, and the level of movement precision required. For example, if the diamond 136 is small in size, a piezoelectric actuator may be used. If the diamond 136 is relatively large or can be grown relatively large, a motorized computer-controllable actuator is preferred. Regardless of the particular actuator employed, the main process controller 346 controls the movement of the diamond actuator member 360 so that the diamond 136 can be automatically moved downward as diamond growth progresses.

[0069] In addition, a holder actuator member 362 protrudes through the stage 324 and is controlled from underneath the stage 324 with holder control, which is shown as a part of the coolant and diamond/holder controls 329 in FIG. 3. The holder actuator member 362 translates along an axis substantially perpendicular to the growth surface and is for maintaining the distance D between an edge of the growth surface of the diamond 136 and a top edge of the holder or sheath 134. A diamond production system can have a diamond actuator member, a holder actuator member, or a combination of both.

[0070] The holder actuator member 362 in FIG. 3 is threaded into the stage 324 and the diamond actuator member 360 is threaded into the holder actuator member 362. By this arrangement, the diamond and holder controls of the coolant and diamond/holder controls 329 shown in FIG. 3 can move the diamond 136, the sheath 134, or both the sheath 134 and the diamond 136. Although the holder actuator member 362 in FIG. 3 is shown as a threaded cylinder with threading on the inside for the diamond actuator member 360 and threads on the outside for threading into the stage 324, the holder actuator member can be of any geometric shape that enables maintaining a specified distance range between an edge of the growth surface of the diamond 136 and the top edge of the holder or sheath 134. Those skilled in the art will realize that components placed within the bell jar, such as the holder actuator member 362 or a combination of both the holder actuator member and the diamond actuator

member, should be vacuum compatible so as to avoid problems in maintaining the desired atmosphere.

[0071] As shown in FIG. 3, a thermal mass 364 is positioned within a recess of the stage 324. The holder or sheath 134 is slidably positioned within thermal mass 364 such that thermal energy is transferred from the sheath 134 to the stage 324. The top surface of the thermal mass 364 can be contoured such that heat can be transferred from the sheath 134 while minimizing the electrical effect of the thermal mass 364 on the plasma 341. Thermal masses 466a, 466b and 466c in FIGS. 4a-4c, respectively, are examples of other contoured thermal masses with different cross-sectional shapes, which in the alternative, can be used in lieu of the thermal mass 364 shown in FIG. 3. A thermal mass can be made of molybdenum. Other materials, such as molybdenum-tungsten alloys or engineered ceramics, having high melting points above the process temperature and a thermal conductivity comparable to that of molybdenum can be used as a thermal mass for transferring heat from a side of the diamond to a stage.

[0072] By minimizing the electrical effect of thermal mass 364 on the plasma 341, the region within the plasma 341 in which the diamond is grown will be more uniform. In addition, higher pressure can be used in growing diamond, which will increase the growth rate of single-crystal diamond. For example, pressures can vary from about 100 torr to about 400 torr, and single-crystal growth rates can be from 50 to 300 microns per hour. Using a higher pressure (above 400 torr) is possible because the uniformity, shape and/or position of the plasma 341 are not as readily affected by thermal mass 364, which is contoured to remove heat from the edges of the growth surface of the diamond and minimizes the electrical effect of the thermal mass 364 on the plasma 341. In addition, less microwave power, such as 1-2 kW, is needed to maintain the plasma 341. Otherwise, a lower pressure and/or increased microwave power would have to be used to maintain the uniformity, shape and/or position of the plasma 341.

[0073] As the diamond 136 grows, both the distance D and the height H increase. As the distance D increases, the heat-sinking capacity of the sheath 134 for the top edges of the growth surface of the diamond 136 decreases. In addition, characteristics of the plasma, such as temperature, change as the growth surface of the diamond 136

extends into the plasma 341. In the diamond production system 300, the growth process is halted when the diamond 136 reaches a predetermined thickness since the distance D and the height H can be controlled by the main process controller 346, via the coolant and diamond/holder controls 329, using the holder actuator member 362 and diamond actuator member 360 during the diamond growing process. This repositioning, either manually or automatically under control of the controller 144, allows the diamond growth on the growth surface of the diamond 136 to occur within a desired region of resonant power within the plasma 341. Further, repositioning allows the infrared pyrometer 142 and any additional instruments to remain focused on the growth surface of the diamond 136, and can maintain an efficient sinking of heat from the edges of the growth surface of the diamond 136.

[0074] FIG. 5 is a diagram of a diamond production apparatus 500 according to an embodiment of the present invention in which a cross-section of deposition apparatus 504 with a specimen holder assembly 520 for moving the diamond 136 during the diamond growth process is depicted. Some of the components of diamond production apparatus 500 are substantially the same as those of diamond production system 100 and 300, and thus, the discussion above with regard to FIG. 1 and FIG. 3 will suffice to describe those components likewise numbered in FIG. 5. For example, the pyrometer 142, deposition chamber floor 122, coolant pipe 128 and bell jar 108 in FIG. 5 are substantially the same as those described in FIG. 1. In another example, the coolant and diamond/holder controller 329 and diamond actuator member 360 in FIG. 5 are substantially the same as those in FIG. 3.

[0075] As shown in FIG. 5, the diamond 136 is mounted on the diamond actuator member 360 and within a contoured thermal mass 566, which acts as a holder. By placing the diamond 136 directly within the contoured thermal mass 566, thermal efficiencies for heat-sinking the diamond 136 are increased. However, the plasma 541 may be more easily affected since the whole contoured thermal mass is moved by the holder actuator 562 in the stage 524 with a diamond holder control, which is shown as a part of the coolant and diamond/holder controls 329 in FIG. 3. Thus, the main process controller 546 should take into account such a factors for appropriately controlling the plasma and/or other parameters of the growth process. In the

alternative, the convex thermal mass 364 shown in FIG. 3, the slant-sided thermal mass 466b in FIG. 4b, a slant-sided/cylindrical apex thermal mass 466c in FIG. 4c or other geometric configurations can be used in lieu of the concave thermal mass 566, in FIG. 5.

[0076] FIG. 6 is a flow diagram illustrating a process 600 in accordance with embodiments of the present invention that can be used with specimen holder assembly shown in FIG. 1. The process 600 begins with step S670 in which an appropriate seed diamond or a diamond in the process of being grown is positioned in a holder. In the specimen holder assembly 120 of FIG. 1 for example, the diamond seed portion 138 is placed in a sheath 134 and the screws 131a-131d are tightened by an operator. Other mechanisms can be used to maintain both the sheath and diamond in position, such as spring loaded collets, hydraulics or other mechanisms can be used in exerting a force against the holder or sheath.

[0077] As referred to in step S672, the temperature of the growth surface of the diamond, either the diamond seed or grown diamond, is measured. For example, the pyrometer 142 in FIG. 1 takes a measurement of the growth surface, which is the top surface of the growing diamond portion 140, and provides the measurement to the main process controller 146. The measurement is taken such that a thermal gradient across the growth surface of the diamond 136 can be determined by the main process controller or at least the temperature of an edge of the growth surface of the diamond are inputted into the main process controller.

[0078] The main process controller, such as main process controller 146 shown in FIG. 1, is used in controlling the temperature of the growth surface, as referred to in S674 in FIG. 6. The main process controller controls the temperature by maintaining thermal gradients of less than 20° C across the growth surface. While controlling the temperature of the growth surface, a determination is made to whether the diamond should be repositioned in the holder, as shown in step S675 of FIG. 6. If the main controller can not control the temperature of the growth surface of the diamond such that all temperature gradients across the growth surface are less than 20° C by controlling the plasma, gas flows and coolant flows, then the growth process is suspended so that the diamond can be repositioned in the holder, as shown in step

S678 of FIG. 6, for better heat-sinking of the diamond and/or better positioning of the diamond within the plasma. If the main controller can maintain all of the thermal gradients across the growth surface of the diamond to be less than 20°C, then the growing of the diamond on the growth surface occurs as shown in step S676 of FIG. 6.

[0079] Measuring the temperature of a growth surface of the diamond, controlling temperature of the growth surface and growing diamond on the growth surface occurs until it is determined that the diamond should be repositioned, as shown in FIG. 6. Although measuring, controlling, growing and the acts of determining are shown and described as steps, they are not necessarily sequential and can be concurrent with one another. For example, the step of growing diamond on the growth surface can occur while measuring the temperature of a growth surface of the diamond and controlling temperature of the growth surface are occurring.

[0080] The repositioning of the diamond, as referred to in step S678, can be done manually or with a robotic mechanism. In addition, a determination can be made of whether the diamond has reached a predetermined or desired thickness, as shown in step S673 of FIG. 6. The determination can be based on an actual measurement via mechanical or optical devices. In another example, the determination can be based on the length of processing time in view of known growth rates for the process. If the diamond has reached the predetermined thickness, then the growing process is complete, as referred to by step 680 in FIG. 6. If the diamond has not reached the predetermined thickness, then the growth process is started again and continues with measuring the temperature of a growth surface of the diamond, controlling temperature of the growth surface and growing diamond on the growth surface until it is determined that the diamond needs to be repositioned, as shown in FIG. 6.

[0081] FIG. 7 is a flow diagram illustrating a process 700 in accordance with embodiments of the present invention that can be used with specimen holder assembly shown in FIG. 3 and FIG. 5. The process 700 begins with step S770 in which an appropriate seed diamond, which can be a grown diamond, manufactured diamond, natural diamond or combination thereof, is positioned in a holder. In the specimen holder assembly 320 of FIG. 3, for example, the diamond seed portion 138 is placed within sheath 134 on the diamond actuator member 360, as shown in FIG. 3. In

another example of a specimen holder assembly, the diamond seed portion 138 is placed within a contoured thermal mass 566 on the diamond actuator 360, as shown in FIG. 5.

[0082] As referred to in step S772, the temperature of the growth surface of the diamond, either the diamond seed or a newly grown diamond portion on the diamond seed, is measured. For example, the pyrometer 142 in FIG. 3 takes a measurement of the growth surface, which is the top surface of the growing diamond portion 140, and provides the measurement to the main process controller 346. In another example, the pyrometer 142 in FIG. 5 takes a measurement of the growth surface, which is the top surface of the seed diamond portion 138, and provides the measurement to the main process controller 546. The measurement is taken such that thermal gradient across the growth surface of the diamond can be determined by the main process controller or at least the temperatures of an edge and the middle of the growth surface are inputted into the main process controller.

[0083] A main process controller, such as main process controller 346 or 546, is used in controlling the temperature of the growth surface, as referred to in S774 in FIG. 7. The main process controller controls the temperature of the growth surface of the diamond such that all temperature gradients across the growth surface are less than 20 °C While controlling the temperature of the growth surface, a determination is made to whether the diamond needs to be repositioned in the holder, as shown in step S775 of FIG. 7. If the main controller can not maintain the temperature of the growth surface of the diamond such that all temperature gradients across the growth surface are less than 20 °C by controlling the plasma, gas flows and coolant flows, then the diamond is repositioned while the diamond is growing as shown in FIG. 7 with the "YES" path from step S775 to both of steps S776 and S778. By repositioning the diamond within the holder, the heat-sinking of the edges of the growth surface is improved. In addition, the growth surface can be positioned within an optimal region of the plasma having a consistency for maintaining all of the thermal gradients across the growth surface of the diamond to be less than 20 °C. If the main controller can maintain all of the thermal gradients across the growth surface of the diamond to be

less than 20 °C, then the growing of the diamond on the growth surface occurs without repositioning as shown in the "NO" path from step S775 to step S776 of FIG. 7.

[0084] Measuring the temperature of a growth surface of the diamond, controlling temperature of the growth surface, growing diamond on the growth surface and repositioning the diamond in the holder occurs until it is determined that the diamond has reached a predetermined thickness. As referred to in step S773 of FIG. 7, a determination is made of whether the diamond has reached a predetermined or desired thickness. The determination can be based on an actual measurement via mechanical or optical devices. For example, a tracking program which records the depth or the amount in terms of distance that the diamond had to be repositioned during the growth process. In another example, the determination can be based on the length of processing time in view of known growth rates for the growth process. If the diamond has reached the predetermined thickness, then the growing process is complete, as referred to by step 780 in FIG. 7. If the diamond has not reached the predetermined thickness, then the growth process continues with measuring the temperature of a growth surface of the diamond, controlling temperature of the growth surface, growing diamond on the growth surface and repositioning the diamond in the holder until it is determined that the diamond needs to be repositioned, as shown in the "NO" path from S773 to within S774 of FIG. 7.

[0085] When implementing processes 600 and 700, diamond growth is usually continued as long as a "step growth" condition can be maintained. In general, the "step growth" condition refers to growth in which diamond is grown on the growth surface of the diamond 136 such that the diamond 136 is smooth in nature, without isolated "outcroppings" or twins. The "step growth" condition may be verified visually. Alternatively, a laser could be used to scan the growth surface of the diamond 136. A change in laser reflectance would indicate the formation of "outcroppings" or twins. Such a laser reflectance could be programmed into the main process controller as a condition for stopping the growth process. For example, in addition to determining if the diamond is a predetermined thickness, a determination can also be made of whether a laser reflectance is being received.

[0086] In general, the methods in accordance with exemplary embodiments of the present invention are designed to create large, colorless, high-quality diamonds with increased {100} growth rates, wherein the growth is along three dimensions. In one embodiment of the invention, oxygen is used in the gas mix at a ratio of about 1-50 % O_2 per unit of CH_4. In another embodiment of the invention, oxygen is used in the gas mix at a ratio of about 5-25 % O_2 per unit of CH_4. Without wishing to be bound by theory, it is believed that the presence of oxygen in the gas mix of the deposition chamber helps to reduce the incorporation of impurities in the diamond, thus rendering the diamonds substantially colorless. During the growth process, the methane concentration is in the range of about 6-12 %. A hydrocarbon concentration greater than about 15 % may cause excessive deposition of graphite inside the MPCVD chamber.

[0087] The process temperature may be selected from a range of about 700-1500 °C, depending on the particular type of single-crystal diamond that is desired or if oxygen is used. Polycrystalline diamond may be produced at higher temperatures, and diamond-like carbon may be produced at lower temperatures. In one embodiment of the invention, the process temperature may be selected from a range of about 700 – 1100 °C. In another embodiment of the invention, the process temperature may be selected from a range of about 900 – 1100 °C. During the growth process, a pressure of about 100-400 torr is used. In one embodiment, a pressure of about 100-300 torr is used. In another embodiment, a pressure of about 160-220 torr is used.

[0088] In one embodiment of the invention, the growth rate of the single-crystal diamond is greater than about 10 μm/hour. In another embodiment, the growth rate of the single-crystal diamond is greater than about 50 μm/hour. In another embodiment, the growth rate of the single-crystal diamond is greater than about 100 μm/hour.

[0089] In one embodiment of the invention, the single-crystal diamond grows to be over 1.2 cm thick. In another embodiment of the invention, the single-crystal diamond grows to be over 5 carats in weight. In another embodiment of the invention, the single-crystal diamond grows to be over 10 carats. In another embodiment of the invention, the single-crystal diamond grows to be over 300 carats.

[0090] In one embodiment, the diamond is grown on up to six {100} faces of an SC-CVD diamond seed. In another embodiment, the diamond grown on up to six {100} faces of the SC-CVD diamond seed is greater than about 300 carats. In another embodiment, the growth of the diamond can be substantially in two dimensions to produce a crystal of large lateral dimension (*e.g.*, a plate of at least about one inch square) by polishing one of the longer surfaces and then growing the diamond crystal in a second orthogonal direction on that surface. In another embodiment, the growth of the diamond can be in three dimensions. In another embodiment, the growth of the diamond is substantially cubic. In another embodiment, the substantially cubic diamond grown along three dimensions is at least one inch in each dimension.

[0091] The gas mix can also include N_2. When N_2 is used, it is added to the gas mix at a ratio of about 0.2-3 % N_2 per unit of CH_4. The addition of N_2 to the gas mix at this concentration enhances the growth rate and promotes {100} face growth.

[0092] FIG. 8 is a UV-VIS spectrum for an HPHT IIa diamond; an SC-CVD diamond produced according to the method of the invention, *e.g.*, with a deposition chamber atmosphere comprising from about 5 % to about 25 % O_2 per unit of CH_4; and an SC-CVD diamond produced with N_2 gas present as a component of the deposition chamber atmosphere. The SC-CVD diamond produced with N_2 gas is light brownish in appearance and exhibited a broad band around 270 nm. This is related to the presence of non-diamond carbon, nitrogen, and vacancies in the diamond. SC-CVD diamonds produced with N_2 gas that have a darker brown appearance show increased absorption below 500 nm and a broad feature centered at 520 nm. This is not seen in natural diamond or HPHT-grown synthetic diamond. The brownish color and the broad band features can be removed by HPHT treatment, *e.g.*, annealing. The spectrum of the diamond produced by the methods of the invention, *e.g.*, with a deposition chamber atmosphere comprising from about 5 % to about 25 % O_2 per unit of CH_4, did not exhibit a broad band at 270 nm or at 520 nm, and is comparable to man-made HPHT-type IIa diamond. Without wishing to be bound by theory, applicants believe that the added oxygen reduces the hydrogen impurity levels and the amount of non-diamond carbon.

[0093] FIG. 9 shows a colorless SC-CVD diamond produced by the method of the invention, *e.g.*, with a deposition chamber atmosphere comprising from about 5 % to about 25 % O_2 per unit of CH_4, on the left and a brownish SC-CVD diamond produced with a N_2, rather than O_2, in the deposition chamber on the right. Both single-crystal diamonds are approximately 5 x 5 x 1 mm in size.

[0094] Figure 10 shows an SC-CVD diamond block formed by deposition on six {100} faces of a HPHT Ib substrate, such as the 4 x 4 x 1.5 mm crystal shown below. This is an attempt to further increase the size of the diamond crystals, wherein gem-quality CVD diamond is grown according to the method of the invention sequentially on the 6 {100} faces of the substrate. By this method, the three-dimensional growth of colorless, single-crystal diamond can produce diamonds about 300 carats in weight and about 1 inch in each dimension.

[0095] FIG. 11 is an IR absorption spectrum (2500-8000 cm^{-1}) for a colorless SC-CVD diamond produced according to the method of the invention, *e.g.*, with a deposition chamber atmosphere comprising from about 5 % to about 25 % O_2 per unit of CH_4, and a brown SC-CVD diamond produced with N_2 gas present as a component of the deposition chamber atmosphere. The spectrum for the brown SC-CVD diamond produced with N_2 gas had peaks at 2931, 3124, 6427, 6857, 7234, and 7358 cm^{-1}. Those peaks are absent in the spectrum for the colorless diamond produced according to the method of the invention with O_2 gas present. The data, therefore, show that there are no near IR or mid IR impurities due to hydrogen in the colorless diamond produced according to the method of the invention with O_2 gas present. This further demonstrates that the method of the invention produces very pure, large single-crystal diamond at a high growth rate.

[0096] The colorless, single-crystal CVD diamond material may be prepared for a range of industrial and other applications, including, but not limited to, uses in electronics, optics, and as a colorless gem.

[0097] Other aspects of the invention can be understood in greater detail from the following examples.

[0098] **EXAMPLE 1**

[0099] A diamond growth process was conducted in the above-described MPCVD chamber in FIG. 1. First, a commercial 3.5x3.5x1.6 mm^3 high pressure high temperature (HPHT) synthetic type Ib diamond seed was positioned in the deposition chamber. The diamond seed has polished, smooth surfaces that were ultrasonically cleaned with acetone. The deposition surface was within two degrees of the {100} surface of the diamond seed.

[00100] Then, the deposition chamber was evacuated to a base pressure of 10^{-3} torr. The infrared pyrometer 142 was focused though a quartz window at an incident angle of 65 degrees on the growth surface of the diamond and had a minimum 2 mm^2 diameter spot size. Diamond growth was performed at 160 torr pressure using gas concentrations of 15% O_2/CH_4, and 12% CH_4/H_2. The process temperature was 1020° C., and gas flow rates were 500 sccm H_2, 60 sccm CH_4, and 1.8 sccm O_2. Deposition was allowed to continue for 12 hours.

[00101] The resulting diamond was 4.2x4.2x2.3 mm^3 unpolished, and represented about 0.7 mm of growth on the seed crystal that was grown at a growth rate 58 microns per hour. The growth morphology indicated that the <100> side growth rate was faster than the <111> corner growth rate. The growth parameter, α, was estimated at 2.5-3.0.

[00102] The deposited diamond was characterized using optical microscopy, x-ray diffraction (XRD), Raman spectroscopy, and photoluminescence (PL) spectroscopy. The optical microscopy and X-ray diffraction study of the resulting diamond confirmed that it was a single-crystal. UV-visible/near infrared transmission spectra of the MPCVD grown diamond separated from the seed diamond is distinct from MPCVD diamond grown in the presence of N_2 gas and matches pure (Type IIa) diamond.

[00103] A number of MPCVD diamonds were produced according to the guidelines of Example 1 while varying the described process temperature. These experiments demonstrate the process temperature ranges for producing various types of diamond in the growth process according embodiments of the present invention.

[00104] Diamond produced by the above methods and apparatus will be sufficiently large, defect free and translucent so as to be useful as, for example, windows in high power laser or synchrotron applications, as anvils in high pressure apparatuses, as cutting instruments, as wire dies, as components for electronics (heat sinks, substrates for electronic devices), or as gems. Other examples of uses or applications for diamond made by the above methods and apparatus include the following:

a.) wear resistant material—including, but not limited to, water/fluid jet nozzles, cutting instruments (*e.g.*, razors, knives), surgical instruments (*e.g.*, surgical blades, cutting blades for surgical instruments), microtone, hardness indentor, graphical tools, stichels, instruments used in the repair of lithographic pieces, missile radomes, bearings, including those used in ultra-high speed machines, diamond-biomolecule devices, microtomes, and hardness indentors;

b.) optical parts—including, but not limited to, optical windows, reflectors, refractors, lenses, gratings, etalons, alpha particle detectors, and prims;

c.) electronics—including, but not limited to, microchannel cooling assemblies; high purity SC-CVD diamonds for semiconductor components, SC-CVD doped with impurities for semiconductor components

d.) anvils in high pressure apparatuses—including, but not limited to, the "Khvostantsev" or "Paris-Edinburgh" toroid shaped anvils that can be used with multiple optical, electrical, magnetic, and acoustic sensors; Bridgman anvils that are relatively large, have variable heights, and include major angles [15]; Multianviles, Drickamer cells, belt apparatus, piston-cylinder apparatus; precompressing samples for laser or magnetic shock wave studies;

colorless, smooth coating for hydrogen and other applications, apparatus for pre-compressing samples for lasers or magnetic shock;

e.) containers—including, but not limited to, 6 edge {100} plated diamonds can be connected to each other to form a container, CVD diamond coating can be further employed to form a vacuum tight container;

f.) laser source-including, but not limited to, annealing SC-CVD diamond to form a stable H3 center (nitrogen aggregate, N-V center, Si center, or other dopants;

g.) superconductor and conducting diamond—including, but not limited to, HPHT annealing with SC-CVD diamond grown with an impurity such as H, Li, N, Mg, or another low atomic weight element with a size approaching that of carbon;

h.) substrate for other CVD diamond growth—using CVD plates as substrates for CVD growth has the advantage over natural or HPT substrates in large size and toughness (to avoid cracking during growth).

[00105] In one embodiment, the present invention is directed to anvils in high pressure apparatuses, wherein the anvils comprise CVD diamond, preferably single-crystal CVD diamond. Anvils comprising single-crystal CVD diamond can be used at higher pressures than anvils made of other materials, such as tungsten carbide. Anvils comprising single-crystal CVD diamond, moreover, are also beneficial in facilitating more and better test results, since the diamond is transparent to neutron, x-ray, and other electromagnetic radiation. Examples of anvil designs that can comprise single crystal CVD diamonds include Bridgman anvils, including, but not limited to, Bridgman anvils that are relatively large, include variable heights, and include major angles and Paris-Edinburgh toroid anvils, including, but not limited to, those discussed in [15].

[00106] In another embodiment, the present invention is directed to a single-crystal CVD diamond that is laser inscribed with identifying marks (*e.g.*, name, date, number) and a method of preparing such a diamond. The identifying marks, which can take the form of, *e.g.,* lines, text, figures, or symbols, can be laser inscribed onto a diamond substrate prior to starting the CVD process to prepare a single-crystal diamond. The mark is transferred to the single-crystal diamond through this process.

[00107] Laser inscription of single crystal diamond can have many applications, including, but not limited to, diamond certification and provenance. Laser inscription can also be used to create "designer" gems, *i.e.*, individualized gems with embedded, customer-requested marks such as text or symbols. The marks inscribed into the diamond cannot be polished off, in part because they can be embedded deep into the diamond.

[00108] Other applications of the laser inscription technology can include producing embedded circuits and electrical contacts in which laser inscription is used to create a

"graphitized" and electrically conductive path in the diamond. Such localized laser cutting can also be useful for removing unwanted regions of poorly crystallized CVD diamond during the synthesis stage (*e.g.*, in much the same way that a dentist would clean out a cavity in a tooth). This latter application can be particularly important during the long synthesis of a very large diamond that may develop problematic growth regions. The applicants have already performed successful work in this area.

[00109] A variety of lasers can be used to perform laser inscription, including, but not limited to, ultraviolet (*e.g.*, excimer) lasers, infrared lasers, high power visible lasers or focused x-ray lasers. In preferred embodiments of the invention, a near-infrared (Nd-YAG) laser built by Bettonville NV of Belgium was used to inscribe marks into single crystal diamond.

[00110] Another embodiment, which is a variation of the above described applications, is the use of focused ion or electron beams. Ions can be implanted to change the conducting properties and introduce specific defects near a diamond surface. For example, one area of great interest is introducing nitrogen defects for quantum computing. The above methods can be used to create regions of unique chemistry in single crystal diamond by "writing" with specific elements (*e.g.*, selective ion implantation) or with electron beams (*e.g.*, controlled defect patterning) within a wafer or block using subsequent overgrowth of diamond.

[00111] The colors of diamond formed by the methods discussed above can be changed by annealing. For example, a yellow or brown diamond can be annealed into a green diamond.

[00112] Single-crystal CVD diamonds of other colors can also be prepared. Examples of such diamonds used in anvils include the following:

1.) mixed red, green, and blue CVD layers inside the anvil to produce a white color;

2.) coating a thin CVD boron layer on the table to make a vivid blue color; and

3.) using a partial blue and green CVD with a yellow seed to produce a rainbow effect.

[00113] Figure 12 shows a cross-sectional view of a water jet cutter. The jewel holds back high pressure (*e.g.*, about 55, 000 psi) water to form a high velocity water jet. This jet of water then enters a venturi where abrasive is introduced. The mixture of abrasive, water, and air, then mixes in the mixing tube to form a jet capable of cutting

steel or just about any other material. Not unexpectedly, the jewel and the mixing tube are placed under an enormous amount of pressure and are thus subject to rapid wear. This is especially true of the mixing tube, due to the presence of the abrasive. In one embodiment, the mixing tube and jewel comprise single-crystal CVD diamond produced by methods previously described. In another embodiment, other components of the water jet comprise single-crystal CVD diamond.

[00114] FIG. 13 shows a cubic container configuration comprising single-crystal CVD diamond. Such a container can be produced, for example, by coating three separate six {100} face plates with CVD diamond using the aforementioned CVD techniques. The face plates prior to coating can be CVD diamonds, single-crystal CVD diamonds, HPHT diamonds, or natural diamonds. These face plates essentially act as seeds on which CVD diamond is coated. The smaller area, thin plates can then be placed on top of a larger area, thicker plate, which contains a substantially square hole created by a laser. The entire assembly can then be placed back into the deposition chamber where an additional CVD diamond coating along all {100} faces will seal the pieces together.

[00115] FIG. 14 shows another container design in which CVD diamond is grown on two plates placed together in a step configuration. The end result is to create a larger plate through the step-like mosaic fusion of smaller plates. The plates will fuse well together on the top surfaces if all of the plates possess 3 {100} faces and are aligned in the same direction (*i.e.*, have an alignment within 10 degrees of each other). The larger plate created using this method can be used as, for example, a seed for further CVD diamond growth.

[00116] FIG. 15a) shows a diamond anvil cell and gasket supported with a binding ring.

[00117] FIG. 15b) shows a beveled diamond anvil. The thick lines show the shape of an anvil surface that would be machined to maximize performance. This is the Toroid-type design previously made of tungsten carbide.

[00118] As the present invention may be embodied in several forms without departing from the spirit or essential characteristics thereof, it should also be understood that the above-described embodiments are not limited by any of the details of the foregoing

description, unless otherwise specified, but rather should be construed broadly within its spirit and scope as defined in the appended claims, and therefore all changes and modifications that fall within the metes and bounds of the claims, or equivalence of such metes and bounds are therefore intended to be embraced by the appended claims.

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The claims defining the invention are as follows:

1. A nozzle comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

   i) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 °C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

   ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

2. The nozzle according to claim 1, wherein all temperature gradients across the growth surface of the diamond are less than about 20 °C.

3. The nozzle according to either claim 1 or 2, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

4. The nozzle according to any one of claims 1-3, wherein the nozzle is used in a high pressure waterjet cutting apparatus.

5. A cutting blade for a surgical instrument comprising a cutting edge comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

   i) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 °C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

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ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

6. The cutting blade according to claim 5, wherein all temperature gradients across the growth surface of the diamond are less than about 20 °C.

7. The cutting blade according to either claim 5 or 6, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

8. A cutting instrument comprising a cutting edge comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

i) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 °C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

9. The cutting instrument according to claim 8, wherein all temperature gradients across the growth surface of the diamond are less than about 20 ^{o}C.

10. The cutting instrument according to either claim 8 or 9, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

11. A wire drawing die comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

i) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of

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900-1400 °C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

5 ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

10 12. The wire drawing die according to claim 11, wherein all temperature gradients across the growth surface of the diamond are less than about 20 °C.

13. The wire drawing die according to either claim 11 or 12, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to
15 about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

14. A bearing comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

i) controlling the temperature of a growth surface of the diamond such that
20 the temperature of the growing diamond crystals is in the range of 900-1400 °C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

25 ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

30 15. The bearing according to claim 14, wherein all temperature gradients across the growth surface of the diamond are less than about 20 °C.

16. The bearing according to either claim 14 or 15, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to
35 about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

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17. A diamond anvil comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

    i) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 ^{0}C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond and

    ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

18. The diamond anvil according to claim 17, wherein all temperature gradients across the growth surface of the diamond are less than about 20 ^{0}C.

19. The diamond anvil according to either claim 17 or 18, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

20. The diamond anvil according to any one of claims 17-19, wherein the single-crystal diamond is substantially colorless.

21. The diamond anvil according to any one of claims 17-20, wherein the anvil is a Bridgman anvil.

22. The diamond anvil according to any one of claim 17-20, wherein the anvil is a Paris-Edinburgh toroid anvil.

23. An etalon comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

    i) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 °C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

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ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

5

24. The etalon according to claim 23, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

10 25. An optical window comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

i) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 °C and the diamond is mounted in a heat sink holder made of a 15 material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber 20 having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

26. The optical window according to claim 25, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % 25 O_2 per unit of CH_4 in the deposition chamber atmosphere.

27. An alpha particle detector comprising a single-crystal diamond, wherein the single-crystal diamond was produced by a method comprising:

i) controlling the temperature of a growth surface of the diamond such that 30 the temperature of the growing diamond crystals is in the range of 900-1400 ^{0}C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond, and

35 ii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

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28. The alpha particle detector according to claim 27, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

5

29. A laser-inscribed single-crystal diamond produced by a method comprising:
    i) laser inscribing a mark onto a diamond substrate prior to starting the CVD process to prepare a single-crystal diamond
    ii) controlling the temperature of a growth surface of the diamond such that the temperature of the growing diamond crystals is in the range of 900-1400 °C and the diamond is mounted in a heat sink holder made of a material that has a high melting point and high thermal conductivity to minimize temperature gradients across the growth surface of the diamond and
    iii) growing single-crystal diamond by microwave plasma chemical vapor deposition on the growth surface of a diamond in a deposition chamber having an atmosphere greater than 150 torr, wherein the atmosphere comprises from about 8 % to in excess of about 30 % CH_4 per unit of H_2.

10

15

20

30. The laser-inscribed single-crystal diamond according to claim 29, wherein the single-crystal diamond is produced by a method further comprising the use of from about 5 to about 25 % O_2 per unit of CH_4 in the deposition chamber atmosphere.

25

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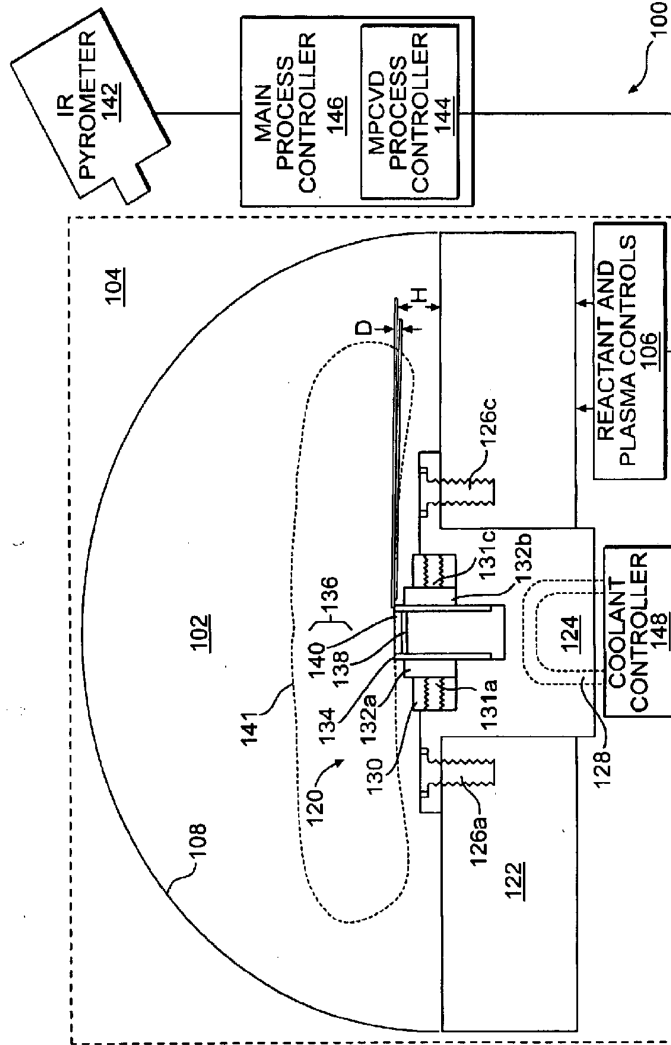

FIG. 1

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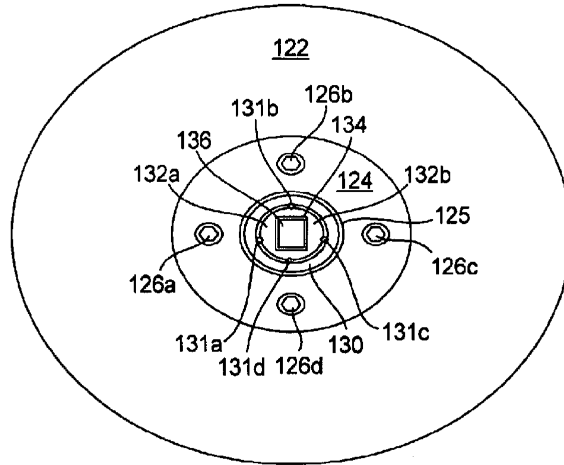

FIG. 2a

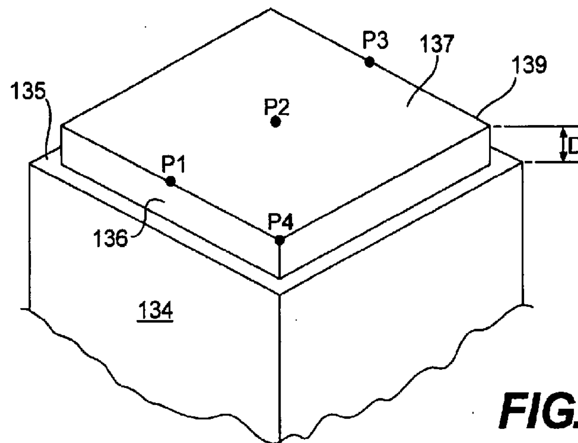

FIG. 2b

3/15

FIG. 3

IR
PYROMETER
142

MAIN
PROCESS
CONTROLLER
346

MPCVD
PROCESS
CONTROLLER
144

300

304

H

D

REACTANT AND
PLASMA CONTROLS
106

126c

136

360

362

324

COOLANT AND DIAMOND/
HOLDER CONTROLS
329

140

138

134

364

341

128

320

108

126a

122

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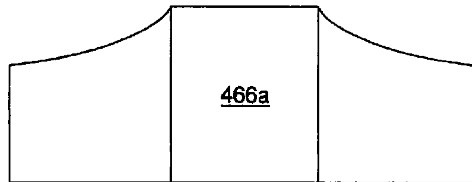

FIG. 4a

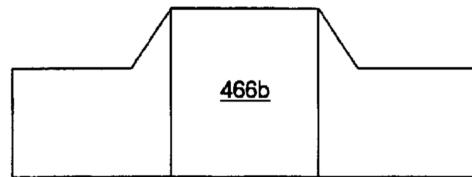

FIG. 4b

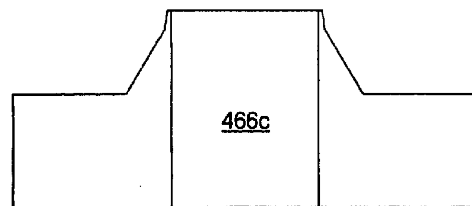

FIG. 4c

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FIG. 5

IR PYROMETER 142

MAIN PROCESS CONTROLLER 546

MPCVD PROCESS CONTROLLER 144

500

504

D

H

REACTANT AND PLASMA CONTROLS 106

126c

562

524

360

136

541

140

138

520

566

128

COOLANT AND DIAMOND/ HOLDER CONTROLLER 329

108

126a

122

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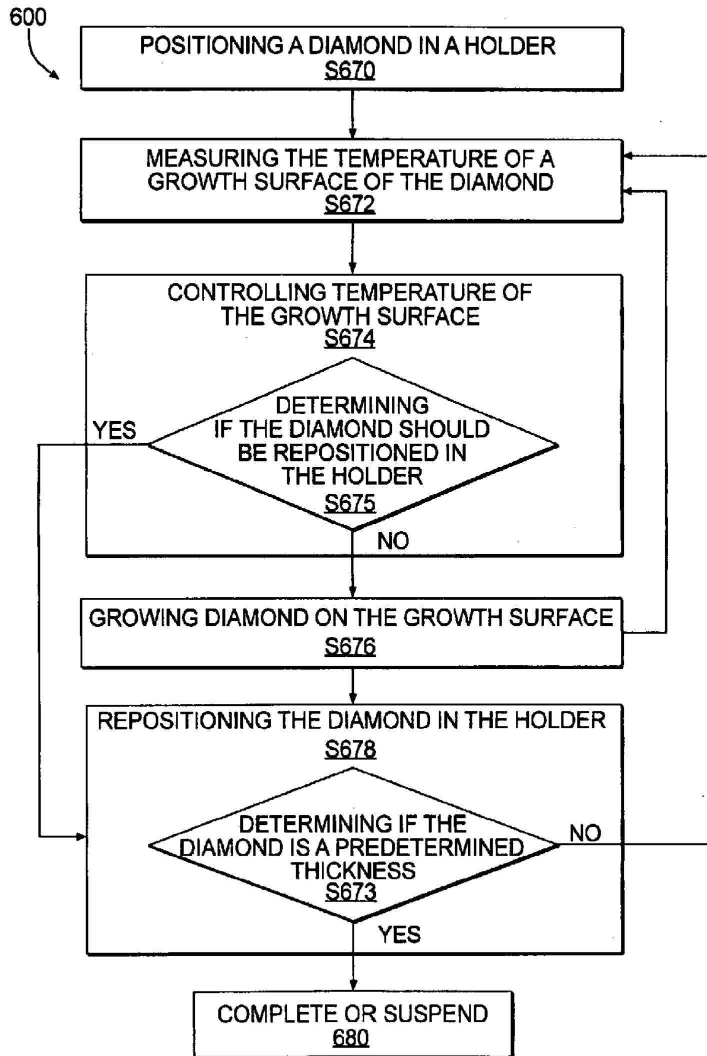

FIG. 6

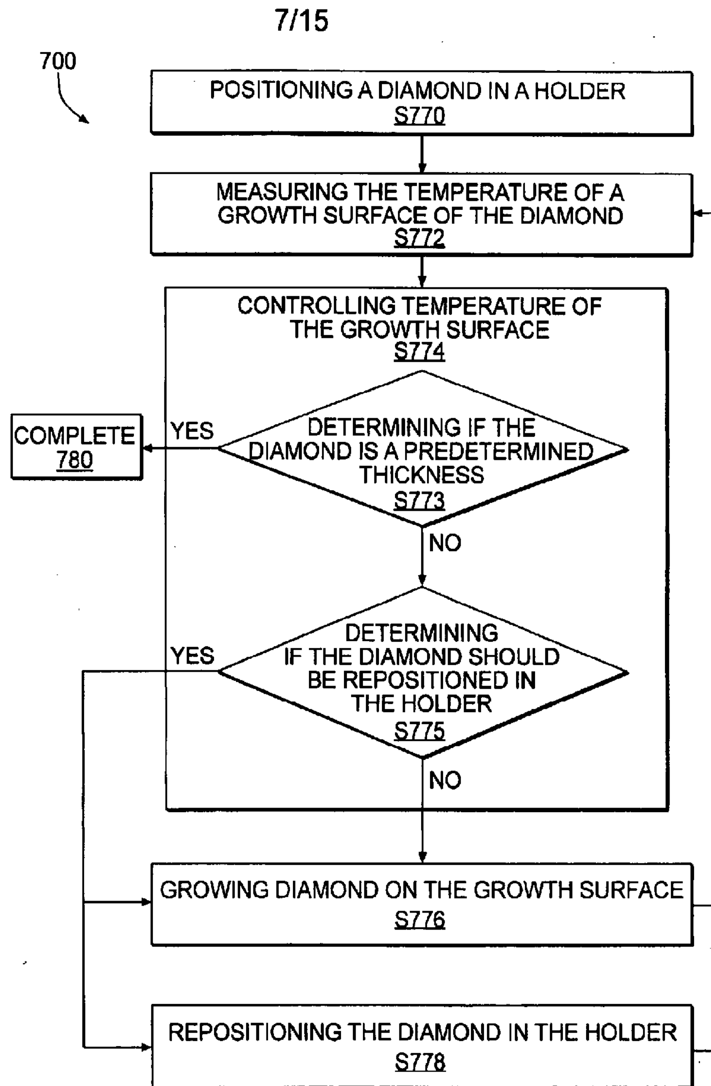

FIG. 7

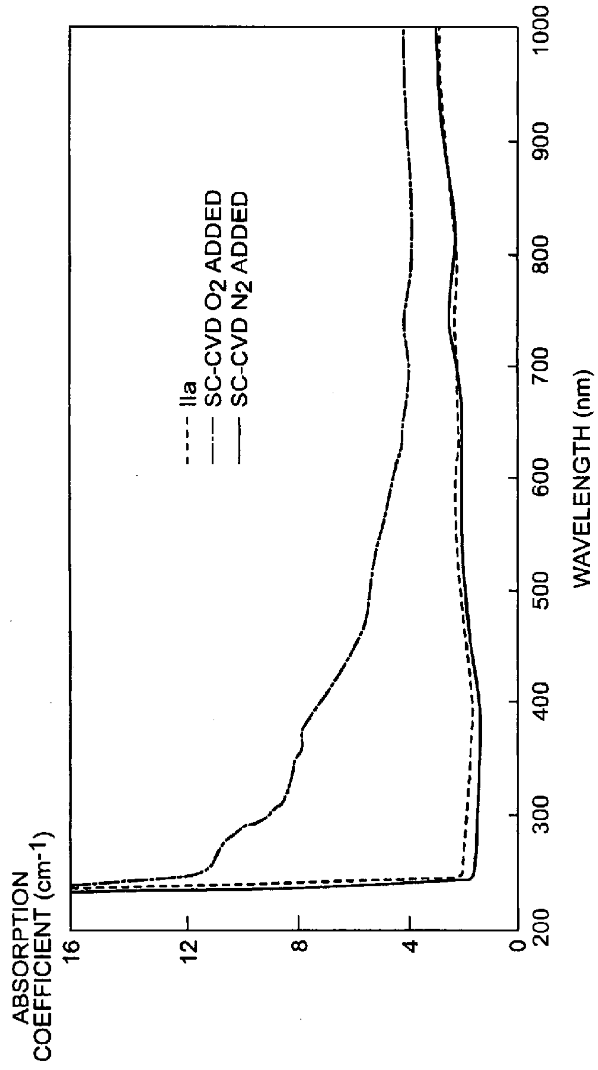

FIG. 8

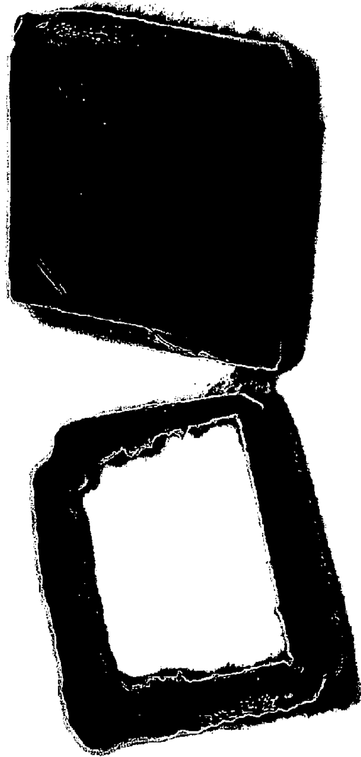

FIG. 9

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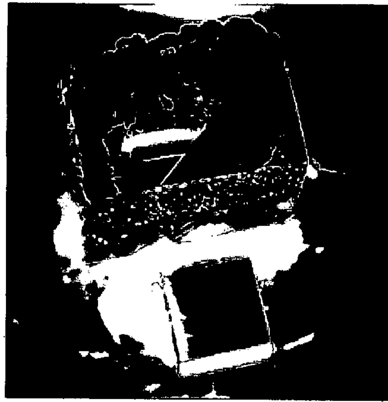

FIG. 10

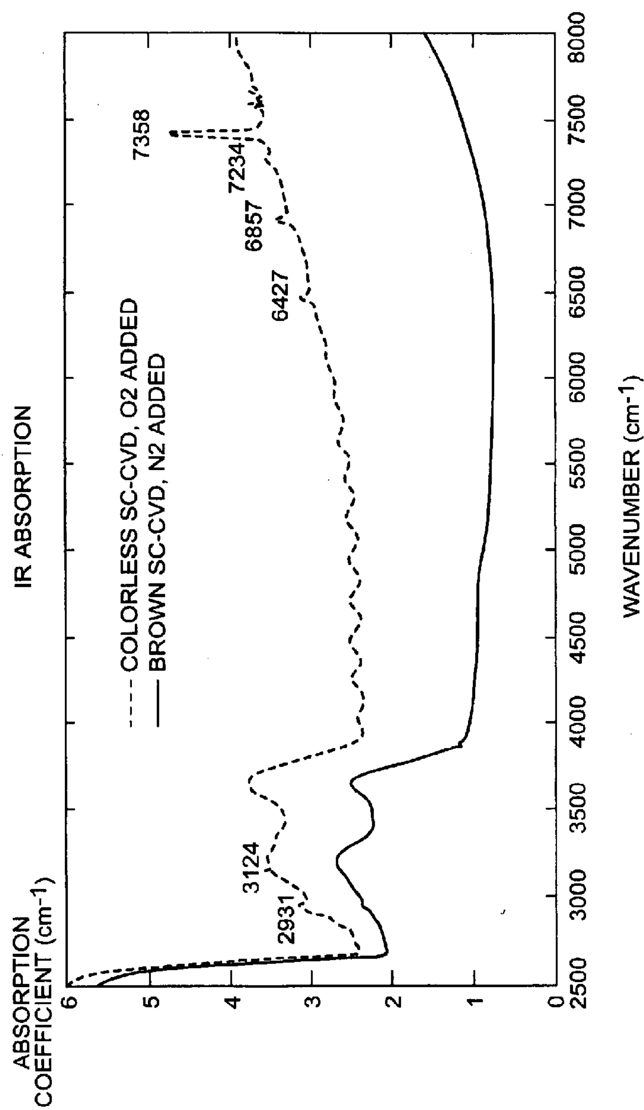

FIG. 11

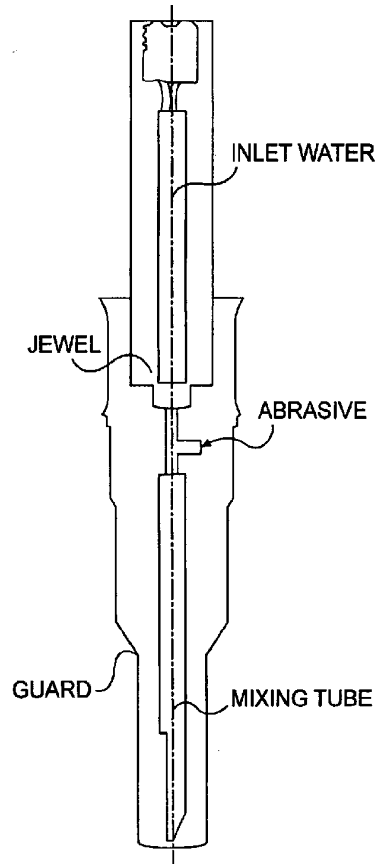

FIG. 12

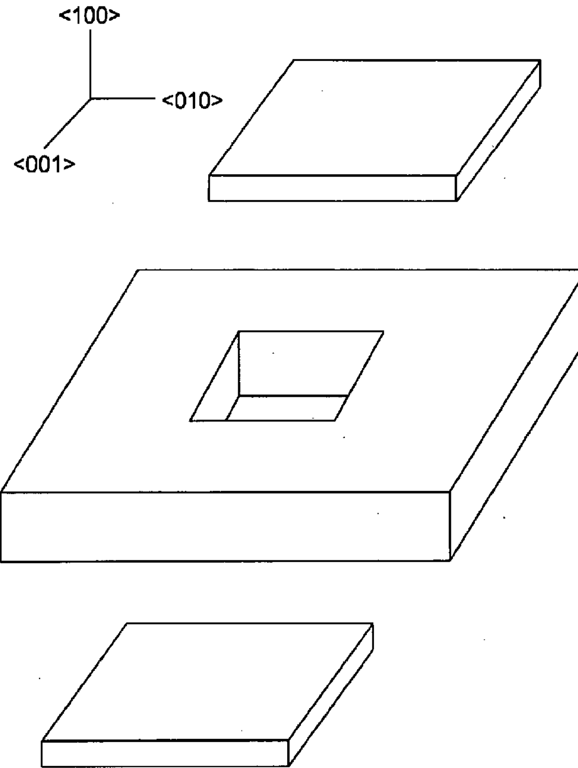

FIG. 13

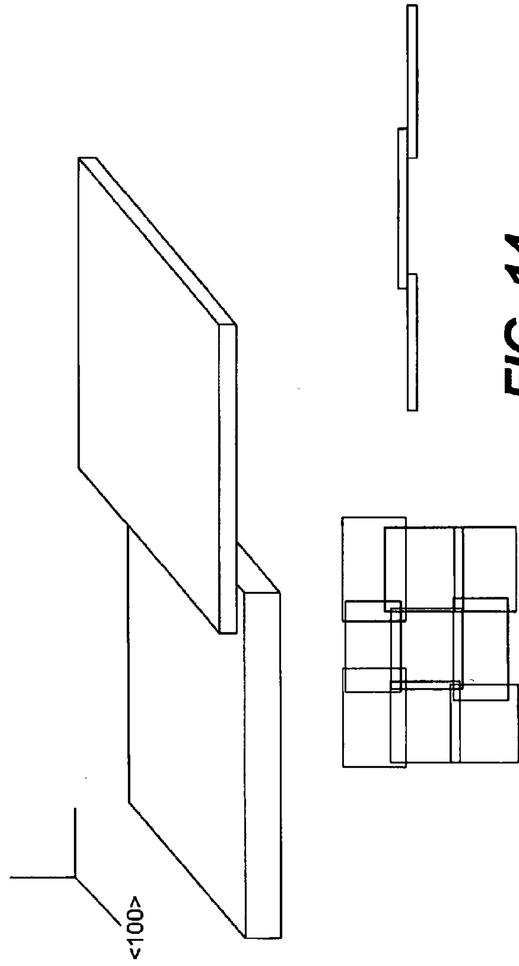

FIG. 14

SUBSTITUTE SHEET (RULE 26)

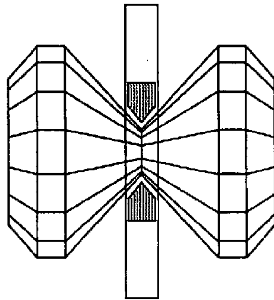

FIG. 15a

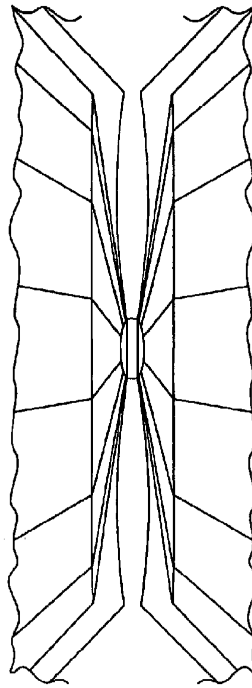

FIG. 15b