PROCESS OF DIAMOND GROWTH FROM C_{70}

FIELD OF THE INVENTION

The present invention relates to a method of growing diamonds by reduction of C_{70} Buckminster fullerenes in the presence of diamond seed particles.

BACKGROUND OF THE INVENTION

Diamond, being the hardest substance known, is of great commercial and scientific value. It is inert to chemical corrosion and can withstand compressive forces and radiation. It is an electrical insulator having extremely high electrical resistance but is an excellent thermal conductor, conducting heat better than most other electrical insulators. Diamond is structurally similar to silicon but is a wide-band-gap semiconductor (5 eV) and so is transparent to UV-visible light and to much of the infrared spectrum. It has an unusually high breakdown voltage and low dielectric constant. These properties, coupled with recent advances, have led to speculation that diamond might find widespread application in high speed electronic devices and devices designed to be operated at high temperature. If it can be doped successfully diamond could become an important semiconductor material on which new or replacement device applications may be based. While silicon chips can withstand temperatures up to 300°C, it is estimated that diamond devices may be able to withstand considerably higher temperatures. Diamond film already find applications as hard protective coatings.

Because of these useful properties, synthetic diamond has great potential in research and commercial applications. Synthetic diamonds are now produced by two known methods: a high pressure process in which carbonaceous material is compressed into diamond using high pressure anvils; and the more recent technique of chemical vapour deposition (CVD) in which diamond films are deposited on an appropriate substrate by decomposing a carbon containing gaseous precursor.

Of recent particular scientific interest are a class of carbon structures known as Buckminster fullerenes which are formed by an integral number of carbon atoms which combine to form a closed, roughly spherical structure. Two prominent fullerenes are C_{60} and C_{70}, which are spherical structures comprising 60 and 70 carbon atoms, respectively. The successful transformation of C_{60} and C_{70} into diamond at high pressure has been disclosed by Manuel Nunez Regueiro, Pierre Monceau, Jean-Louis Hodeau, Nature, 355, 237-239 (1992) and Manuel Nunez Regueiro, L.Abello, G.Lucazeau, J.L.Hodeau, Phys. Rev. B, 46, 9903-9905 (1992). The transition of C_{60} to diamond has also been studied by Hisako Hirai, Ken-ichi Kondo and Takeshi Ohwada, Carbon, 31, 1095-1098 (1993). It is also known that C_{70} can accelerate the nucleation of diamond thin film formation on metal surfaces using CVD as disclosed by R. J. Meilunas, R. P. H. Chang, S. Liu, M. M.Kappes, Appl. Phys. Lett., 59, 3461-3463 (1991), and R. J. Meilunas, R. P. H. Chang, S. Liu, M. M.Kappes, Nature, 354, 271 (1991).

A high growth rate of diamond film using fullerene precursors in an argon microwave plasma with or without hydrogen has been reported by D.M.

Gruen, S. Liu, A.R. Krauss and X. Pan, J. Appl. Phys., 75, 1758-1763 (1994), and D.M. Gruen, S. Liu, A.R. Krauss, J. Luo and X. Pan, Appl. Phys. Lett., 64, 1502-1504 (1994).

Recently, dispersed diamond particles with diameters in the range of 20-150 Å have been observed in fullerene-rich soot as disclosed by Vladimir Kuznetsov, A. L. Chuvilin, E.M.Moroz, V.N. Kolomiichuk, Sh. K. Shaikhutdinov, Yu. V. Butenko, Carbon, 32, 873-882 (1994), and Vladimir L. Kuznetsov, Andrey L.Chuvilin, Yuri V. Butenko, Igor Yu. Malkov, Vladimir M. Titov, Chem. Phys. Lett., 222, 343-348 (1994).

United States Patent Nos. 5,370,855, 5,462,776, 5,328,676 and 5,209,916 issued to Gruen disclose methods of conversion of fullerenes to diamond. The methods comprise subjecting the fullerenes to highly energetic environments such as radio frequency plasma discharges, electron beams, intense laser beams to break down potassium modified fullerenes. Growth of diamond onto diamond seed substrates heated to 1000 to 1200°C is disclosed in Patent No. 5,462,776. A drawback to all these methods of fullerene conversion is the fact that at such high temperatures the diamond structure is prone to conversion to graphite. Another drawback is the expense of the energy imparting devices such as lasers, RF generators and the like.

It would be very advantageous and of potentially significant commercial value to be able to grow single crystal diamond particles with much larger particle sizes at relatively low temperatures in an environment not requiring capital intensive equipment.

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SUMMARY OF THE INVENTION

It is an object of the present invention to provide an economical process for growing single crystal diamonds which does not require high temperatures or pressures.

The present invention provides a process for the formation of diamond particles of mean diameters in excess of 400 μm, grown from diamond powder nucleation seeds of approximately 1.5 μm mean diameter. C_{70} is reduced in the presence of reducing agents such as selenium or phosphorous at moderate temperatures and pressure.

In one aspect of the invention there is provided a process for growing diamonds. The method comprises reducing a quantity of C_{70} in the presence of diamond seed particles to cause at least some of the diamond seed particles to grow.

In another aspect of the invention, a process for growing diamonds is provided which comprises providing diamond seed particles, and providing a quantity of C_{70} powder and a reducing agent both in flow communication with the diamond powder. The process includes heating the C_{70}, the reducing agent and the diamond powder under vacuum at an effective temperature and for an effective period of time to cause some of the C_{70} to be reduced by the reducing agent and deposit onto at least some of the diamond seed particles causing the particles to grow larger.

In this aspect of the invention the preferred reducing agent is selenium or phosphorous, the effective temperature is about 550°C and the effective period of time is from about 18 days to about 60 days.

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In another aspect of the invention there is provided a process for growing diamonds. The process comprises providing a plurality of diamond seed particles having a mean diameter and providing a quantity of C_{70} powder and a reducing agent. The C_{70} powder and the reducing agent are in flow communication with the diamond seed particles. The process includes the step of heating the C_{70} powder to produce C_{70} in the vapour phase, and heating the reducing agent and the diamond seed particles under vacuum at a temperature of from about 500°C to about 600°C and for a period of time of from about 18 days to about 60 days to cause a portion of the C_{70} in the vapour phase to be reduced by the reducing agent and deposit onto and increase the mean diameter of at least one of the diamond seed particles.

BRIEF DESCRIPTION OF THE DRAWINGS

The method of diamond growth from C_{70} forming the subject invention will now be described, reference being had to the accompanying drawings, in which:

Figure 1 illustrates an apparatus used for growing diamonds from diamond seeds according to the present invention;

Figure 2 is a scanning electron micrograph (SEM) of C_{70} polycrystalline powder used in the method according to the present invention;

Figure 3 is an SEM of a sample of the diamond seeds (average size ~1.5 μm) used in the method of the present invention;

Figure 4 is an SEM of several diamond particles found in the lower portion of the capillary shown in Figure 1 after the assembly was heated at

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550°C for 20 days in the presence of selenium;

Figure 5 displays a typical laser micro-Raman spectrum of the C_{70} polycrystalline powder of Figure 2;

Figure 6 displays a laser micro-Raman spectrum of one of the particles shown in Figure 4 in the wavelength range 1000 to about 1700 cm^{-1};

Figure 7 displays a laser micro-Raman spectrum of one of the particles shown in Figure 4 in the wavelength range 500 to about 1700 cm^{-1};

Figure 8 is shows the x-ray diffraction of one of the grown diamond particles shown in Figure 4;

Figure 9 shows the structure of a diamond particle grown according to the method of the present invention calculated from the x-ray diffraction pattern of Figure 8;

Figure 10 shows the structure of C_{70}; and

Figure 11 shows the structure of C_{60}.

DETAILED DESCRIPTION OF THE INVENTION

Referring to Figure 1, approximately 18 to 20 mg of C_{70} (98 %), approximately 11 mg of elemental selenium powder (99.5%, -325 Mesh particle size, Alfa) or red phosphorous powder (99%, -100 Mesh particle size, Alfa) and trace quantities of diamond seed powder (average diameter of 1.5 μm) were placed generally at 10 in a 1 cm diameter x 10 cm long pyrex tube 12. A trace quantity (< 1mg) of diamond powder shown generally at 14 was loaded into a small pyrex capillary (1.0 mm x 50 mm) 16, which was then set into the larger pyrex tube 12 as shown in Figure 1. The entire tube assembly was evacuated

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and sealed under vacuum (~$2x10^{-5}$ torr). After heating the tube assembly at a temperature of about 550°C in a tube oven (not shown) with controllable temperature for 20 to 30 days, various portions of the product were examined using laser micro-Raman Spectroscopy and scanning electron microscopy (SEM).

Crystallite sizes and shapes of the diamond seeds and the reaction produces were examined using scanning electron microscopy (HITACHI model S-570, Japan). The identification of the crystallites as diamond was accomplished using Laser micro-Raman spectroscopy. An important advantage of micro-Raman spectroscopy is that the sample crystallite can be located by a charge coupled device (CCD) camera at high magnification. This enabled both the size of the crystallite and its identity to be determined simultaneously. A Kr ion laser tuned to 530.87 nm was used as the excitation source. An approximately 2 mW beam was focused down to a 3 micrometer diameter spot. Raman spectra were detected in a back scattering geometry using a triplemate spectrometer (SPEX Industries Inc. model 1877D) equipped with a microscope (Micromate model 1482D) and a liquid nitrogen cooled CCD detector (Princeton Instruments Inc. Model LN/CCD).

An SEM image of the C_{70} powder that was used in the above-described experiment is shown in Figure 2. The plate-like crystallites are shown for the purpose of comparison with diamond crystallites. Figure 3 shows an SEM image of a sample of the diamond powder that was used as seed diamond. Examination of several such samples showed that particle diameters rarely exceeded 2 μm and no particle with a diameter in excess of 3 μm was seen. In

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contrast, Figure 4 shows four crystallites with average diameters of approximately 400 μm that were found among the reaction products of the fullerene seeded with small diamond particles and with selenium used as the reducing agent after 20 days of heating at 550°C. Only approximately 1% of the diamond seeds were found to be enlarged to this extent. However, on a volume basis the overall enlargement of the individual seeds was substantial.

The micro-Raman spectrum of one of these crystallites is shown in Figure 6 over the wavelength range 1000 to about 1700 cm^{-1}. The characteristic single peak at approximately 1328 cm^{-1} is unequivocal proof that the particle is diamond. The micro-Raman spectrum shown in Figure 7 is similar to the spectrum of Figure 6 but was taken in the wavelength range 500 to about 1700 cm^{-1}. For comparison, the Raman spectrum of C_{70} that was used in this work is shown in Figure 5. There is no such peak at 1328 cm^{-1}. The 26 relatively strong vibrational mode frequencies obtained from the spectrum of Figure 5 are in good agreement with values previously disclosed in R. A. Jishi, M.S. Dresselhaus, G. Dresselhaus, Kai-An Wang, Ping Zhou, A.M. Rao and P.C. Eklund, Chem. Phys. Lett., **206**, 187 (1993). These vibrational mode frequencies are also in good agreement with group theoretical analysis, see M. S. Dresselhaus, G. Dresselhaus and R. Saito, Phys. Rev. B, **45**, 6234 (1992). In all C_{70} has 53 Raman active modes.

The x-ray diffraction pattern shown in Figure 8 for one of the grown diamond particles in Figure 4 clearly shows the single crystal cubic structure of diamond and this is confirmed from the crystal structure shown in Figure 9 calculated from the x-ray diffraction pattern of Figure 8.

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Most of the larger diamond particles that were produced were found in the capillary 16 (Figure 1) in which the seed diamonds were deposited. This strongly suggests that gas-phase C_{70} was responsible for the growth of the seed diamonds. C_{70} has a substantial vapour pressure at 550°C. The Raman spectrum of the material that remained at the bottom of the larger tube 10 after 20 days corresponded to that of unreacted C_{70}.

Analogous experiments were also conducted using C_{60} instead of C_{70}. These experiments using C_{60} did not produce any measurable growth in the size of the diamond seed particles based on comparison of SEMs taken before and after prolonged exposure of the seeds to C_{60} under essentially the same conditions of temperature, pressure and time as with the C_{70}.

In addition to selenium and phosphorous, other elemental reducing agents such as sodium, potassium and sulphur are contemplated by the inventors to be effective in reducing C_{70} and at temperatures higher than in the range 500 to 600°C.

The following is a possible growth mechanism proposed by the inventors. The mechanism is speculative, so it will be understood that the following is meant to be a non-limiting explanation. The structure of C_{70} is shown generally at 40 in Figure 10 and can be compared to the structure of C_{60} shown at 70 in Figure 11. The carbon atoms 42 comprising C_{70} are hybridized intermediately between sp^2 (as in graphite) and sp^3, the hybridization of carbon in diamond. When one of the bonds is broken in a fullerene, the two carbons comprising the broken bond have a choice between sp^2 and sp^3 hybridization according to the nature of the reaction partner that reacts at the broken bond.

Referring to Figure 11, C_{60} has two types of C-C bonds; a so-called "single bond" 44 at the edges between pentagonal and hexagonal faces, and a "double bond" 46 at the edges between hexagonal faces. However, all carbon atoms are vertices of both hexagonal and pentagonal faces. Referring to Figure 10, C_{70} has, additionally, C-C bonds 50 that are edges separating two hexagonal faces and, also, vertices of hexagonal faces only. The inventors speculate that it is these additional carbon-carbon bonds 50 in C_{70} that break to initiate diamond growth.

It is speculated that the diamond seed acts as a template whose surface dangling bonds ensure that the carbon atoms of the newly ruptured C-C bond of the C_{70} molecule adopt the sp^3 hybridization required to continue the diamond growth. Ultimately all of the carbon atoms of the C_{70} molecule could be incorporated into the diamond.

Although the process in accordance with the present invention occurs at relatively low temperatures and pressures, it makes use of the free energy stored in the C_{70} molecule during its formation at the very high temperatures of the carbon arc used to generate it. This increase in free energy (over that of the graphite precursor in the form of the electrodes of the arc) manifests itself in the intermediate hybridization characteristic of the fullerenes. Recent theory predicts the involvement of a non-planar intermediate which has one sp^3 and one sp hybridized carbon, see Robert L. Murray, Douglas L. Strout, Gregory K. Odom and Gustavo E. Scuseria, Nature, 366, 665-667 (1993).

In order to channel this free energy into diamond formation some of the C-C bonds in C_{70} must be induce to rupture. This is achieved by the

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presence of materials such as selenium or phosphorous that donate electrons to the C_{70} and, therefore, facilitate bond breaking.

The present invention advantageously provides an economical method of growing diamonds from seed diamond particles with C_{70} which does not require high pressures or temperatures as in the known methods. The result that C_{70}, but not C_{60}, can be readily reduced in the presence of a reducing agent was completely unexpected. While the process has been described with respect to the preferred process, those skilled in the art will appreciate that numerous variations of this process may be made to grow diamonds which still fall within the ambit of the following claims.

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THEREFORE WHAT IS CLAIMED IS:

1. A process for growing single crystal diamonds, comprising;

reducing vapour phase C_{70} in the presence of diamond seed particles at an effective pressure and effective temperature to cause at least some of the diamond seed particles to grow.

2. The process according to claim 1 wherein the C_{70} is reduced using a reducing agent selected from the group consisting of selenium and phosphorous.

3. The process according to claim 2 wherein the effective temperature is about 550°C.

4. A process for growing single crystal diamonds, comprising:

providing a plurality of diamond seed particles;

providing a quantity of C_{70} powder and a reducing agent, said C_{70} powder and said reducing agent being in flow communication with said diamond seed particles; and

heating said C_{70} powder to produce C_{70} in the vapour phase, and heating said reducing agent and said diamond seed particles at an effective pressure and effective temperature and for an effective period of time to cause a portion of said C_{70} in the vapour phase to be reduced by said reducing agent and deposit onto and increase the size of at least some of said diamond seed particles.

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5. The process according to claim 4 wherein said reducing agent is selected from the group consisting of selenium and phosphorous.

6. The process according to claim 4 wherein said reducing agent is selected from the group consisting of sodium, potassium and sulphur.

7. The process according to claim 4 wherein said effective temperature is a temperature greater than about 500°C.

8. The process according to claim 5 wherein said effective temperature is in the range from about 500°C to about 600°C and said effective period of time is from about 18 days to about 60 days.

9. The process according to claim 8 wherein said effective pressure is below about $2x10^{-6}$ torr.

10. A diamond particle grown from a diamond seed particle according to the process of claim 7 wherein the diamond particle has a characteristic absorption peak at about 1328 cm^{-1} as determined by laser micro-Raman spectroscopy.

11. A process for growing single crystal diamonds, comprising:

providing a plurality of diamond seed particles having a mean diameter;

providing a quantity of C_{70} powder and a reducing agent, said C_{70} powder and said reducing agent being in flow communication with said diamond seed particles; and

heating said C_{70} powder to produce C_{70} in the vapour phase, and heating said reducing agent and said diamond seed particles under vacuum at a temperature of from about 500°C to about 600°C and for a period of time of from about 18 days to about 60 days to cause a portion of said C_{70} in the vapour phase to be reduced by said reducing agent and deposit onto and increase the mean diameter of at least one of said diamond seed particles.

12. The process according to claim 11 wherein the step of providing a plurality of diamond seed particles comprises providing diamond seed particles having a mean diameter of about 1.5 microns.

13. The process according to claim 12 wherein the step of heating comprises increasing the mean diameter of said diamond seed particles to at least 10 microns.

14. The process according to claim 13 wherein said reducing agent is selected from the group consisting of selenium and phosphorous.

15. The process according to claim 13 wherein said reducing agent is selected from the group consisting of sodium, potassium and sulphur.

16. The process according to claim 14 wherein said temperature is about 550^{0}C.

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