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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 October 2006 (19.10.2006)

PCT

(10) International Publication Number
WO 2006/110004 A1

(51) International Patent Classification:
C23C 16/27 (2006.01)

(21) International Application Number:
PCT/KR2006/001368

(22) International Filing Date: 13 April 2006 (13.04.2006)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
10-2005-0030824 13 April 2005 (13.04.2005) KR

(71) Applicant *(for all designated States except US)*: **KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY** [KR/KR]; 39-1, Hawolgok-Dong, Sungbook-Ku, Seoul 136-791 (KR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **LEE, Jae-Kap** [KR/KR]; Hyundai Apt. 103-1704, 34, Junggye-bon-Dong, Nowon-Gu, Seoul 139-932 (KR). **JOHN, Phillip** [GB/GB]; Department of Chemistry, Riccarton, Edinburgh, EH14-4 AS (GB).

(74) Agent: **PARK, Jang-Won**; Jewoo Bldg. 5th Floor, 200, Nonhyun-dong, Gangnam-Ku, Seoul 135-010 (KR).

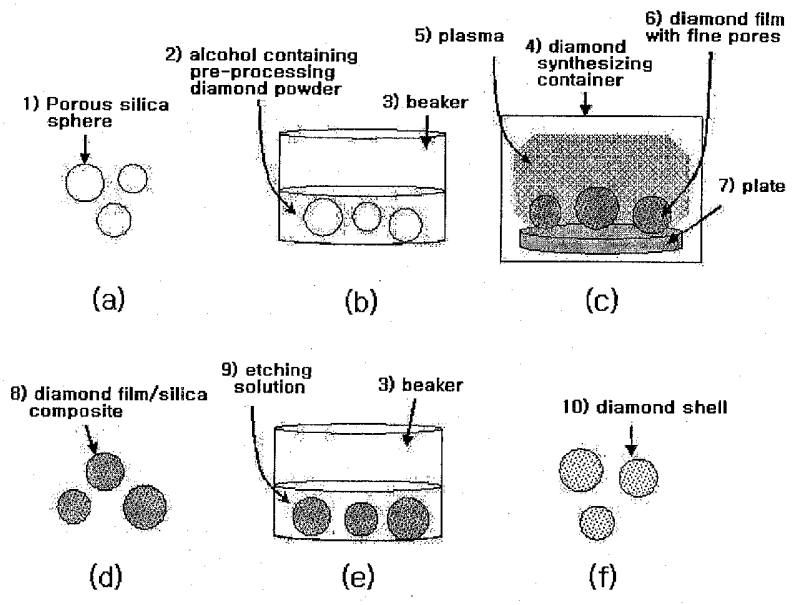
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LC, LK,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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

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

(54) Title: DIAMOND SHELL FABRICATED BY USING POROUS PARTICLE AND THE FABRICATION METHOD THEREOF



(57) Abstract: A hollow diamond shell with a size of a few micrometer to hundreds of micrometer and having a geometrical shape and its fabrication method are disclosed. A diamond film is deposited by a CVD method and porous grits are used as a victim substrate to be etched later, so that the substrate can be easily removed by a capillary phenomenon that an etching solution can be intensively absorbed in a substrate etching process. Thus, a perfect diamond shell with only a plurality of fine pores with a nano size without any conspicuous opening can be obtained. Also, a diamond shell with a small opening of below 10 percent of the surface area of grits can be fabricated by controlling a nuclear generation of diamond particles.

WO 2006/110004 A1

DIAMOND SHELL FABRICATED BY USING POROUS PARTICLE AND THE FABRICATION METHOD THEREOF

TECHNICAL FIELD

The present invention relates to a diamond shell fabricated by using a porous particle and its fabrication method and, more particularly, to a complete diamond shell having fine pores of nano size without any opening portion fabricated by using a porous particle as a matrix used as a victim frame during a process of fabricating a diamond shell and its fabrication method.

BACKGROUND ART

Artificial diamond is synthesized by a high pressure and high temperature (HPHT) method, a detonation method, or a chemical vapor deposition (CVD) method.

Diamond synthesized by the HPHT (synthesis conditions: about 50,000 air pressure and 1,400°C) developed in 1955 has cubo-octahedron grit or irregular powder form with a size of below a few hundreds μm. Diamond obtained by a single crystal growth method performed also under the HPHT has a bulk form with a size of a few mm^3. Diamond obtained by a detonation method (about 100,000 air pressure, 1,000°C) has a powder form close to a spherical shape with a size of a few nm.

The general shape of diamond obtained by the HPHT method and the detonation method has such grit (or powder) form as natural diamond.

This is because volume of an equipment that can generate a high pressure (above about 50,000 air pressure) to obtain diamond, a high temperature and high pressure phase of carbon, is limited.

Meanwhile, in 1980s, the CVD method (primary synthesizing conditions: about 100 Torr and 700°C), by which diamond can be synthesized at below an atmospheric pressure, was developed so that more diverse types of diamond can be fabricated. According to the CVD synthesis method, a gas is activated by using heat or plasma in a certain vacuum container and deposited in a type of a polycrystalline film on a surface of a matrix(substrate) maintained at about 700°C. In this case, diamond is limited to be deposited on the surface of the matrix that contacts with vapor phase. In the CVD method, the synthesis area depends on volume of plasma generated in the used equipment, and the shape of diamond film depends on the shape of the used matrix. The diamond film is deposited with a thickness of a few nm ~ a few mm on the platy matrix. It is used in the state of being attached on the matrix like an insert tool or a drill (direct coating: a thin film of below tens of μm) or used in a type of free standing film separated from the matrix(tens of μm ~ a few mm). In addition, a diamond free standing film in a dome shape with a diameter of a few cm^2 can be fabricated by using a matrix with a bent portion. In addition, by inducing a uniform nuclear generation in vapor phase according to the CVD method, a spherical diamond powder with a size of a few hundreds of nm can be synthesized.

However, the related art diamond synthesizing methods cannot

fabricate diamond with a hollow shell structure.

DISCLOSURE OF THE INVENTION

Therefore, an object of the present invention is to provide a method for fabricating a diamond shell with an opening smaller by 10% than a shell surface (referred to hereinafter as 'diamond shell with an opening') or a diamond shell with fine pores of a nano (1-1000nm) size without any conspicuous opening(referred to hereinafter as 'perfect diamond shell).

To achieve these and other advantages and in accordance with the purpose of the present invention, as embodied and broadly described herein, there is provided a method for fabricating a diamond shell comprising: preparing a porous matrix having a geometrical shape such as a spherical or polyhedral shape; inserting the porous matrix in a diamond synthesis vacuum container, decomposing a raw material gas of diamond by plasma or thermal energy to deposit a uniform diamond film with one or more pores through which a liquid phase can pass on the porous matrix by a CVD method to obtain a diamond/matrix composite (complex body); and putting the composite in an etching solution to remove the porous matrix by a capillary phenomenon that the porous matrix absorb the etching solution. In this case, the thickness of the shell wall can be within the range of 5 percent to 10 percent of the size of the shell.

In addition, in the present invention, after the hollow diamond shell is inserted in the diamond synthesis vacuum container by using the hollow diamond shell as a matrix, a row material gas of diamond is decomposed

by plasma or thermal energy to synthesize a diamond film by the CVD method, to thereby obtain a hollow diamond shell whose shell wall has a thickness 10 percent or greater of the shell size.

In the method for fabricating the hollow micro-diamond shell, the present invention provides the method for fabricating a perfect diamond shell having only fine pores with a nano size, which cannot be fabricated by a related art by using porous silica as a victim matrix. In the present invention, a diamond shell with an opening smaller by 10 percent than a surface area can be fabricated by using a selective pre-processing method. Such diamond shell having the chemical stability, the inherent properties of diamond and biocompatible characteristics can be used as a container for keeping a bio-material such as DNA or bacteria or a container for putting a vapor material such as a hydrogen gas, as well as a liquid phase such as medicines or perfume, and uniformly supplying it over time. In addition, the diamond shell can be used as a filler with a light weight and high strength in a bio-ceramic field such as artificial bones or in the fields of a sub-marine, aircraft, a spacecraft and military supplies, and also used as a low dielectric constant heat-radiation filler in a semiconductor industry. In addition, a perfect hollow diamond shell with a wall thickness of 10 percent to 30 percent of the shell size can be used as a structure material that requires a light weight and high strength, and a high crystalline diamond shell without a pure white color can be used as jewelry in a novel form.

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.

In the drawings:

FIG. 1 is a schematic view showing a process of fabricating a diamond shell according to the present invention; and

FIG. 2 is a schematic view showing a change in a size of pores generated while nuclear pores of diamond are grown to a film on a matrix, of which FIG. 2a shows a case that density of nuclear generation is high and FIG. 2b shows a case that density of nuclear generation is low.

MODES FOR CARRYING OUT THE PREFERRED EMBODIMENTS

Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

According to one embodiment of the present invention, porous silica particles of a size of micrometer with a geometrical shape such as a spherical or polyhedral shape are prepared as a matrix. The size of the pore of the porous silica particles can be different depending on a fabrication method. In case of using a sol-gel method, the size of the pore

of the porous silica particles can be 10Å~1,000Å (the size of the matrix is 1μm~100μm), and in case of using an emulsion method, the size of the pore of the porous silica particles can be 10Å~1μm (the size of the matrix is

10μm~5mm). In this respect, however, the material and size of the matrix and the size of the pore are not limited thereto.

The porous matrix is a metal oxide including at least one of SiO_2, Al_2O_3 and $BaTiO_3$, or polymer, and an organic or inorganic material that can be easily deposited by a diamond film and etched by chemicals can be used. In addition, a porous a matrix with a hollow type can be used as the matrix.

The prepared porous silica particles are deposited through a general CVD diamond synthesizing process. A pre-processing step is selectively performed to facilitate synthesizing of diamond film, and a step of synthesizing the diamond film is performed by using a general CVD device to obtain a diamond/silica composite. Thereafter, the silica of the composite is removed in an etching step to fabricate a diamond shell. Each step will be described in detail as follows.

In the pre-processing step, a porous matrix 1 are put in a beaker 3 in which fine diamond powder with a size of below 1μm has been distributed, vibrated in an ultrasonic bath during a certain time to form a scratch or a remnant on the surface of the matrix, so that a diamond nucleus can be easily formed during its synthesizing. The pre-processing

step is commonly used for synthesizing general diamond (refer to FIG. 1b).

The pre-processed porous silica matrix is deposited during a certain time in a CVD diamond synthesizing device and then undergoes a synthesizing step so as to be a diamond/silica composite (refer to FIG. 1c). In this case, the thickness of the film differs depending on the synthesis

variables such as composition or a deposition time, and preferably, is about 5 percent to 10 percent of the general shell size. During the synthesizing step, an opening or pores is(are) to be formed on the diamond film, which will now be described in detail.

Next, the composite 8 is put in an etching solution 9 and undergoes the etching step for removing the matrix (FIG. 1e) to thereby fabricate diamond shells with fine pores or an opening. The etching solution can differ depending on the material and the purpose of the matrix.

The formation of the opening or the pores of the diamond shells can be primarily controlled in the pre-processing step by using the two following methods. One method is that a portion of the surface of the matrix is intentionally prevented from being pre-processed (selective pre-processing), on which a diamond film cannot be formed, whereby a diamond shell with an opening can be fabricated. Another method is that the pre-processing time is changed. This method is used for fabricating a perfect diamond shell without a plurality of fine pores without any opening. A pre-processing time in the general diamond film synthesizing (on the

silicon substrate) takes about one hour. If the pre-processing time is shorter than that, the nuclear density can be reduced, and in this case, as described in detail in the following synthesizing step, fine pores can be formed.

After the pre-processing step, the pores can be finally controlled in the film synthesizing step. The synthesizing step includes a step of generating nuclear particles on the pre-processed porous matrix and

growing the nuclear particles. In a general diamond film synthesis, spherical diamond nuclear particles with a size of a few to tens of nm are irregularly generated on the surface of the matrix, and then, the nuclear particles are grown to form a diamond film with a columnar structure (FIG. 2). Accordingly, pores are inevitably generated between nuclear particles in the film formation step. The size of the pores is in inverse proportion to the nuclear density. Thus, the size of the pores is small when the nuclear density is high (when the pre-processing time takes long) (FIG. 2a), whereas if the nuclear density is low (when the pre-processing time takes short), the size of the pores is large (FIG. 2b). In the step of forming the film, the size of the pores can be in the range from a few nano to a few micrometer and is reduced when the thickness of the film increases. During the process, the size of pores formed in the diamond film can be controlled to be variable from a few Å to a few μm (e.g., 1Å to 5μm).

In order to fabricate the diamond shells, the diamond film/silica composite fabricated according to the above-described method is put in a

a matrix etching solution. The etching solution infiltrates into the silica matrix through the opening or the pores of the diamond film, and then, soaked up into the matrix by the capillary phenomenon of the porous matrix to thereby temporarily etch the entire a matrix so as to be removed. In this case, because there is no possibility that the shells are broken due to the partial etching that appears when non-porous silica is used, the perfect diamond shells with the fine pores can be stably fabricated.

In addition, in order to fabricate the diamond shell with an opening or

the perfect diamond shells with fine pores without any conspicuous opening according to the selective pre-processing method, it is important to allow conditions for forming the uniform diamond film on the entire surface of the matrix during the diamond synthesizing.

Meanwhile, in the process of depositing diamond (C) on the silica (SiO_2) matrix, a silicon carbide (SiC) layer can be generated between the diamond film and the silica matrix, namely, on the silica surface. This is generally similar to a phenomenon that when diamond is deposited on the silicon (Si) substrate on which diamond film synthesizing is performed, a silicon carbide (SiC) layer is generated. Silica is easily etched in hydrofluoric acid (HF), but the silicon carbide is not dissolved in the hydrofluoric acid. Thus, when the diamond shells are fabricated after silica is used as the matrix, a solvent for removing the silicon carbide layer together with silica should be used.

Actually, under the conditions that input power was 15kW, methane composition of hydrogen gas was 10 percent, pressure was 100 Torr, a gas flow was 200 sccm, a diamond film/porous silica a matrix composite (blue color, opaque) was deposited in a multi-cathode DC PACVD diamond synthesizing apparatus for one hour was etched in a 10-percent HF aqueous solution for 24 hours. Thereafter, results of observing the composite using a scanning electron microscopy (SEM) show diamond shells. A layer of hundreds of nm was observed in the shells, and the layer was determined as the silicon carbide (SiC) according to an AES analysis result. This means that carbon atoms was intruded into silica (SiO_2) during synthesizing to form the silicon carbide layer. Because silicon carbide is not etched in the HF, the sample was additionally etched for 10 minutes in a boiling Murakami solution (3g, NaOH, 30g K-hexacyanoferrae(III), 60 ml water).

When the sample was observed by using the SEM, silicon carbide layer could not be observed. The thickness of the diamond is about 10μm, which means that the silicon carbide layer was removed by the Murakami etching. In addition, it was observed that the color of the diamond shells was changed from the black (opaque) to a gray color (translucent) during the Murakami etching. It is noted that diamond is translucent, the remaining silicon carbide layer makes the diamond film/silica composite and the composite without only silica as silica has been removed have black color (opaque). Meanwhile, when the fabricated diamond film/silica

composite was etched in the boiling Murakami solution for 10 minutes, silica and silicon carbide could be removed, without performing the hydrofluoric acid (HF) etching.

As mentioned above, the hollow diamond shells can be fabricated through the three steps of the pre-processing step performed on the surface of the porous silica matrix, the step of fabricating the diamond film/silica composite having a small opening (or fine pores), and the etching step performed on the porous matrix. By changing the shape of the matrix to a spherical, tetrahedron or hexagonal shape and the size of each matrix, diamond shells with various shapes and sizes can be fabricated. In addition, by changing the diamond synthesizing conditions, diamond shells having

diamond films with various surface tissues and crystallinity can be fabricated.

By etching the diamond film/porous silica composite in the hydrofluoric acid (HF) to remain the silicon carbide layer on the diamond shell, a diamond/silicon carbide composite shell can be fabricated. The composite shell would have excellent mechanical characteristics such as high ductility or the like owing to the silicon carbide. In addition, by using the hollow porous silica shell as the substrate, a diamond film/hollow porous silica shell composite can be obtained in the synthesizing step.

By continuously performing the CVD diamond synthesizing by using the thusly fabricated diamond shell and diamond/silicon carbide composite

shell as a matrix, a perfect hollow diamond shell that has thick shell wall (10 percent of the shell size or greater) and does not have fine pores can be fabricated. The shells would have compression strength as high as the particle-type diamond.

The present invention will now be described in detail with reference to the accompanying drawings.

FIG. 1 is a schematic view showing a process of fabricating a diamond shell according to the present invention.

As the matrix, porous silica spheres 1 are prepared as substrate particles (a) and put in a beaker 3 in which alcohol 2 containing pre-processing diamond powder is held, on which ultrasonic vibration pre-processing is performed for one hour (b). During the pre-processing process, the size of an opening of the shell can be controlled. The pre-processed silica particles are put in a diamond synthesizing chamber 4 in which plasma 5 is formed to deposit a diamond film. After the synthesizing is completed, the diamond film/substrate composite (d) is boiled in the Murakami solution for 10 minutes to etch silica matrix out (e) to obtain hollow spherical diamond shells 11.

FIG. 2 shows formation of the diamond film and a change in the size of pores when density of nuclear generation is high (FIG. 2a) and when density of nuclear generation is low (FIG. 2b). It is noted that when the nuclear density is low, larger pores are generated. The estimate size of the pores is within the range of a few Å to hundreds of nm.

In the present invention, by using the porous silica as the matrix, the fine size of the opening or the pores of the shells that allows the solution to pass therethrough can be controlled to be smaller to thereby fabricate a perfect diamond shell. The diamond shells can be used as a liquid-phase container of bio molecules, chemicals, medicines, perfume, etc, and also as a vapor-phase container such as the hydrogen gas. In addition, the perfect hollow diamond shells without fine pores can be used for a structure material that requires to be light and have high strength or as jewelry.

The present invention will be explained in more detail in the following examples. It is to be understood that these examples are merely illustrative and it is not intended to limit the scope of the present invention to these examples.

Embodiment 1

A porous matrix was pre-processed in an ultrasonic bath for one hour before being synthesized, and used diamond powder had the size of 1μm. Diamond was synthesized on the surface of porous silica spheres with a diameter of 25μm~30μm by using a multi-cathode DC power plasma CVD method. The synthesis conditions were that the inputted power was 15kW, methane composition of hydrogen gas was 10 percent, pressure was 100 Torr, and a gas flow was 200 sccm. Time for the synthesizing was one hour. When the surface of silica was observed by

using the SEM, it was confirmed that a diamond film was deposited except for a portion (5 percent to 10 percent of the entire surface) of each matrix, and in this respect, the portion on which the film was not deposited is considered as a portion that contacted with a plate 7. The composite has a block color (completely opaque), and the surface tissue includes a surface (100) and a mixture of the surfaces (100) and (111).

When a silica structure greater than 2mm was used as the matrix, it is not possible to uniformly deposit a diamond film on the surface. Presumably, this is because when the matrix greater than 2mm is used, plasma can be concentrated onto the upper surface of the matrix particles to cause a big temperature difference between the upper and lower surfaces of the matrix during diamond synthesizing. Reversely, if a silica substrate smaller than 200nm is used, grits get tangled each other, failing to obtain independent grits after the diamond synthesizing.

Embodiment 2

A diamond film was synthesized under the same conditions as the Embodiment 1 except that the methane composition of hydrogen gas was 11 percent. When the surface of silica was observed by using the SEM, the result was that the surface tissue largely includes the surface 100 and other synthesizing behaviors were similar to the Embodiment 1. The color of the composite was also black (completely opaque).

Embodiment 3

Porous matrix was pre-processed for 10 minutes under the same conditions as the Embodiment 1. The diamond synthesizing conditions were the same as the Embodiment 1, and after diamond was synthesized for 30 minutes, the matrix was re-arranged and then diamond was again synthesized for 30 minutes (two-step synthesizing) to deposit a uniform diamond film on the entire surface of the matrix. The color of the composite was black (completely opaque) and the surface tissue include the surface 100 and the mixture of the surfaces (100) and (111), and the mixtures of the surfaces (100) and (111) were more observed. It is not easily to fine pores (opening) even with the SEM, because the film was uniformly synthesized on the entire surface of the matrix through the two-step synthesizing. Pores with the size of a few μm were found occasionally. Raman analysis results of the diamond shell show that there is a conspicuous diamond peak near 1332cm-1 and a gentle peak between 1350cm-1 ~1500cm-1 corresponding to a non-diamond phase (sp2) carbon. This confirms that the shell contains the non-diamond shape.

When the silica structure greater than 2mm was used through two-step synthesizing, the film could be deposited uniformly. In this case, however, it is not possible to uniformly synthesize the film. Presumably, it is estimated that plasma can be concentrated onto a portion of the surface of the matrix during synthesizing, causing a large temperature difference

between the portion of the surfaces of the matrix during the diamond synthesizing.

Meanwhile, in the diamond synthesizing step, by optimizing the deposition conditions according to a used synthesizing apparatus, the diamond film can be uniformly synthesized on the entire surface of the matrix without performing the above-described two-step synthesizing.

Embodiment 4

The matrix/diamond composite fabricated in Embodiment 1 was etched in 10-percent hydrofluoric acid aqueous solution for 24 hours. After etching, it was observed that the color of grits was black (completely opaque). When grits was observed by using the SEM, shell-shaped diamond was observed, and in this respect, a layer of few hundreds of nm in the shell was also observed. The layer was determined as silicon carbide (SiC) according to an AES analysis result. This means that, during the synthesizing, a carbon element infiltrated into silica (SiO_2) to form a silicon carbide layer. The silicon carbide is not etched by the hydrofluoric acid. In this manner, the diamond/silicon carbide composite shell was fabricated.

Embodiment 5

The matrix/diamond composite fabricated in Embodiment 1 was etched in a 10-percent hydrofluoric acid aqueous solution for 24 hours,

and then etched again in a boiling Murakami solution (3g NaOH 30g K-hexacyanoferrae(III), 60ml water) for 10 minutes. After etching, particles were changed to have a gray color (translucent). The result of observing the sample by using the SEM shows that there was no silicon carbide layer. The thickness of the diamond layer was about 10μm. This means that a silicon carbide layer was removed according to the Murakami etching. It can be noted that the change in the color of the particles to the gray color from the black color, it can be noted that the silicon carbide layer causes the black color (opaque).

Embodiment 6

The matrix/diamond composite fabricated in Embodiment 1 was directly etched in the Murakami solution (3g NaOH 30g K-hexacyanoferrae(III), 60ml water), not in the hydrofluoric acid aqueous solution, for 10 minutes. After etching, the diamond particles (shells) were changed to have a gray color (translucent). The outer appearance of the particles was the same as before being etched. This means that silica and silicon carbide layer of the particles (shells0 were removed. Accordingly, perfect diamond shells without nano pores could be obtained.

Embodiment 7

A diamond film containing a methane composition of 6 percent under the same conditions as Embodiment 3 was deposited for two hours

(two-step synthesizing and each step was performed by one hour) to fabricate a diamond film/matrix composite. The composite has the size of 30μm~35μm and the black color and was opaque. The composite was etched in the boiling Murakami solution as shown in Embodiment 6 for 10 minutes. After the etching, it was noted that the outer appearance of the grits (diamond shells) was the same as before being etched but the color was changed to a white color. This means that silica and a silicon carbide layer of the shells were removed. When a shell was broken down and its tissue was observed by the SEM, it was noted that it has an pore with the size of a sub-μm and the thickness of the film was 8μm. The piece of the broken diamond shell was transparent. It was also noted that the white color of the diamond shell was caused by diffusion of light due to the concavo-convex surface of the diamond shell.

Embodiment 8

The perfect hollow diamond shell having the nano air pore fabricated in Embodiment 7 was used as a matrix and synthesizing was performed by two steps (each step was performed two hours) for four hours under the diamond synthesizing conditions of Embodiment 7. The shell had the white color. Results of observation by using the SEM showed that the size of the shell was increased to 50μm to 60μm without an air pore. Accordingly, a perfect diamond shell was obtained without an air pore.

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.

CLAIMS

1. A method for fabricating a diamond shell comprising:

preparing a porous matrix having a geometrical shape such as a spherical or polyhedral shape;

inserting the porous matrix in a diamond synthesis vacuum container, decomposing a raw material gas of diamond by plasma or thermal energy to deposit a uniform diamond film with one or more pores through which a liquid phase can pass on the porous matrix by a CVD method to obtain a diamond/matrix composite; and

putting the composite in an etching solution to remove the porous matrix by a capillary phenomenon that the porous matrix absorb the etching solution.

2. The method of claim 1, wherein the size of the porous matrix is within the range of 200nm to 5mm.

3. The method of claim 1, wherein the porous matrix is a metal oxide comprising at least one of SiO_2, Al_2O_3 and $BaTiO_3$, or polymer, and is made of an organic or inorganic material that can be deposited by a diamond film and easily etched by chemicals.

4. The method of claim 1, wherein in order to increase a nuclear generation speed and density of diamond, a pre-processing step is

performed such that the porous matrix is put in a beaker in which fine diamond powder has been distributed, vibrated in an ultrasonic bath during a certain time to form a scratch or a remnant on the surface of the porous matrix.

5. The method of claim 4, wherein during the pre-processing step, selective pre-processing is performed such that the pre-processing diamond powder does not contact with a certain portion of the surface of the porous matrix so that a diamond film cannot be formed on the certain portion in a follow-up process, to thereby form an opening.

6. The method of claim 1, wherein, in the step of fabricating the diamond/matrix composite, the size of a pore of the diamond film is controlled to be 1Å~5μm by controlling the nuclear density and the thickness of the film.

7. The method of claim 4, wherein, in the pre-processing step on the porous matrix, the size of their pore of the diamond film is controlled to be 1Å~5μm by controlling the nuclear density or the thickness of the film according to a change of the pre-processing time.

8. The method of claim 1, wherein, in the step of fabricating the diamond/matrix composite, the porous matrix is synthesized during a certain time, re-arranged, and then synthesized again, in order to uniformly

deposit a diamond film on the surface of the porous matrix.

9. The method of claim 1, wherein the porous matrix contains silica (SiO_2) and is etched to be removed by using a hydrofluoric acid as the etching solution, and a porous silicon carbide layer formed between the porous matrix and the diamond film remains.

10. The method of claim 1, wherein the porous matrix contains silica (SiO_2), and a porous silicon carbide layer formed between the porous matrix and the diamond film and the porous matrix are simultaneously removed by using a boiling Murakami solution as the etching solution.

11. A method for fabricating a diamond shell, wherein a hollow diamond shell having a geometrical shape such as a spherical or polyhedral shape according to claim 1 is prepared and inserted as a matrix in a diamond synthesis vacuum container, and a row material gas of diamond is decomposed by plasma or thermal energy to synthesize a diamond film by a CVD method, in order to obtain a thick hollow diamond shell with a thickness 10 percent or greater of the shell size.

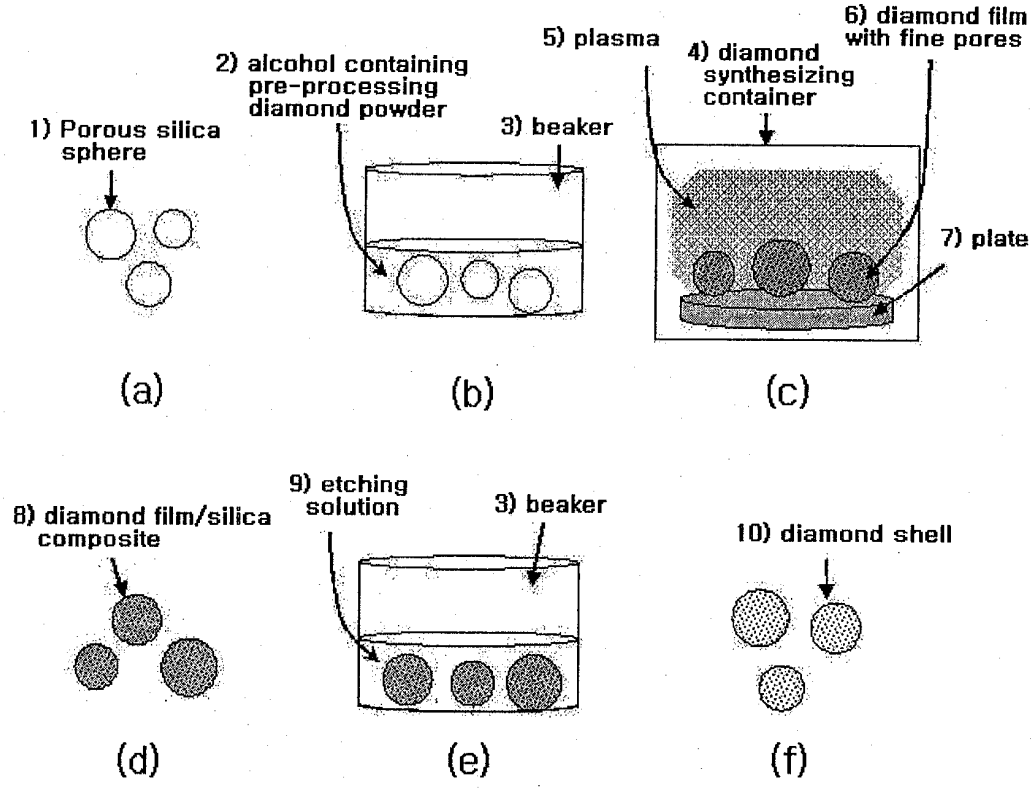
12. A method for fabricating a diamond shell, wherein a hollow diamond/silicon carbide composite shell having a geometrical shape such as a spherical or polyhedral shape according to claim 9 is prepared and inserted as a matrix in a diamond synthesis vacuum container, and a row

material gas of diamond is decomposed by plasma or thermal energy to

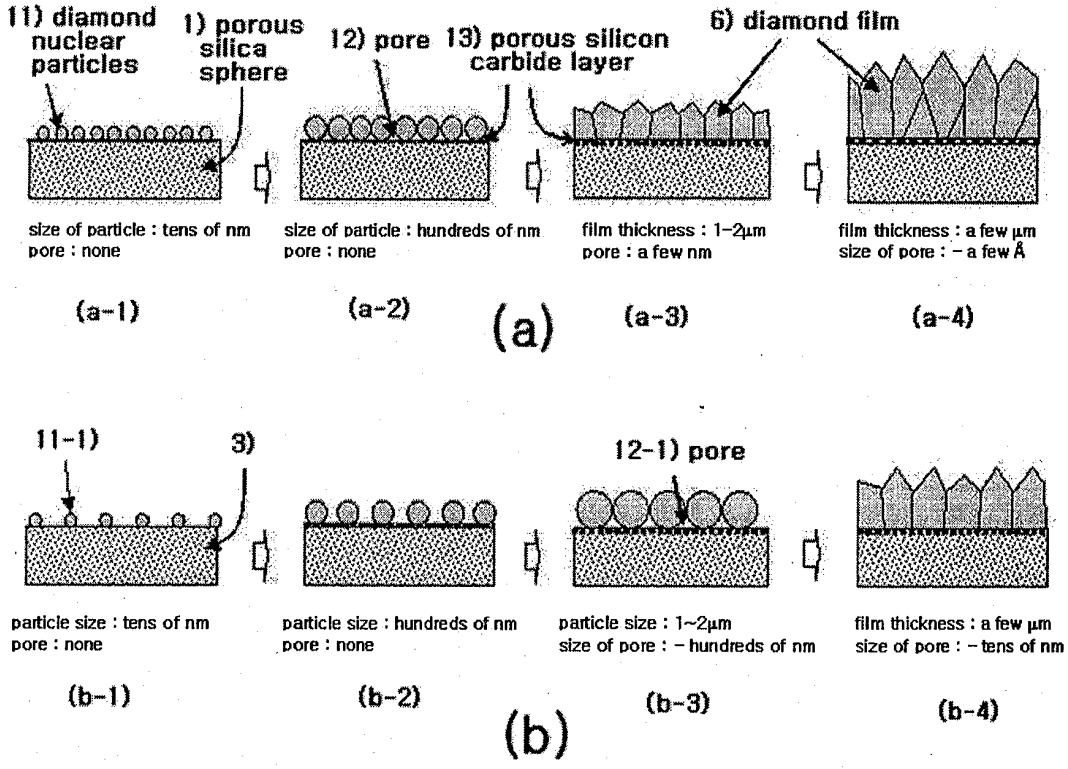
synthesize a diamond film by a CVD method, in order to obtain a thick hollow diamond/silicon carbide composite shell with a thickness 10 percent or greater of the shell size.

13. A diamond shell fabricated according to claim 1.

[Fig. 1]


1) Porous silica sphere
2) alcohol containing pre-processing diamond powder
3) beaker
5) plasma
4) diamond synthesizing container
6) diamond film with fine pores
7) plate
(a)
(b)
(c)
8) diamond film/silica composite
9) etching solution
3) beaker
10) diamond shell
(d)
(e)
(f)

[Fig. 2]


11) diamond nuclear particles
1) porous silica sphere
12) pore
13) porous silicon carbide layer
6) diamond film
size of particle : tens of nm
pore : none
size of particle : hundreds of nm
pore : none
film thickness : 1-2μm
pore : a few nm
film thickness : a few μm
size of pore : - a few Å
(a-1)
(a-2)
(a)
(a-3)
(a-4)
11-1)
3)
12-1) pore
particle size : tens of nm
pore : none
particle size : hundreds of nm
pore : none
particle size : 1~2μm
size of pore : - hundreds of nm
film thickness : a few μm
size of pore : - tens of nm
(b-1)
(b-2)
(b)
(b-3)
(b-4)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2006/001368

A. CLASSIFICATION OF SUBJECT MATTER

C23C 16/27(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8 C23F 4/04, C01B 31/06, C30B 25/00, C30B 29/04, C16/00

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

Korean Patents and applications for inventions since 1975.
Korean Utility models and applications for Utility models since 1975.
Japanese Utility models and applications for Utility models since 1975.

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

Patent and Utility Search System at KIPO.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6261469 A (ANVAR ZAKHIDOV et al.) 17 July 2001 See the abstract, claims 1-4,17-20 and example 13.	1 - 3, 8, 9, 11 - 13
Y	US 6261469 A (ANVAR ZAKHIDOV et al.) 17 July 2001 See the abstract, claims 1-4,17-20 and example 13.	4
A	US 6261469 A (ANVAR ZAKHIDOV et al.) 17 July 2001 See the abstract, claims 1-4,17-20 and example 13.	5 - 7, 10
Y	US 6051152 A (PAUL M. NATISHAN et al.) 18 April 2000 See the abstract, example 1, column 3, lines 5-13.	4
Y	JP 05-345697 A (NISSAN MOTOR CO., LTD.) 27 December 1993 See paragraph [0004].	4
A	KR 10-2002-0023502 A (KINIK COMPANY) 29 March 2002 See the abstract and claims 1-15.	1 - 13
E	WO 2006/043786 A1 (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY et al.) 24 April 2006 See the abstract and claims 1-10.	1 - 5, 9, 10, 13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 JULY 2006 (18.07.2006)	**19 JULY 2006 (19.07.2006)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer LEE, SUNG JOON Telephone No. 82-42-481-5530

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2006/001368

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6261469 A	17.07.2001	CA2343915AA	11.10.2002
		EP01121334A1	08.08.2001
		EP1121334A1	08.08.2001
		JP14527335	27.08.2002
		JP2002527335T2	27.08.2002
		US2001019037A1	06.09.2001
		US2001019037AA	06.09.2001
		US6261469B1	17.07.2001
		US6261469BA	17.07.2001
		US6517763B1	11.02.2003
		US6517763BA	11.02.2003
		WO0021905A1	20.04.2000
		WO0200021905A1	20.04.2000
US 6051152 A	18.04.2000	NONE	
JP 05-345697 A	27.12.1993	NONE	
KR 10-2002-0023502 A	29.03.2002	NONE	
WO 2006/043786 A1	27.04.2006	KR 1020060034545 A	24.04.2006