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(54) **METHOD TO GROW CARBON THIN FILMS CONSISTING ENTIRELY OF DIAMOND GRAINS 3-5 NM IN SIZE AND HIGH-ENERGY GRAIN BOUNDARIES**

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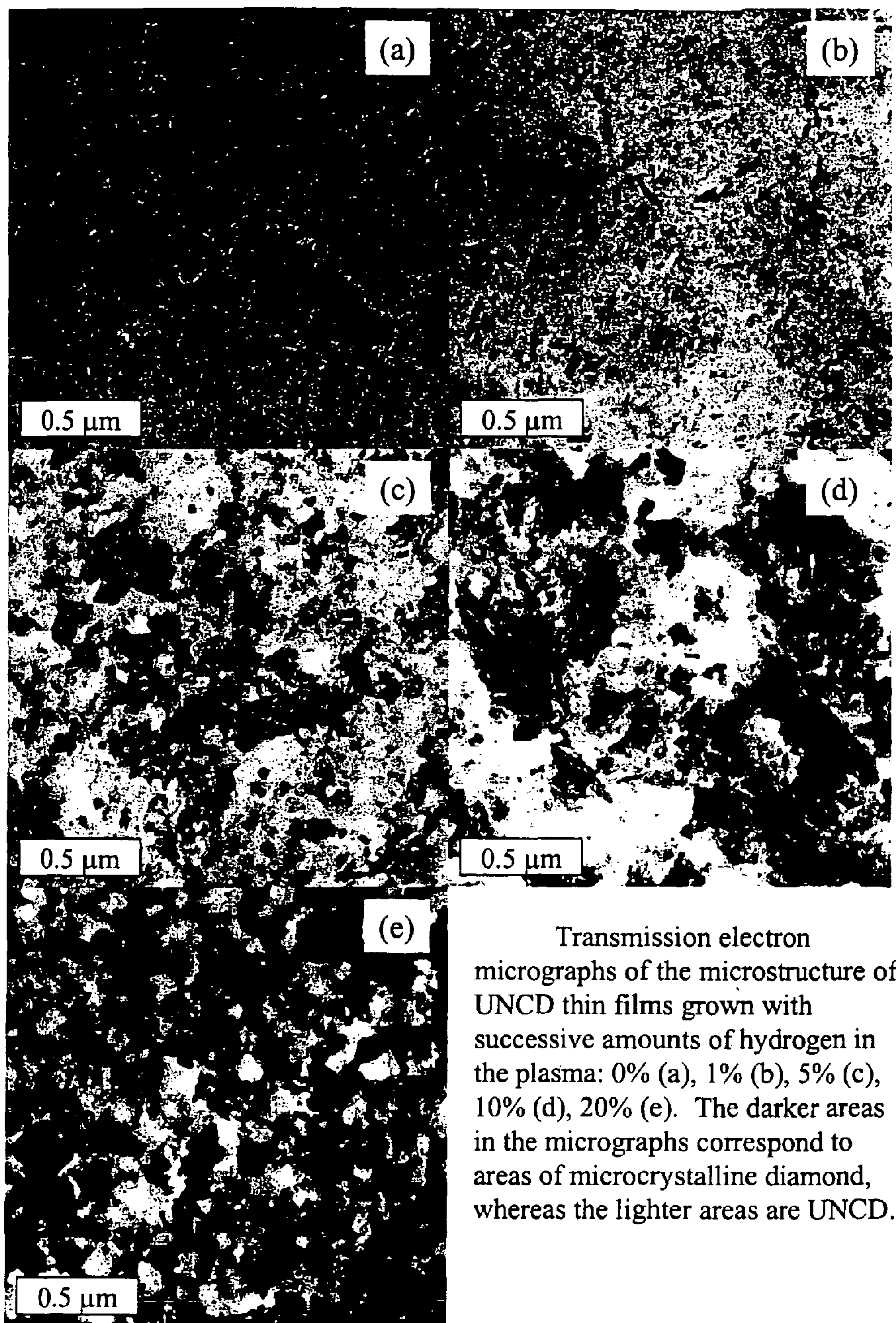
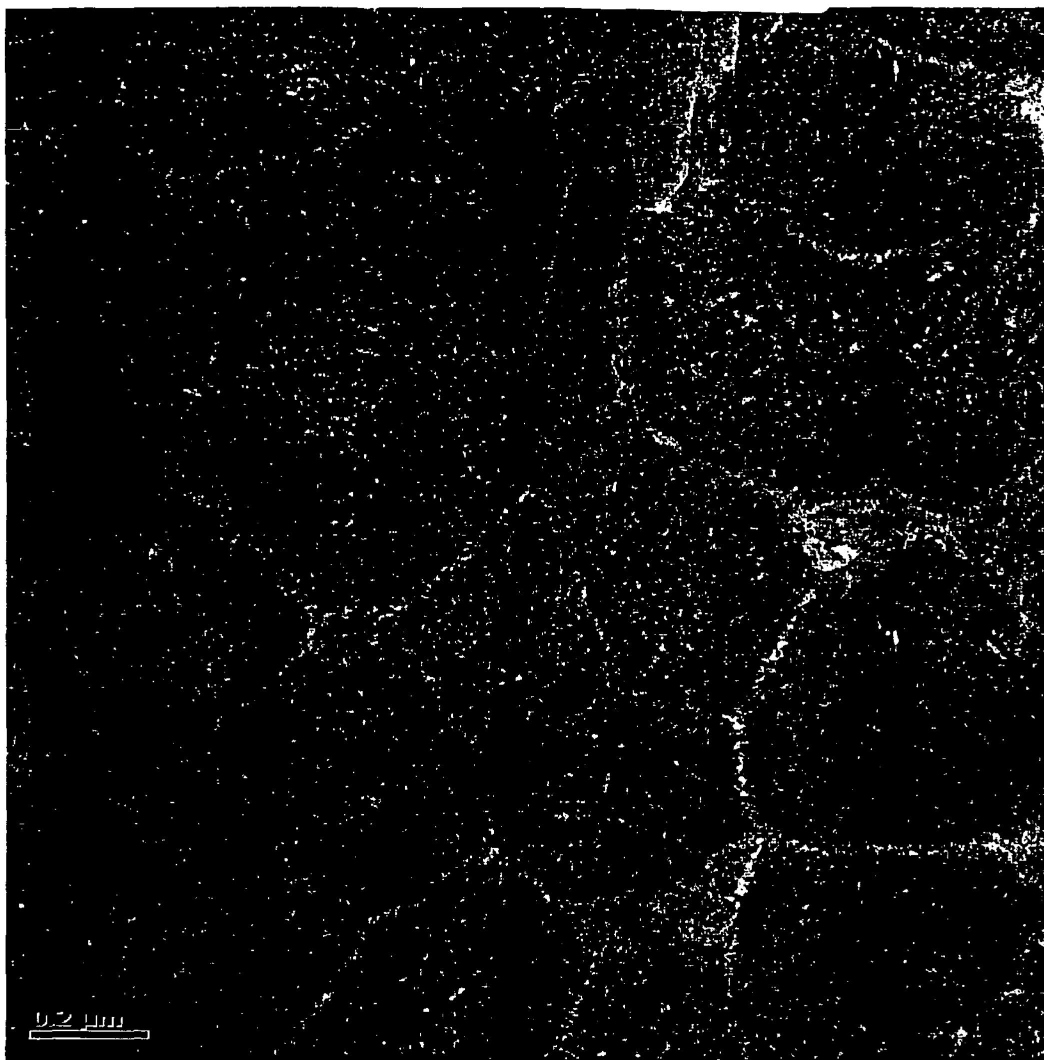
(57) **ABSTRACT**

An ultrananocrystalline diamond (UNCD) having an average grain size between 3 and 5 nanometers (nm) with not more than about 8% by volume diamond having an average grain size larger than 10 nm. A method of manufacturing UNCD film is also disclosed in which a vapor of acetylene and hydrogen in an inert gas other than He wherein the volume ratio of acetylene to hydrogen is greater than 0.35 and less than 0.85, with the balance being an inert gas, is subjected to a suitable amount of energy to fragment at least some of the acetylene to form a UNCD film having an average grain size of 3 to 5 nm with not more than about 8% by volume diamond having an average grain size larger than 10 nm.



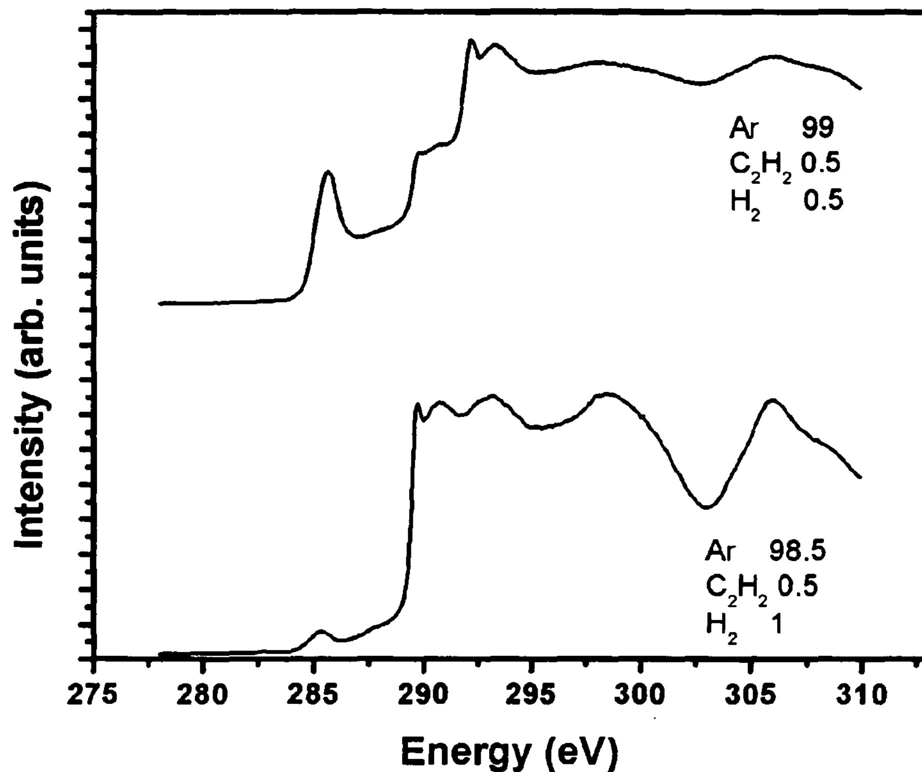
Transmission electron micrographs of the microstructure of UNCD thin films grown with successive amounts of hydrogen in the plasma: 0% (a), 1% (b), 5% (c), 10% (d), 20% (e). The darker areas in the micrographs correspond to areas of microcrystalline diamond, whereas the lighter areas are UNCD.

FIG. 1



TEM micrograph of a carbon film grown using an $Ar/C_2H_2/H_2$ plasma using 0.5 % H_2 at 800 °C. Note the presence of a large amount of non-diamond carbon.

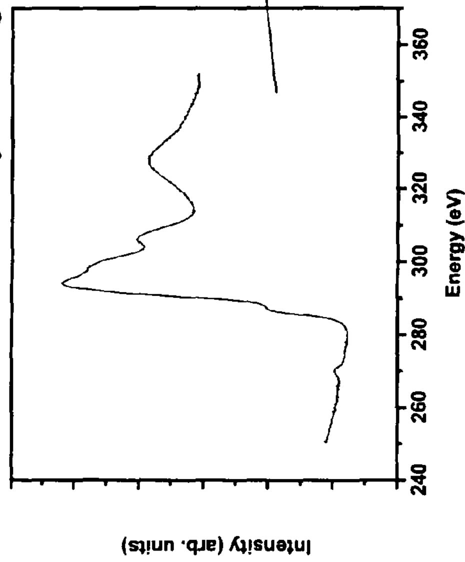
FIG. 2



x-ray absorption data, taken on beamline 8.0.1 at the Advanced Light Source (LBNL), showing the change in local bonding structure of the diamond film grown using two different gas mixtures. The relative percentages of Ar, C_2H_2, and H_2 are shown. Reduction in the amount of hydrogen below a critical point (upper curve) leads to much more sp2-bonded carbon in the film (the peak at 285.5 eV is much larger).

FIG. 3

EELS of Sample #96



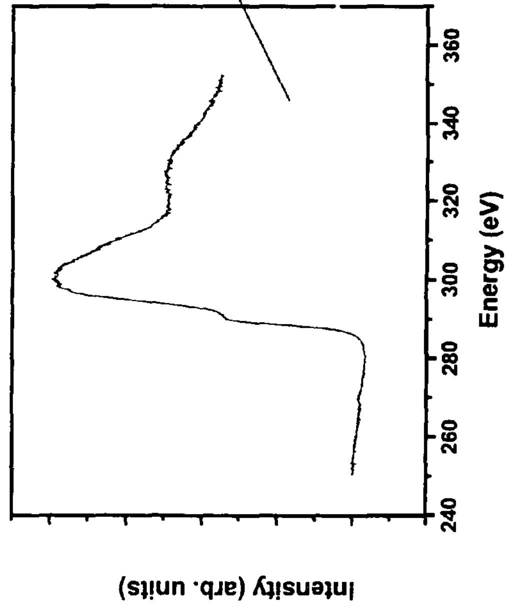


FIG. 4

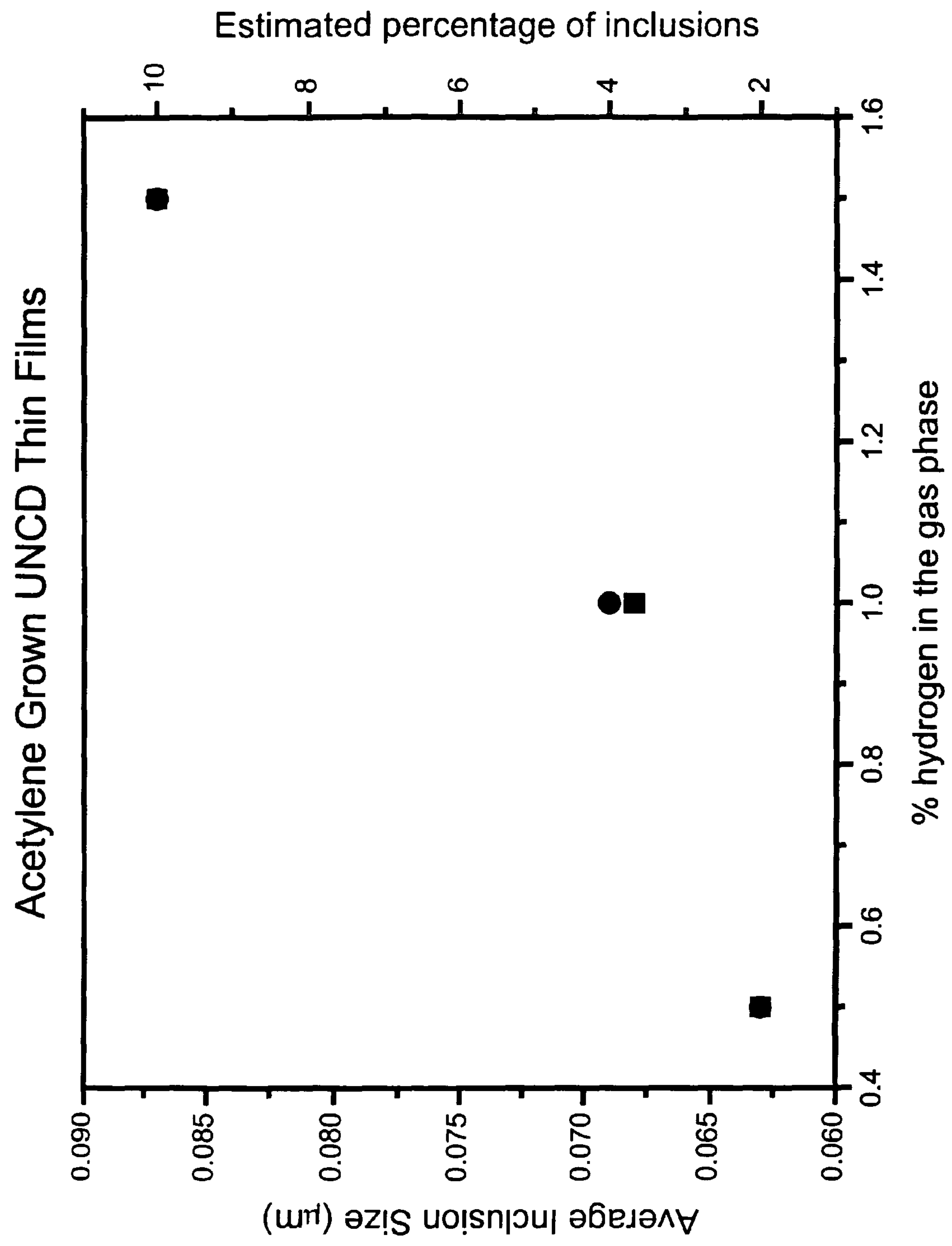


FIG. 5

NEXAFS of C2H2 Films varying hydrogen concentration

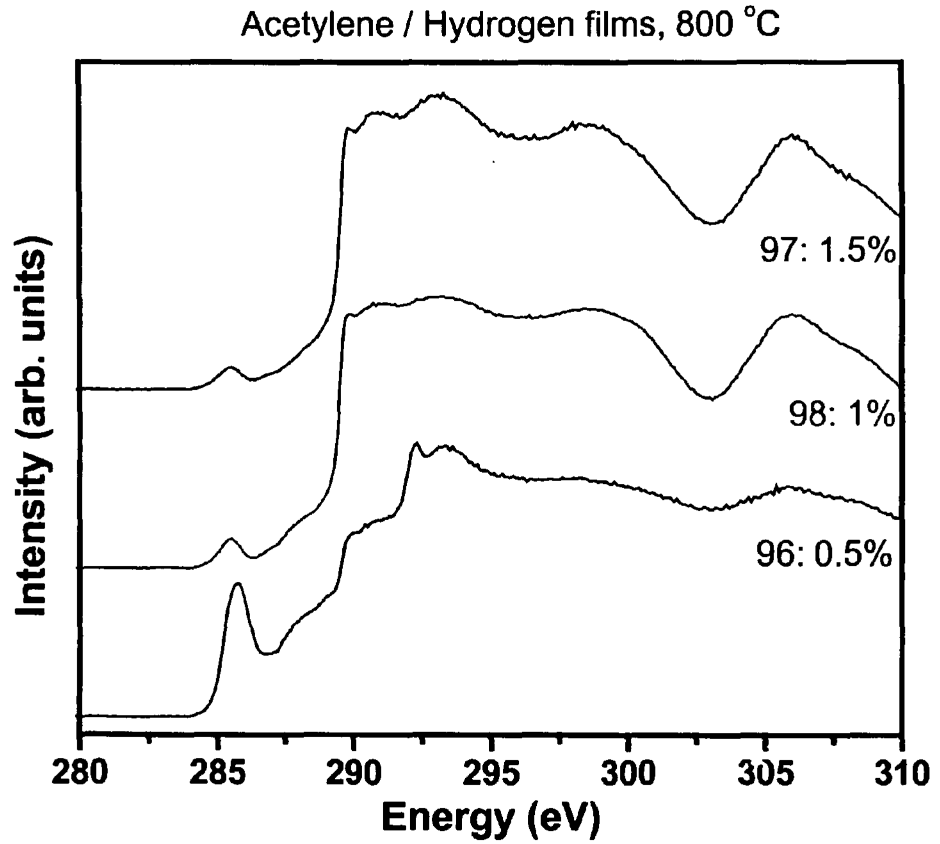
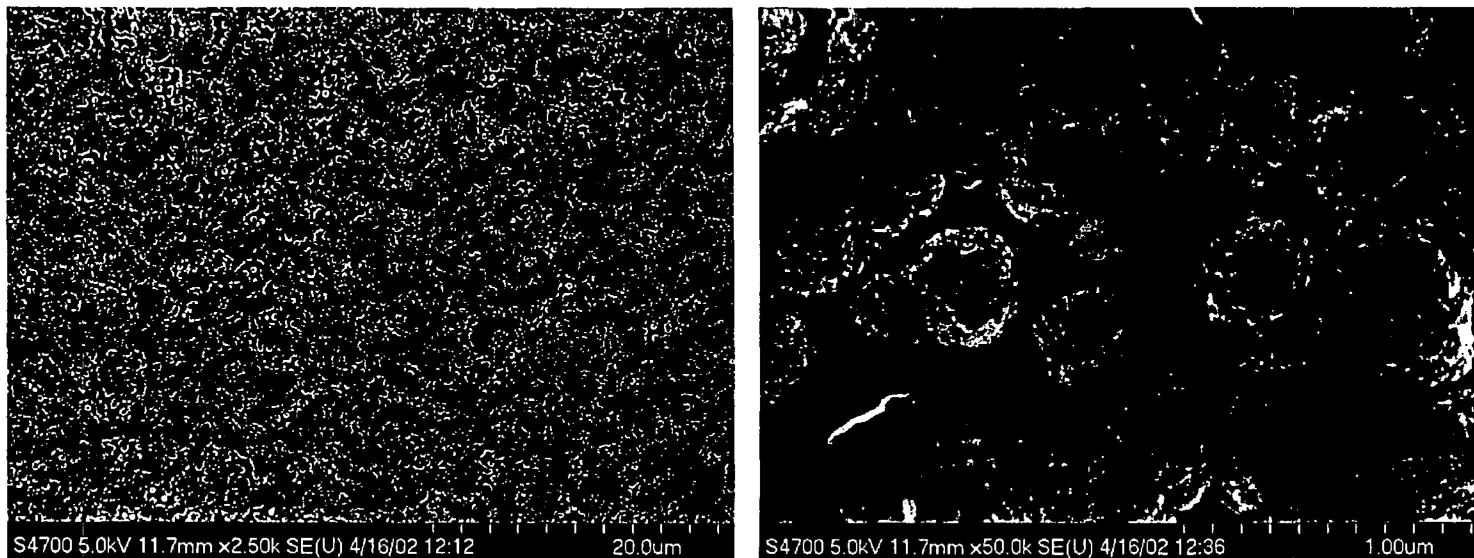


FIG. 6

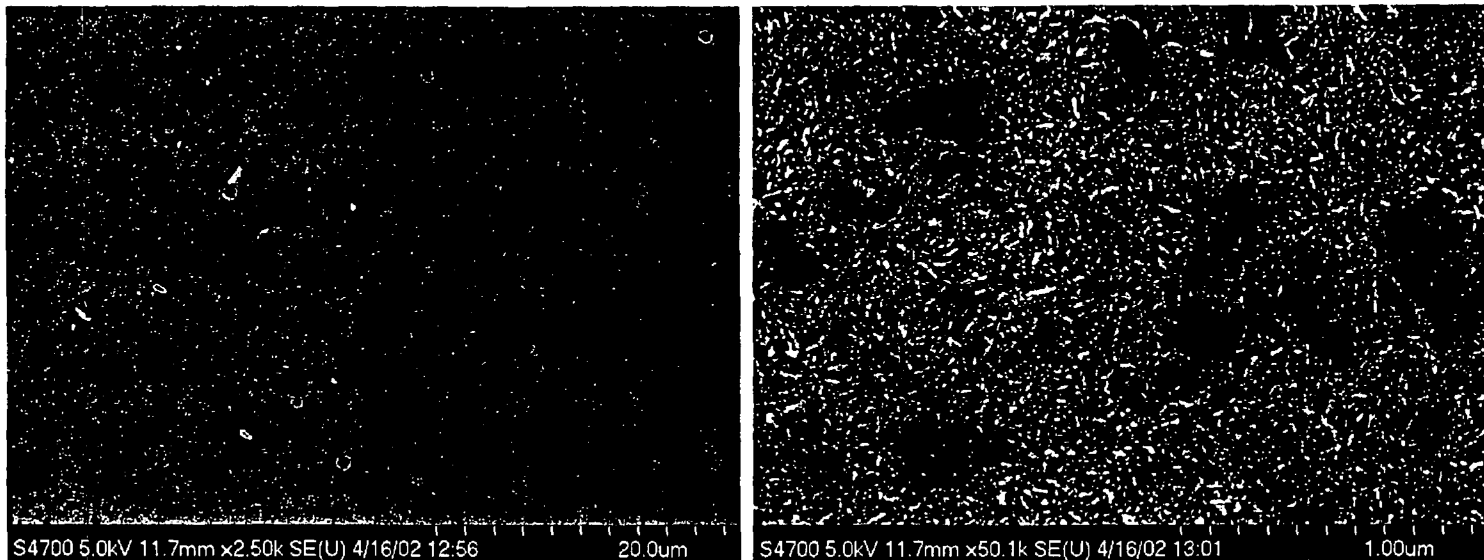
Sample #96: Surface Morphology of Acetylene Grown UNCD



Growth Conditions:
- Gas Composition Ar 99 / C_2H_2 0.5 / H_2 0.5
- Pressure 200 mbar
- Power 850 W
- Temperature 800 °C
- Time 3 hours
- Thickness: 0.45 μm

FIG. 7

Sample #97: Surface Morphology of Acetylene Grown UNCD

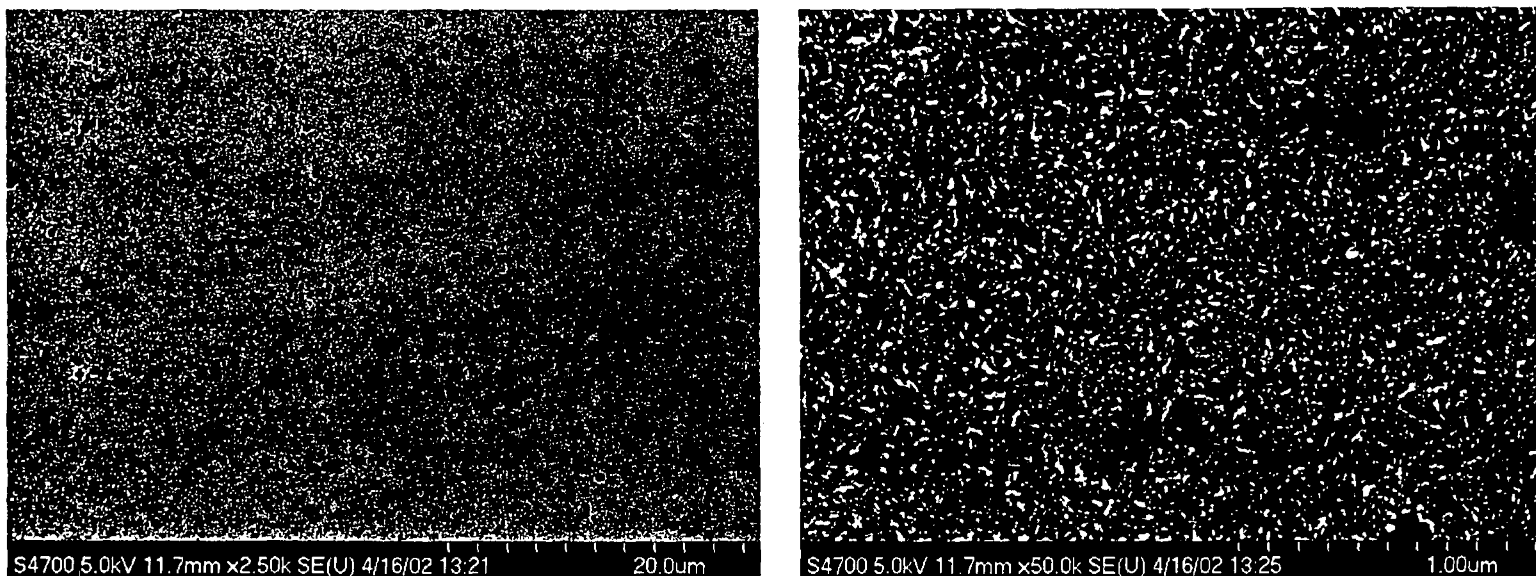


Growth Conditions:

- Gas Composition Ar 98.5 / C_2H_2 0.5 / H_2 1
- Pressure 200 mbar
- Power 850 W
- Temperature 800 °C
- Time 3 hours
- Thickness 0.79 μm

FIG. 8

Sample #98: Surface Morphology of Acetylene Grown UNCD

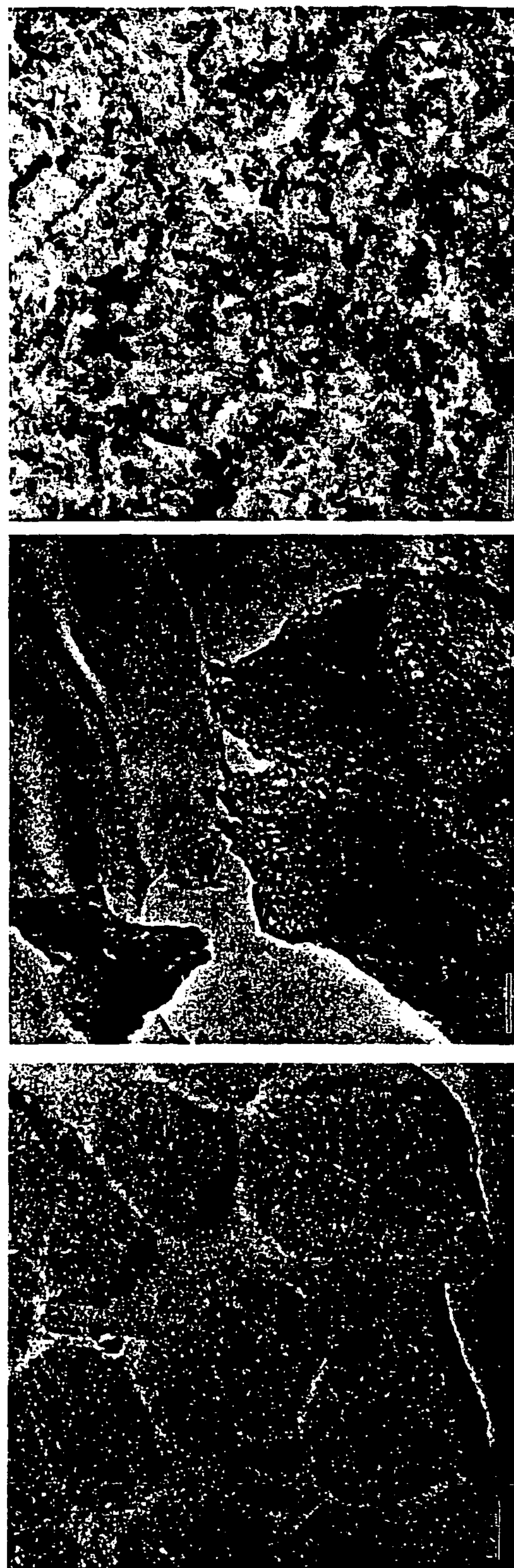


Growth Conditions:

- Gas Composition Ar 98 / C_2H_2 0.5 / H_2 1.5
- Pressure 200 mbar
- Power 850 W
- Temperature 800 °C
- Time 3 hours
- Thickness: 1.1 μm

FIG. 9

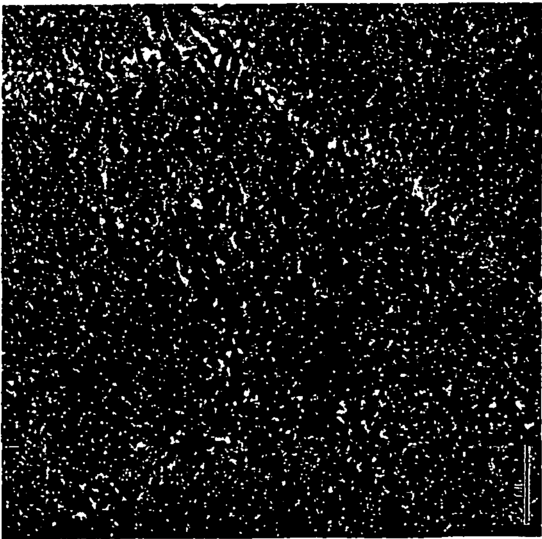
Comparison of low-res TEM of Acetylene films



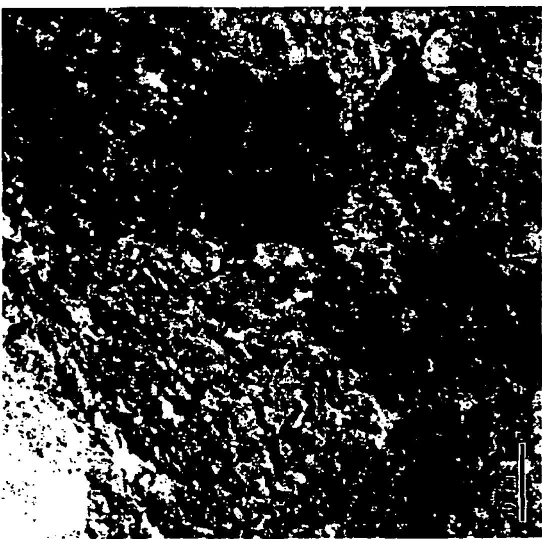
96: 0.5% H_2 98: 1% H_2 97: 1.5% H_2

FIG. 10

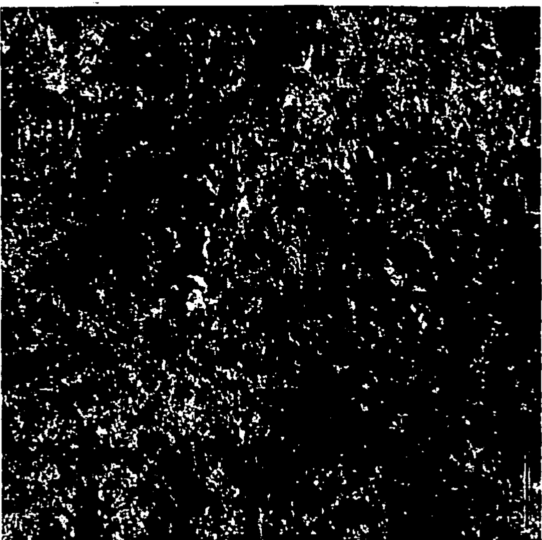
Comparison of low-res TEM of Acetylene films



96: 0.5% H_2



98: 1% H_2



97: 1.5% H_2

FIG. 11

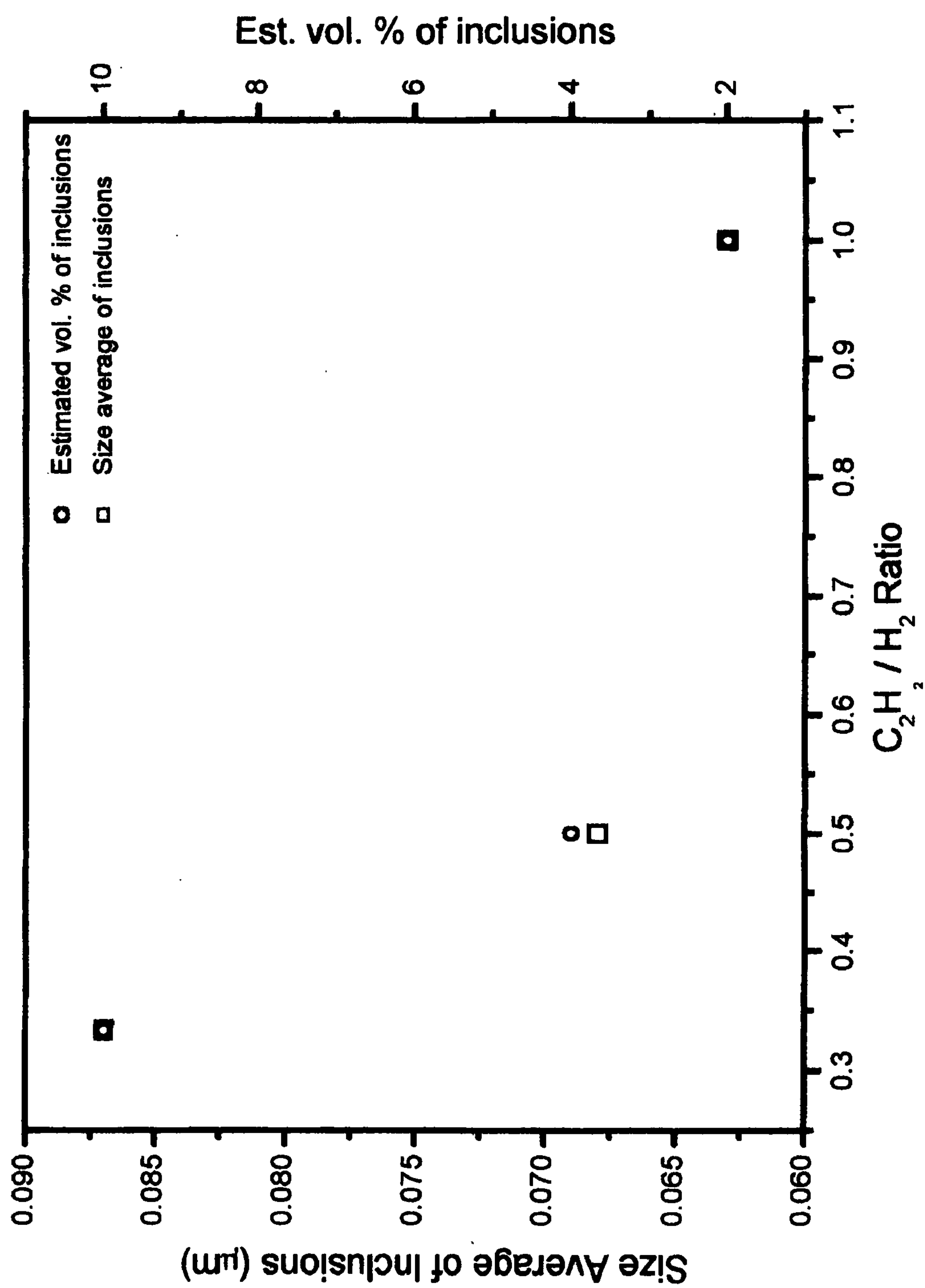


FIGURE 12

METHOD TO GROW CARBON THIN FILMS CONSISTING ENTIRELY OF DIAMOND GRAINS 3-5 NM IN SIZE AND HIGH-ENERGY GRAIN BOUNDARIES

RELATED APPLICATION

[0001] This application, pursuant to 37 C.F.R. 1.78(c), claims the benefit of U.S. Provisional Application Ser. No. 60/482,973 filed on Jun. 26, 2003.

[0002] The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy (DOE) and The University of Chicago representing Argonne National Laboratory.

BACKGROUND OF THE INVENTION

[0003] The overarching goal of diamond thin film research is to develop techniques and practices that allow the deposition of films on a variety of substrates that retain most if not all of the outstanding properties of natural diamond (hardness, electron mobility, thermal conductivity, etc.). This work has been going on for many years and has resulted in a number of thin film deposition technologies for growing diamond (>95% crystalline sp^3 bonded carbon) films. The two major techniques are plasma enhanced chemical vapor deposition (PECVD, using either RF or microwave frequencies) and hot-filament CVD reactors, although other forms of CVD also exist as well for diamond deposition (i.e. arc-jet and oxyacetylene flame growth.

[0004] The previous technology is based on the use of plasma chemistries that grow diamond films with micrometer size gains and low-energy grain boundaries, using a typical gas mixture of 1% CH_4. These films are commonly referred to as microcrystalline diamond (MCD), and have a distinct columnar structure where the grain size (and roughness) increase with increasing film thickness. Diamond growth in these films proceeds via chemical reactions at the growing surface wherein a methyl radical adsorbs unto a site following the abstraction of hydrogen from this site. The presence of atomic hydrogen in the plasma is critically needed in order to abstract hydrogen from the surface as well as to etch the non-diamond carbon during growth. These films consist of >99% diamond bonded carbon but are imperfect renderings of diamond as a thin film, suffering from many drawbacks that ultimately limit their commercialization. Many companies setup to commercialize MCD in the early 90's failed as a consequence of these limitations.

[0005] Nanocrystalline diamond films (NCD) can be grown by increasing the content of CH_4 in the CH_4/H_2 plasma to about 4-5%. NCD films, which consist of nanometer-sized grains of diamond (sp^3) bonded carbon, have shown some promise as commercially viable carbon coatings, but a key challenge in these films is the control of their nanoscale morphology and uniformity of the bonding structure, so as to retain the properties of natural diamond. These films are often, but not always two-phase materials, with nanometer sized (>50 nm) grains of diamond-bonded carbon imbedded in an amorphous, sp^2-bonded carbon matrix. They are consequently not as hard as natural diamond. Additionally, even in the best of cases (phase-pure nanocrystalline diamond films) these films require a very high initial nucleation density in order to form nanometer grains, and the grain size of these films increases with film thickness, limiting the thickness of the NCD films.

[0006] Over the past several years work at Argonne National Laboratory (ANL) has lead to the invention of an alternative diamond film technology: Ultrananocrystalline Diamond (UNCD) as described in U.S. Pat. No. 5,989,511, the disclosure of which is incorporated by reference, which is based on a fundamentally different chemistry. UNCD films are typically grown using gas mixtures consisting of 99% Ar with 1% CH_4 (a 99/1 plasma) that claims C_2 dimers as the species that play a key role in the nucleation of the UNCD films and might contribute to the growth process as well. The C_2 dimers are produced by plasma assisted breakdown and reaction of the parent molecules. The so called UNCD films were thought to consist entirely of diamond grains 3-5 nm in size (with crystalline sp^3 coordinated carbon atoms) with high-energy, high angle twist grain boundaries (with disordered sp^2 coordinated carbon atoms). It is the nanoscale structure of these films that give them a unique combination of material properties, including exceptional hardness, 20 nm rms as deposited roughness, low film stress, low as-deposited friction coefficient, high electronic conductivity when doped with nitrogen or boron, and many other properties.

[0007] Recent work, however, has shown that for the 99/1 plasma chemistry most typically used about 10% of the carbon in a UNCD film does not have the UNCD nanoscale bonding structure, but instead consists of large inclusions (~100 nm) of heavily twinned-dendritic inclusions of crystalline sp^3-bonded carbon. In short, carbons films grown using 99/1 plasmas are not pure UNCD, but consist of a mixture of UNCD and MCD, with the MCD portion greater than 8% by volume and generally more than 10% by volume of the diamond. The addition of hydrogen to the gas mixture leads to the very rapid increase in the volume fraction of MCD in the films relative to the UNCD component, increasing to 50% MCD for 5% added hydrogen by volume (94% Ar/1% CH_4/5% H_2) and >90% MCD for 20% added hydrogen. Recent TEM results shown in **FIG. 1** dramatically illustrate this UNCD+MCD structure directly. **FIG. 1** illustrates differences in a 1% methane plasma with varying added hydrogen. Most of the films grown prior to about 1998 were grown using significant amounts of added hydrogen.

[0008] In addition, further recent work has also shown that, when the amount of hydrogen gas is reduced below a certain level, which is dependent to some extent on substrate temperature, as will be explained, the resulting film consists of a large amount of sp^2-bonded carbon, and is thus useless for applications that require either nanocrystalline or ultrananocrystalline films nanocrystalline applications.

SUMMARY OF THE INVENTION

[0009] The present invention solves the problem of growing thin films of a carbon material of ultrananocrystalline diamond (UNCD), on surfaces of insulator, semiconductor, and/or conductor materials. The present invention is based on the discovery that only for a certain, narrow range of plasma compositions, in which the amount of hydrogen gas is precisely controlled, a film of "pure UNCD" is grown, where "pure UNCD" means that the UNCD film microstructure is characterized by grains of 3-5 nm in size with sp^3

bonded carbon atoms, and atomic wide (~0.4 nm) grain boundaries with carbon atoms bonded in sp^2, sp^3, and other local geometries and wherein the volume percent of microcrystalline diamond (MCD) in the film is less than about 8. This invention therefore serves to identify and describe the synthesis of a "pure UNCD" film.

[0010] Accordingly, it is an object of the present invention to provide an ultrananocrystalline diamond film having an average grain size between 3 and 5 nm with up to about 8% by volume diamond having an average grain size greater than 10 nm.

[0011] Another object of the present invention is to provide a method of manufacturing an UNCD film comprising forming a vapor of acetylene and hydrogen that is thermally stable at 1000° K in an inert gas other than He wherein the volume ratio of acetylene to hydrogen is greater than 0:35 and less than about 0.85 with the balance being an inert gas, subjecting the vapor to a suitable amount of energy to fragment at least some of the acetylene, and contacting the fragment containing vapor and a substrate, and forming an UNCD film having an average grain size of 3 to 5 nm with not more than about 8% by volume diamond having an average grain size larger than 10 nm on the substrate.

[0012] Yet another object of the present invention is to provide a method of manufacturing UNCD film comprising forming a vapor of C_2H_2 and H_2 in an inert gas of Ar and/or Kr and/or Xe wherein the C_2H_2 to H_2 to volume ratio is greater than 0.35 and less than 0.85, with the balance being the inert gas, fragmenting a portion of the C_2H_2 by providing microwave energy to the vapor, and contacting the vapor containing acetylene fragments and a substrate maintained at a temperature less than about 600° C. to form an UNCD film having an average grain size of 3 to 5 nm with not more than about 8% by volume diamond having an average grain size larger than 10 nm on the substrate.

[0013] Still another object of the invention is to provide a method of manufacturing UNCD film, comprising forming a vapor of a carbon containing compound that does not form methyl radicals upon fragmentation and hydrogen that is thermally stable at 1000° K in an inert gas other than He wherein the concentration of hydrogen is less than 1.5% by volume, with the balance being an inert gas, objecting the vapor to a suitable amount of energy to fragment at least some of the carbon containing vapor, and contacting the fragment containing vapor and a substrate, and forming an UNCD film having an average grain size of 3 to 5 nm with not more than 8% by volume diamond having an average grain size larger than 10 nm on the substrate.

[0014] A final object of the present invention is to provide a UNCD film made according to the various methods set forth above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

[0016] FIGS. **1**(*a-e*) are transmission electron micrographs (TEMs) of prior art UNCD thin films grown in a methane plasma with successive amounts of added hydrogen in the plasma;

[0017] **FIG. 2** is a TEM micrograph of a carbon film grown using an argon/acetylene/hydrogen plasma with 0.5% added hydrogen by volume at 800° C.;

[0018] **FIG. 3** is a graph of near Edge X-ray Absorption Fine Structure (NEXAFS) taken on a beam line **8.0.1** at the Advanced Light Source (LBNL) showing the change in local bonding structure of the diamond film grown using two different gas mixtures;

[0019] **FIG. 4** (*a-b*) are a Electron Energy Loss Spectroscopy (EELS) obtained from the samples shown in **FIG. 2** with **4**(*a*) showing the grain region and **4**(*b*) from the grain boundary;

[0020] **FIG. 5** is a graphical representation of the relationship for acetylene grown UNCD thin films wherein the added hydrogen to the plasma is varied and the average inclusion size and the estimated percentages of inclusions in the films thereof;

[0021] **FIG. 6** is a NEXAFS representation of three acetylene films with different hydrogen concentrations grown at 800° C.;

[0022] **FIGS. 7-9** are SEMs of the surface morphology of the films of **FIG. 6**;

[0023] **FIG. 10** is a low resolution TEM of the acetylene films illustrated in **FIGS. 6-9** at 0.2 micron scale;

[0024] **FIG. 11** is a low resolution TEM like **FIG. 10** but at a 50 nm scale; and

[0025] **FIG. 12** is a graph like **FIG. 5** using the volume ratio of acetylene to hydrocarbon rather than the % hydrogen.

DESCRIPTION OF PREFERRED EMBODIMENT

[0026] The Innovative Plasma Systems GmbH (IPLAS) microwave plasma system has allowed the inventors to examine carbon films grown using acetylene-based (instead of methane-based) plasmas, i.e. using $Ar/C_2H_2/H_2$ gas mixtures. In methane plasmas, the methane thermally decomposes to C_2H_2 and H_2, so that a 99/1 plasma in facts contains 1.5% H_2 (see **FIG. 1***a*) that comes from a combination of the added hydrogen and from the methane. Thus, the amount of H_2 in the plasma can be reduced below 1.5% using acetylene-based plasmas.

[0027] Recent TEM data obtained from a film grown using a 99% Ar/1% C_2H_2/0.5% H_2 plasma at 800° C. is shown in **FIG. 2**, which shows a very different morphology compared with normal UNCD films (**FIG. 1***a*) and illustrates that even with C_2H_2 the hydrogen concentrations are very important as the material of **FIG. 2** is unsatisfactory.

[0028] **FIG. 3** shows x-ray absorption data obtained from two samples grown using the same parameters in every way except the percentage Near Edge X-ray Absorption Fine Structure (NEXAFS) of hydrogen gas in the plasma.

[0029] **FIG. 4** shows nanoprobe EELS (electron energy loss spectroscopy) data taken from different regions of the film shown in **FIG. 2**. The grain boundaries (b) consist of

mostly disordered sp^2-bonded carbon, whereas the grains (a) consist of a mixture of sp^2 and crystalline sp^3-bonded carbon (i.e. diamond).

[0030] The film grown using 98% Ar/1% C_2H_2/1% H_2 (**FIG. 3**, bottom graph) shows a spectrum characteristic of normal UNCD, whereas a reduction in the relative percentage of hydrogen to 0.5% leads to a film with a roughly 50/50 mixture of sp^2 and sp^3 bonded carbon, as previously illustrated in FIGS. **2** and FIGS. **4**(*a*) and (*b*). Accordingly, it has been found that even when using acetylene as a carbon source only strict control of acetylene and hydrogen concentration produce "pure UNCD" films.

[0031] The basis for the present invention is the discovery that only for a certain, narrow range of plasma compositions, in which the amount of hydrogen gas used is finite and is finely controlled, will the growth of a carbon film that is "pure UNCD" occur. This invention includes both "pure UNCD" film and method of making same.

[0032] The presence of C_2-dimers is a necessary but not a sufficient condition for the growth of a "pure" UNCD film, as seen by the prior art methane based UNCD films. To grow a film consisting of "pure" sp^3-bonded diamond grains 3-5 nm in size, and whose grain boundaries are high-energy, high-angle twist grain boundaries, one must:

[0033] 1. Maximize the amount of material grown through the C_2-dimer reaction pathway.

[0034] 2. Minimize the amount of material grown through the methyl radical (CH_3—, H^+) reaction pathway.

[0035] 3. Minimize the amount of sp^2-bonded carbon that is not bonded within the grain boundaries.

[0036] Use of a noble-gas-based plasma chemistry that leads to the production of C_2-dimers, and produces a maximal amount of C_2 relative to CH_3^- and other hydrocarbon radicals without significant production of methyl radicals.

[0037] Fine control of the amount of hydrogen in the plasma. The presence of a minimal amount of hydrogen gas in the gas mixture should be precisely controlled, depending on temperature and the content of other gases, in order to

[0038] stabilize the growing diamond nanocrystals, by terminating the growing diamond surfaces with hydrogen.

[0039] promote the formation of C_2 dimers in the plasma.

[0040] promote the growth of diamond nanocrystals in the 3-10 nm size range.

[0041] etch the non-diamond carbon that is not bonded within the grain boundaries, and

[0042] stabilize the noble gas discharge.

[0043] Growth between 300-800° C. temperatures must be high-enough to promote the C_2-dimer reaction pathway but not too high as to desorb the hydrogen terminating the growing diamond surfaces. Since the hydrogen desorption from the growing film is a strong function of temperature, the amount of added hydrogen needed to maintain the hydrogen termination of the surface is dependent on temperature, with less hydrogen needed as the temperature is lowered.

[0044] The gas mixture should be precisely controlled so that the soot production in the plasma and reactor is held to a minimum. This involves the fine adjustment of the flow of carbon-source gas relative to the other gases.

[0045] The gas mixture, gas flow rates, microwave power, if a microwave power source is used, total pressure, substrate temperature, and other process parameters must also be dynamically controlled in order to maintain the optimal growth of "pure" UNCD.

[0046] When acetylene is used in combination with other gases in the plasma, the volume ratio of acetylene to hydrogen should be greater than 0.35 and less than about 0.7 to produce a UNCD film which contains less than about 8% by volume of the larger MCD crystallites. Using acetylene ensures that the least amount of CH_3— radical is produced during the manufacture of the inventive "pure UNCD" materials. There is a relationship between the temperature at which the film is grown and the amount of non-diamond carbon produced. Preferably, the substrate temperature at which the acetylene based material is grown is at 600° C. or less. Below 500° C. growth rate diminishes severely, however, growth rates as low as 300° C. are still acceptable, but not necessarily preferred, whereas temperatures as high as 800° C. may be used but are not preferred.

[0047] The precise amount of hydrogen needed in the plasma and hence the volume ratio of acetylene to hydrogen is dependant upon the temperature at which the diamond film is grown. For typical UNCD deposition conditions (temp.=800° C.), the amount of added hydrogen in the plasma must be kept >0.5% in order to produce a "pure UNCD" film with no graphitic phase present. As the growth temperature is reduced, the amount of hydrogen needed to produce a "pure UNCD" film decreases to 0.5%, until at 600° C., a "pure UNCD" film is formed under these conditions. The tentative explanation for this is that as the temperature is reduced, the amount of hydrogen thermally desorbed from the growing diamond surface is reduced, allowing for the maintenance of stable diamond nuclei even under the extremely hydrogen-poor conditions found here.

[0048] **FIG. 5** disclose the relationship for acetylene grown UNCD thin films between the percent added hydrogen to the gas phase and the average inclusion size on the left hand Y axis and the estimated percent of inclusions on the right hand Y axis, with the square data points referring to the average inclusion side and the circular data points referring to the estimated percent of inclusions. As seen from **FIG. 5**, 8 volume percent inclusions resulted from approximately 1.37% added hydrogen in the plasma phase and at about 1.2% added hydrogen there was less than 6 volume percent inclusions.

[0049] The data point at 0.5% added H_2 represents about 50% sp^2 material (see **FIG. 2**) which is completely unsatisfactory for UNCD purposes. However, it is believed that approximately 0.75% added hydrogen produces an acceptable "pure UNCD" although it is clear from the data that as the hydrogen content diminishes below about 0.75% hydrogen, the greater the chance that significant amounts of sp^2 material is formed. At 1% added hydrogen, a very good

material as illustrated in **FIGS. 6-11** is formed. **FIG. 6** is a NEXAFS graph of 3 acetylene films grown at microwave power of about 850 watts at temperatures of about 800° C. and pressure of 20 millibar. The films were grown over a period of about 3 hours and had thicknesses of 0.45 microns for sample **96**, 0.79 microns for sample **97** and 1.1 micron for sample **98**. In all cases, temperature refers to the substrate temperature not, of course, the plasma temperature. **FIG. 6** shows that there is a significant amount of graphite or $-sp^2$ material at the 285 eV energy level and therefore sample **96** at 0.5% added hydrogen is unsatisfactory material, as previously discussed. Although the NEXAFS data does not distinguish between material in samples **97** and **98**, the sample **97** material which is the last data point of 1.5% added hydrogen in **FIG. 5** shows that the volume percent of inclusions is approximately 10%, an amount which excludes this material as "pure UNCD" film.

[**0050**] Referring now to **FIGS. 7-9**, inclusive, there are shown differences in the surface morphology of acetylene UNCD films with hydrogen concentrations of 0.5%, 1.5% and 1%, respectively. As clearly may be seen sample #**98**, **FIG. 9** has the least dark material which is the MCD, while having the most amount of lighter material, "pure UNCD".

[**0051**] Referring now to **FIGS. 10 and 11**, there are low resolution TEMs of films for samples **96**, **97** and **98**, the three data points in **FIG. 5**. As seen from **FIGS. 10 and 11**. **FIG. 12** is the data of; **FIG. 5** expressed as the volume ratio of acetylene to hydrogen for the x-axis rather than the volume percent of hydrogen as in **FIG. 5**. As can be seen, good films are made for acetylene to hydrogen ratios of greater than 0.35 and less than about 0.85 but the range of 0.35 to 0.7 is preferred. For ratios of about 0.4 films having less than 6% of inclusions greater than 10 nm are produced.

[**0052**] When looking at the TEM images, what we see are areas of brighter regions and darker regions. On closer examination (higher magnification), we can see a difference in the local nanostructure of these regions. While both regions are undoubtedly made up of diamond (i.e. each have the same lattice spacing as (111) diamond), the regions of the darker areas exhibit a nanostructure similar to heavily faulted microcrystalline diamond, in that there are no small grains, just a large grain with a number of different types of defects, such as stacking faults and twinning planes (common in fee materials). The lighter regions, however, show a much different nanostructure—these areas exhibit the nano-sized grains commonly referred to when discussing UNCD thin films.

[**0053**] The difference in the contrast of these areas of differing structure in the low resolution images is due to the fact that the microcrystalline diamond inclusions more strongly diffract the electron beam than the nanocrystalline diamond regions in this film. This difference in contrast was increased in the electron microscope by inserting an objective aperture into the path of the electron beam, which effectively blocked off more strongly diffracted beams from contributing to the image.

[**0054**] Although the above description of "pure UNCD" films has concentrated on acetylene films grown with microwave induced plasmas, it should be understood that other hydrocarbon compounds that do not readily form methyl radicals such as fullerenes and/or anthracene may be used in the present invention to provide "pure UNCD" film. Moreover, a variety of different power sources and plasmas may be used and the invention is not limited to microwave plasma but includes PECVD using RF as well as hot-filament CVD reactors.

[**0055**] While there has been disclosed what is considered to be the preferred embodiments of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention

1. An ultrananocrystalline diamond (UNCD) having an average grain size between 3 and 5 nanometers (nm) with not more than about 8% by volume diamond having an average grain size larger than 10 nm.

2. The UNCD of claim 1, wherein diamond having an average grain size larger than 10 nm is present in an amount less than 6% by volume.

3. The UNCD of claim 1, wherein diamond having an average grain size larger than 10 nm is present in an amount in the range of from about 3% by volume to not more than about 8% by volume.

4. The UNCD of claim 1, wherein said UNCD has grain boundaries of about 0.4 nm.

5. The UNCD of claim 1, wherein said UNCD is essentially sp^3-bonded diamond.

6. The UNCD of claim 1, wherein substantially all sp^2-bonded carbon present is at the UNCD grain boundaries.

7. The UNCD of claim 1, wherein the UNCD grain boundaries are high energy.

8. The UNCD of claim 1, wherein the UNCD grain boundaries are high-angle twist.

9. An UNCD having average grain size between 3 and 5 nm with diamond having average grain size larger than 10 nm present in the range of from about 3% by volume to not more than 8% by volume and wherein the UNCD is essentially sp^3 bonded diamond and wherein substantially all sp^2 bonded carbon present is at the UNCD grain boundaries.

10. A method of manufacturing UNCD film, comprising forming a vapor of acetylene and hydrogen that is thermally stable at 1000° K in an inert gas other than He wherein the volume ratio of acetylene to hydrogen is greater than 0.35 and less than 0.85, with the balance being an inert gas, subjecting the vapor to a suitable amount of energy to fragment at least some of the acetylene, and contacting the fragment containing vapor and a substrate, and forming an UNCD film having an average grain size of 3 to 5 nm with not more than about 8% by volume diamond having an average grain size larger than 10 nm on the substrate.

11. The method of claim 10, wherein the fragment containing vapor has substantially no methyl radicals and the ratio of C_2H_2 to H_2 is greater than 0.35 and less than about 0.7.

12. The method of claim 10, wherein the substrate temperature is maintained at about 600° C. or lower during film formation.

13. The method of claim 10, wherein the energy is microwave energy.

14. The method of claim 10, wherein the inert gas is argon.

15. The method of claim 10, wherein the UNCD film has diamond with average grain sizes larger than 10 nm present in a volume percent in the range of from about 3% to not more than about 8%.

16. The method of claim 10, wherein the UNCD is deposited at a rate of not less than 0.2 micrometers per hour while the substrate is maintained at a temperature of less than about 600° C.

17. The method of claim 10, wherein the UNCD is deposited at a rate of not less than 0.4 micrometers per hour while the substrate is maintained at a temperature of less than about 400° C.

18. A method of manufacturing UNCD film, comprising forming a vapor of C_2H_2 and H_2 in an inert gas of Ar and/or Kr wherein the C_2H_2 to H_2 volume ratio is greater than 0.35 and less than 0.85, with the balance being the inert gas, fragmenting at least some of the C_2H_2 by providing microwave energy to the vapor, and contacting the vapor containing acetylene fragments and a substrate maintained at a temperature less than about 600° C. to form an UNCD film having an average grain size of 3 to 5 nm with not more than about 8% by volume diamond having an average grain size larger than 10 nm on the substrate.

19. The method of claim 18, wherein the inert gas is argon.

20. The method of claim 19, wherein the UNCD film has diamond with average grain sizes larger than 10 nm present in a volume percent in the range of from about 3% to not more than about 8% and the C_2H_2 to H_2 ratio is greater than 0.35 and less than about 0.7.

21. The method of claim 20, wherein the UNCD is deposited at a rate of not less than 0.2 micrometers per hour while the substrate is maintained at a temperature of less than about 600° C.

22. The method of claim 18, wherein the UNCD is deposited at a rate of not less than 0.4 micrometers per hour while the substrate is maintained at a temperature of less than about 400° C.

23. A UNCD film made according to the method of claim 18.

24. A UNCD film made according to the method of claim 21.

25. A method of manufacturing UNCD film, comprising forming a vapor of a carbon containing compound that does not readily form methyl radicals upon fragmentation and hydrogen that is thermally stable at 1000° K in an inert gas other than He wherein the concentration of hydrogen is less than 1.5% by volume, with the balance being an inert gas, subjecting the vapor to a suitable amount of energy to fragment at least some of the carbon containing vapor, and contacting the fragment containing vapor and a substrate, and forming an UNCD film having an average grain size of 3 to 5 nm with not more than 8% by volume diamond having an average grain size larger than 10 nm on the substrate.

26. The method of claim 25, wherein the carbon containing compound is one or more of a fullerene, acetylene and anthracene.

27. An article of manufacture made by the method of claim 26.

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