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(54) SYNTHESIS OF CARBON NANOTUBES BY SELECTIVELY HEATING CATALYST

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(57) **ABSTRACT**

A catalytic chemical vapor deposition method and apparatus for synthesizing carbon nanotubes and/or carbon nanofibers (CNTs) on a substrate involves selectively heating a catalyst for CNT synthesis on or near the surface of the substrate. Selective heating of the catalyst is achieved using inductive heating from a radio frequency source. Selective heating of the catalyst prevents heating of the substrate and enables the synthesis of CNTs on temperature sensitive substrates.

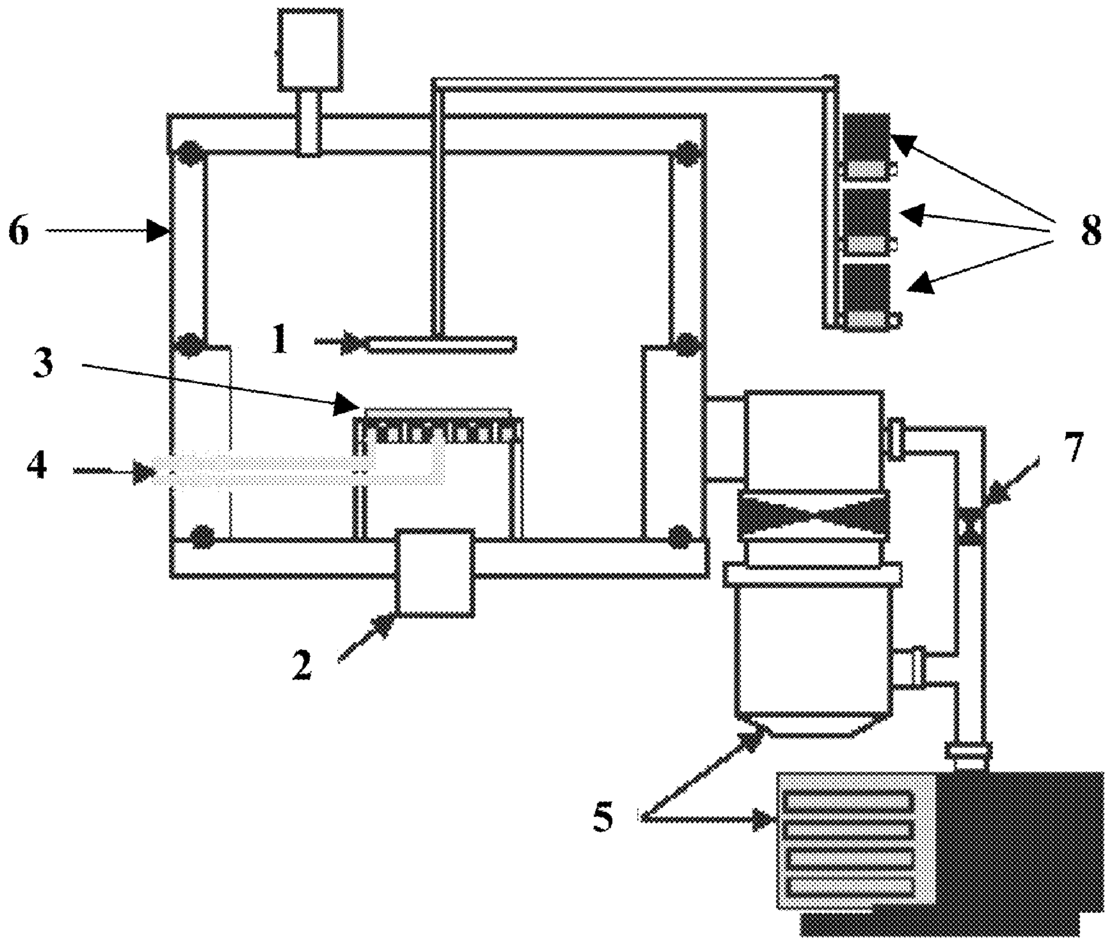


FIG. 1

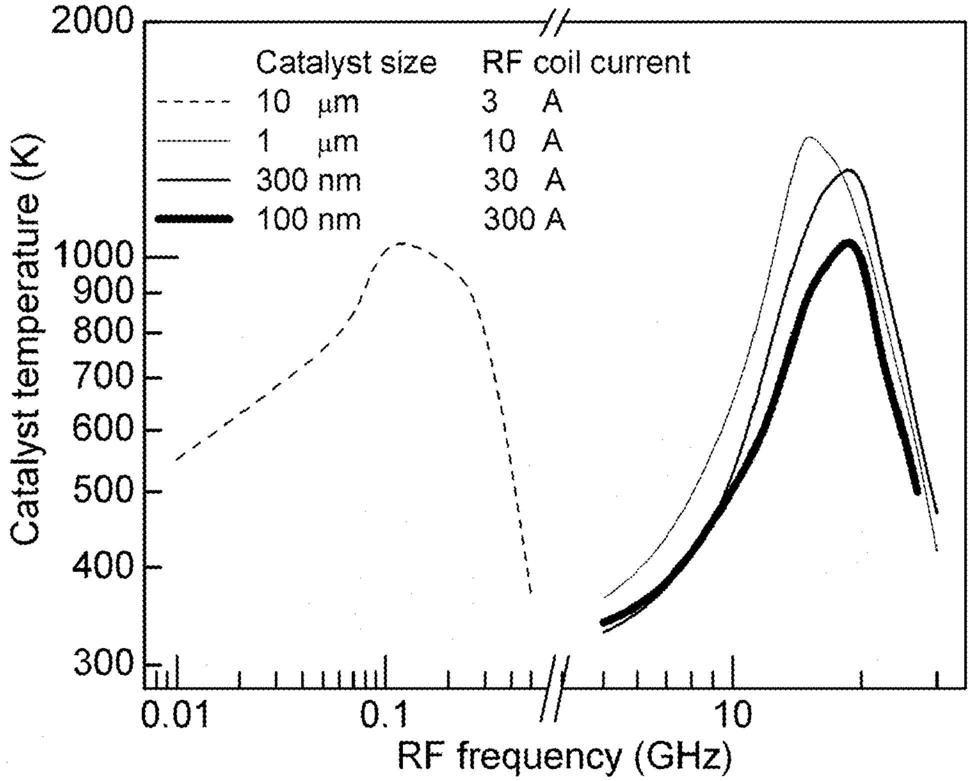
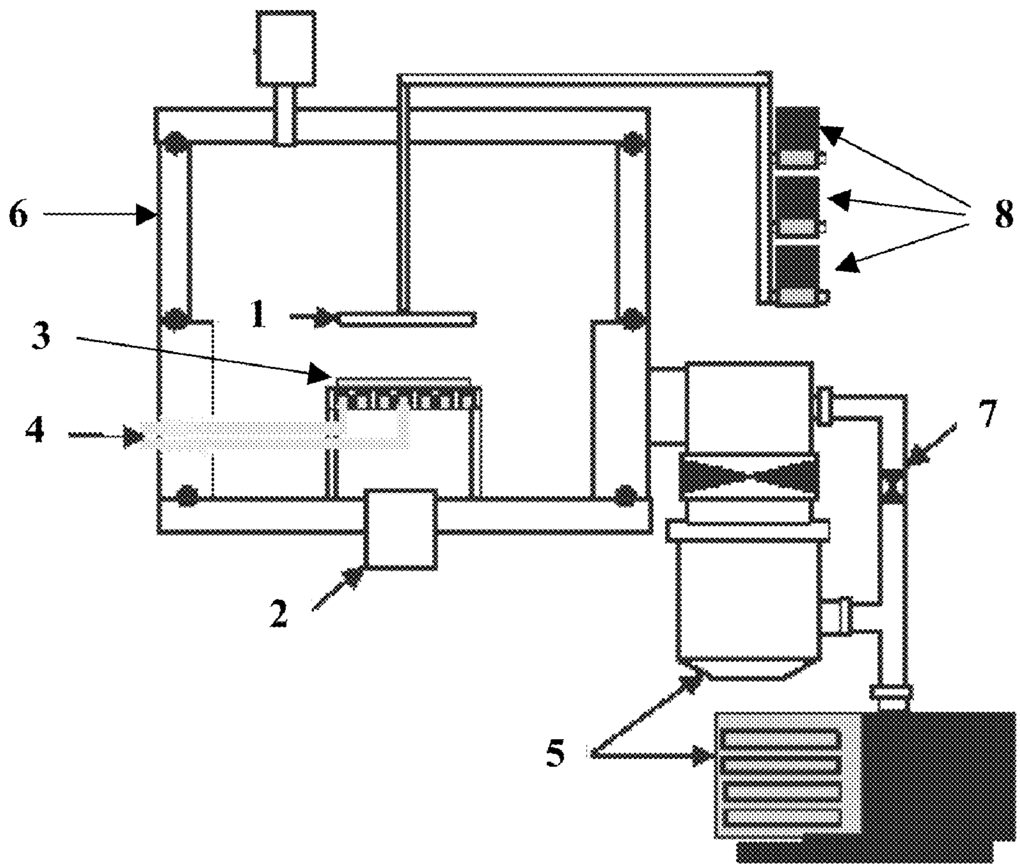

2000
Catalyst size
RF coil current
10 μm
3 A
1 μm
10 A
300 nm
30 A
100 nm
300 A
1000
900
800
700
600
500
400
300
Catalyst temperature (K)
0.01
0.1
10
RF frequency (GHz)

FIG. 2



SYNTHESIS OF CARBON NANOTUBES BY SELECTIVELY HEATING CATALYST

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Divisional of and claims priority under 35 U.S.C. 121 to application Ser. No. 11/668,741, filed 30 Jan. 2007.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] The U.S. Government may have certain rights in this invention pursuant to SBIR Contract OII-0611099 awarded by the National Science Foundation.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention

[0004] The present invention pertains to the synthesis of carbon nanotubes by catalytic chemical vapor deposition methods. Specifically, the present invention involves methods and apparatus, for making carbon nanotubes comprising the selective heating of catalysts and their products.

[0005] 2. Description of Related Art

[0006] Carbon nanotubes (CNTs) are graphitic filaments/whiskers with diameters ranging from 0.4 to 500 nm and lengths in the range of several micrometers to millimeters. The designation "CNT" is often used to call all types of vertically aligned carbon tubular structures including single-wall CNTs, multi-wall CNTs, and carbon nanofibers. CNTs exhibit a variety of desirable and unique electronic and mechanical properties. The useful properties of CNTs, coupled with their unusual molecular symmetry, have opened new frontiers in the manufacturing of electron field emission sources, nanodiodes, nanotransistors, biological probes, scanning probe microscopy tips, composite polymers, and hydrogen and energy storages.

[0007] Catalytic Chemical Vapor Deposition (CCVD) and Plasma Enhanced Catalytic Chemical Vapor Deposition (PECCVD) syntheses of CNTs are often used to synthesize CNTs directly on substrates. Both methods involve temperatures high enough (above 500° C.) to provide the energies needed for the chemical reactions that produce CNTs. In a PECCVD method, this heat is provided by plasma. Plasma-assisted growth of CNTs is typically conducted in a DC plasma reactor. Such a reactor comprises a grounded anode and a powered cathode. The wafer substrate used for the synthesis of CNTs is placed either on the anode or cathode. The electrode holding the wafer typically has a heating source which is used to increase the wafer temperature and consequently enable CNT formation. A disadvantage of DC systems is the formation of high negative bias on the wafer in these systems (>300 V). Recently, microwave reactors have come into use for the synthesis of CNTs. Plasma in such a reactor is sustained by the microwave source, and an additional DC or RF power supply may independently control the energy of ions striking the wafer.

[0008] High crystalline quality material can typically be produced only at very high temperatures, such as 500° C. or higher. This heating often damages the substrate or causes device integration problems. WO 03/011755 A1 discloses a method for making CNTs on a substrate wherein the temperature of the substrate is maintained at a temperatures ranging from 30° C. to 300° C. This method uses a radio frequency (RF) source to generate plasma that enhances chemical vapor deposition by providing the energy required for the reactions that produce CNTs. One advantage disclosed for this method is the replacement of a filament used to generate plasma by a RF source. The amount of heat transferred to substrate by RF-generated plasma is less than that transferred from a filament, making it possible to maintain lower substrate temperatures during CNT synthesis.

[0009] The method of the present invention provides selective heating of only catalyst particles, thereby applying high temperature only to the catalyst surfaces where CNT-forming reactions occur and preventing excessive heating of the substrate. This is achieved by heating from an RF source tuned to efficiently heat catalyst. This allows catalytically grown nanostructures on temperature-sensitive materials without damaging substrate structure. In contrast to WO 03/011755 A1, the present method does not require plasma or an RF source to generate plasma and uses a RF source tuned to a frequency that heats catalyst specifically and is dependent on the size of catalyst particles.

BRIEF SUMMARY OF THE INVENTION

[0010] In one embodiment, the present invention is a method for synthesizing CNTs on a substrate comprising the selective heating of a catalyst by a RF source.

[0011] In another embodiment, the present invention is an article of manufacture comprising CNTs synthesized on a substrate using a method comprising the selective heating of a catalyst by a RF source.

[0012] In yet another embodiment, the invention is an apparatus for the synthesis of CNTs comprising an RF source positioned and tuned to specifically and efficiently heat catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1** is a graph showing the results for simulations of inductive catalytic particle heating using various frequencies of RF energy.

[0014] FIG. **2** is a schematic of a reactor for low-temperature synthesis of VACNTS/VACNFs.

DETAILED DESCRIPTION OF THE INVENTION

Definitions:

[0015] The term "carbon nanotubes" (CNTS) is used herein in a generic sense to include single-walled and multi-walled carbon nanotubes, carbon nanofibers, carbon nanofilaments, and carbon nanoropes.

[0016] A radio frequency (RF) source is used herein to describe a device that generates electromagnetic fields having frequencies of between 1 GHz and 100 GHz.

[0017] The term "catalyst" is used with the art accepted meaning and, in the case of catalytic CNT synthesis includes metals such as Ni, Fe, Co, Cu, Al, V, Y, Mo, Pt, Pd and their binary and ternary alloys. A catalyst may be sputter deposited in thin films on substrates and exist as nanoparticles with a size typically ranging from 1 nm to 1 mm. A 'temperature-sensitive" substrate in the context of the present disclosure is a substrate that can be damaged or rendered incapable of integration into a larger system by exposure to elevated temperatures and includes graphite, glass, plastics, silicon, textiles, papers, and organic polymers.

Selective Heating of Catalysts Using RF Electromagnetic (EM) Energy

[0018] Inductive heating of metal samples using RF electromagnetic fields is used in biology and medicine. For example, macromolecules such as DNA can be heated to temperatures up to 70° C. using inductively heated metal particles of a few nm in size. These methods, however, are not sufficient or compatible with CNT growth, in part, because heating of catalyst for the efficient synthesis of CNTs requires temperatures an order of magnitude higher than those used in bio-medical applications.

[0019] A computational study of inductive heating of Ni catalytic particles by RF electromagnetic fields was performed. The propagation of the fields produced by a RF antenna toward catalytic nanoparticles was modeled by solving the time-dependent equation for the vector magnetic potential A given by

$$\frac{1}{\mu_0\mu_r}\vec{\nabla}^2\vec{A} = \varepsilon_0\varepsilon_r\frac{\partial^2\vec{A}}{\partial t^2} + \sigma\frac{\partial^2\vec{A}}{\partial t^2} + \vec{j}_{coil}\sin(2\pi\omega t), \quad (1)$$

where μ_0 and μ_r are the vacuum and relative permeability, respectively; ϵ_0 and ϵ_r are the vacuum and relative permittivity and σ is the conductivity, j_{coil} and w are the current and frequency of rf antenna. Oscillating magnetic fields produced by the antenna resulted in oscillating electric fields interacting with the catalyst. Because of the skin-effect, the rf electric fields penetrate inside catalyst only within the skin depth and induced electric current, $\vec{J}=\sigma\vec{E}$, where electric field is $\vec{E}=-\partial\vec{A}/\partial t$. Inductive heating of catalytic particle, $H_{ind}=\vec{J}\cdot\vec{E}$, can be thought of as joule heating with the conductive currents generated by the time varying field. The heat transfer equation accounting for inductive heating of catalyst can be written as

$$c_p\rho_m\frac{\partial T}{\partial t} - \nabla(\kappa\nabla T) = H_{ind} \quad (2)$$

where c_p is the specific heat, r_m is the density of material, k is the thermal conductivity.

[0020] A 2-Dimensional computational investigation of inductive heating of catalytic particles of size varied from 100 nm to 10 mm was performed using CFD-ACE® multi-physics software. RF fields for inductive heating of catalyst were generated by a RF antenna located 2 cm from the catalytic particle surrounded by SiO_2 glass representing the temperature-sensitive surface of a substrate in a CCVD reactor. The current of the RF antenna j_{coil} was increased with decreasing size of the particle to ensure that the catalyst temperature remained in excess of 1000 K.

[0021] Temperatures of catalytic particles ranging in size from 10 mm to 100 nm obtained at various frequencies of a RF antenna are given in FIG. **1**. The frequency required for efficient heating of catalyst increases as the size of particle decreases. For example, efficient inductive heating of catalyst particles 10 mm and 100 nm in diameter was achieved at frequencies of 100 MHz and 20 GHz, respectively. The current of the RF antenna must be substantially increased as the size of catalyst particles decreases in order to maintain heating of catalyst to temperatures in excess of 1000 K. For example, 10 mm catalyst was heated by a RF antenna operating at 3 A to a temperature of about 1000 K, while a RF antenna with 300 A current was required to achieve a similar temperature for a 100 nm catalytic particle. A pulsed RF antenna can be used to minimize heat transfer from catalyst particles to substrate.

EXAMPLE

Selective Heating of Catalyst Using a RF Source

[0022] Low-temperature growth of vertically aligned CNT (VACNT) may be performed in a mixture of acetylene and ammonia gas at several Torr of total pressure flowing at around 60 and 80 sccm respectively, 700° C., and a bias of 500 V between substrate and a showerhead anode that maintains a current of 200 mA. An example of a system for low-temperature synthesis of CNT is shown in FIG. **2**. The system comprises a 13.56 MHz RF source **1** for creating plasma discharge and an additional pulsed RF power source **2** with tunable frequency in the GHz range for inductively heating catalytic nanoparticles. A nonconducting substrate **3** is used to eliminate substrate Joule heating and a cooling system **4** is used for active cooling of the substrate. The system is initially evacuated to approximately 10^{-6} Torr using, for example, coupled turbo and mechanical pumps **5** so that the chamber **6** can be evacuated first mechanically and then using the turbo pump. To maintain stable plasma, an active pressure control device such as a mechanized throttle valve **7** is used. Mass flow controllers **8** regulate the flow of the carbon bearing feedstock gas, the promoter (ammonia) and oxygen.

What is claimed is:

1. A method for forming carbon nanotubes on a substrate comprising the step of:

providing a catalyst distributed on the surface of the substrate and

simultaneously delivering a supply of hydrocarbons to the catalyst and selectively heating the catalyst using a radio frequency source using a catalytic chemical vapor deposition process, to form carbon nanotubes on the substrate.

2. The method of claim **1**, wherein the radio frequency source is tuned to a frequency that heats catalyst specifically.

3. The method of claim **2**, wherein the radio frequency source is tuned to a frequency that is dependent on the size of catalyst particles.

4. The method of claim **1** wherein the catalyst is in the form of nanoparticles distributed on a substrate.

5. The method of claim **1** wherein the catalyst is selected from the group consisting of Ni, Fe, Co, Cu, Al, V, Y, Mo, Pt, Pd and their binary and ternary alloys.

6. The method of claim **1** further comprising the step of actively cooling the substrate during carbon nanotube formation.

7. The method of claim **1** wherein the catalytic chemical vapor deposition process is a plasma enhanced catalytic chemical vapor deposition process.

8. The method of claim **1** wherein the radio frequency electromagnetic field is generated by an radio frequency source other than that used to that used to sustain discharge in the plasma-enhanced chemical vapor deposition process.

9. The method of claim **6** wherein the radio frequency used is between 1 GHz and 100 GHz.

10. The method of claim **1** wherein the carbon nanotubes are aligned.

11. The method of claim **1** wherein the substrate is a temperature-sensitive substrate.

12. The method of claim **1** wherein a supply of oxygen gas is supplied to the catalyst simultaneously with the supply of hydrocarbon gas.

13. An apparatus for catalytic chemical vapor deposition synthesis of carbon nanotubes on a substrate comprising:

a) a catalyst distributed on the surface of the substrate,

b) a means of delivering a supply of hydrocarbons to the catalyst,

c) a radio frequency source for creating plasma discharge, and

d) a radio frequency source positioned to selectively heat the catalyst by induction.

14. The apparatus of claim **13** wherein the radio frequency source for creating plasma discharge produces radio waves having a frequency of 13.56 MHz and the radio frequency source positioned to selectively heat the catalyst by induction produces radio waves having a frequency of between 1 and 100 GHz.

15. The apparatus of claim **13** wherein the radio frequency source positioned to selectively heat the catalyst by induction is a tunable radio frequency source.

16. The apparatus of claim **13** further comprising mass flow controllers to regulate the flow of hydrocarbons delivered to the catalyst.

17. The apparatus of claim **13** further comprising a means for delivering oxygen to the catalyst.

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