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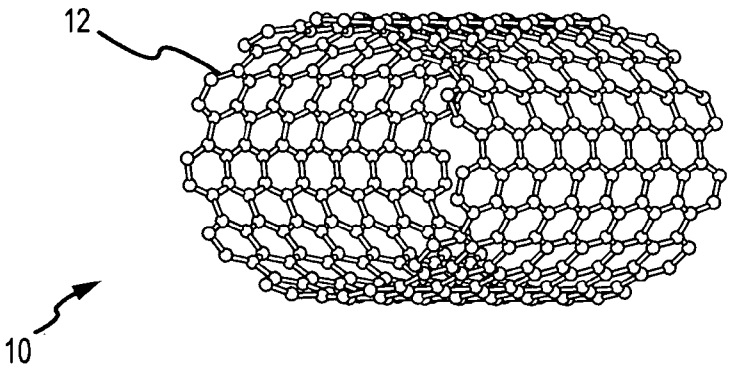

FIG.1
(PRIOR ART)

(57) Abstract: Ion implantation is used to grow nanotubes out of carbon and other materials. Catalytic materia! is placed on or in a membrane that physically and possibly environmental Iv separates an implantation chamber or region from a growth chamber or region. High-energy ions are implanted into the catalytic material from one side to grow nanotubes on an exposed surface in the growth chamber Ion implantation via the membrane provides for greater flexibility to separate and independently control the implantation and growth processes.

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System and Method for Nanotube Growth via Ion Implantation using a Catalytic Transmembrane

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to nanotube (NT) growth of carbon and other materials using an ion implantation process.

Description of the Related Art

Carbon nanotubes (CNTs) have stimulated a great deal of interest in the microelectronic and other industries because of their unique properties including tensile strengths above 35 GPa, elastic modulus reaching 1 TPa, higher thermal conductivity than diamond, ability to carry 1000x the current of copper, densities below 1.3g/cm^3 and high chemical, thermal and radiation stability. CNTs have great promise for devices such as field effect transistors, field emission displays, single electron transistors in the microelectronic industry, and uses in other industries. Commercialization of CNTs will depend in large part on the ability to grow and network CNTs on a large cost-effective scale without compromising these properties.

As illustrated in Figure 1, a CNT **10** is a hollow cylindrical shaped carbon molecule. The cylinderical structure is built from a hexagonal lattice of sp^2 bonded carbon atoms **12** with no dangling bonds. The properties of single-walled nanotubes (SWNTs) are determined by the graphene structure in which the carbon atoms are arranged to form the cylinder. Multi-walled nanotubes (MWNTs) are made of concentric cylinders around a common central hollow.

CNTs are commonly grown using several techniques such as arc discharge, laser ablation and chemical vapour deposition (CVD). In CVD the growth of a CNT is determined by the presence of a catalyst, usually a transition metal such as Fe, Co or Ni, which causes the catalytic dehydrogenation of hydrocarbons and consequently the formation of a CNT. CVD generally produces MWNTs or SWNTs of relatively poor quality due mostly to the poorly controlled diameters of the nanotubes. However, CVD

is relatively easy to scale up and can be integrated with conventional microelectronic fabrication, which favors commercialization.

The way in which nanotubes are formed at the atomic scale is not precisely known. The growth mechanism is still a subject of scientific debate, and more than one mechanism might be operative during the formation of CNTs. As shown in Figures 2a and 2b, a catalyst **20** is deposited on a support such as silicon, zeolite, quartz, or inconel **22**. At elevated temperatures, exposure to a carbon containing gas causes the catalyst to take in carbon, on either the surfaces, into the bulk, or both. This thermal diffusion process of neutral carbon atoms occurs at energies of a few electronvolts (eV). A precursor to the formation of nanotubes and fullerenes, C_2, is formed on the surface of the catalyst. From this precursor, a rodlike carbon **24** is formed rapidly, followed by a slow graphitization of its wall. The CNT can form either by 'extrusion' (also know as 'base growth' or 'root growth') shown in Figure 2a, in which the CNT grows upwards from the catalyst that remains attached to the support, or the particles can detach from the substrate and move at the head of the growing nanotube, labelled 'tip-growth', as shown in Figure 2b. Depending on the size of the catalyst particle either SWNT or MWNT are grown. A typical catalyst may contain an alloy of Fe, Co or Ni atoms having a total diameter of 1 to 100 nm (on the order of 1,000 atoms for 1 nm diameter of catalyst).

As shown in Figure 3, to synthesize CNTs **24** using CVD the support **22** and catalytic material **20** are placed inside an environmentally-controlled chamber **32**. The sample is heated until the temperature is great enough (400 °C) that the introduction of hydrogen along with a buffer gas (Argon) "reduces" (removes the oxide) the particle. A plurality of gas feeds **34** introduce a process gas including a mixture of a carbon-containing growth gas **36**, typically a hydrocarbon C_xH_y such as Ethylene (C_2H_4), Methane (CH_4), Ethanol (C_2H_5OH), or Acetylene (C_2H_2) or possibly a non-hydrocarbon such as carbon-monoxide (CO), an inert buffer gas **38** such Argon (Ar) to control pressure inside the chamber and prevent released hydrogen atoms from exploding and possibly a scrubber gas **40** such as H_2O or O_2 to periodically or continuously clean the surface of the catalyst. An energy source **42** such as a heating coil provides the energy necessary (e.g. a few eV) to heat the catalyst to a temperature which allows it to 'crack' the hydrocarbon molecules into reactive atomic carbon **44.** The reactive carbon

44 is absorbed into the surface of catalytic material **20** causing the CNT to grow from the same catalytic surface. A pump system **46** including a vacuum and/or pressure pump controls the pressure inside the chamber to produce conditions both conducive to absorption of carbon atoms into the catalytic material and growth of CNTs from the catalytic material. A number of electrical ports **48** are provided to accommodate pressure sensors, thermocouples and the like to monitor conditions inside the chamber.

SUMMARY OF THE INVENTION

The present invention provides a system and method for growing nanotubes out of carbon and other materials using an ion implantation process that facilitates sustained growth of high quality nanotubes.

This is accomplished by implanting ions into a catalyst to grow nanotubes. In the case of carbon nanotubes (CNTs), a catalyst is placed on or in a membrane that physically and possibly environmentally separates an implantation chamber from a growth chamber. An ion beam is used to implant carbon ions into the catalyst to grow CNTs on an opposing surface exposed to the growth chamber. The carbon ions can be implanted directly into the catalyst or indirectly via "knock on" or "sputtering" processes that amplify the number of implanted carbon ions. Ion implantation via the membrane provides for greater flexibility to separate and independently control the implantation and growth processes.

These and other features and advantages of the invention will be apparent to those skilled in the art from the following detailed description of preferred embodiments, taken together with the accompanying drawings, in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1, as described above, is a diagram of a carbon nanotube;

FIGs. 2a-2b, as described above, are diagrams illustrating root and tip CNT growth;

FIG. 3, as described above, is a diagram of a conventional CVD process using a single feedstock-growth chamber to grow CNTs on a substrate;

FIGs. 4a and 4b are diagrams of an ion implantation process through a membrane that supports the catalyst and separates the implantation and growth chambers for

nanotube growth in accordance with the present invention;

FIGs. 5a and 5b are a diagram of a simple membrane and catalyst configuration and a frequency plot of ion implantation depths;

FIG. 6 is a diagram of an embodiment of the ion implantation process using a membrane to separate the implantation and growth chambers in accordance with the present invention;

FIG. 7 is a diagram of an exemplary embodiment of a gasket that seals the implantation and growth chambers from the external environment and each other;

FIG. 8 is a section view of an exemplary membrane including an array of catalytic nano-particles formed therein;

FIGs. 9a-9b are section and plan views of an exemplary strip heater for heating the catalyst;

FIG.10 is a section view of a membrane for direct implantation of ions into the catalyst;

FIGs. 11a and 11b are sections views of an alternate embodiment of the membrane to facilitate a "lift-off" growth process;

FIGs. 12a-12c are diagrams of an implantation process that sputters carbon ions from a target that are back scattered onto the catalyst;

FIG. 13 is a section view of an alternate embodiment of the membrane for growing an array of nanotubes from a sheet of catalytic material;

FIG. 14 is a diagram of a hybrid CVD and ion implantation process for growing nanotubes; and

FIG. 15 is a diagram of an alternate embodiment for growing CNTs in a closed-cavity.

DETAILED DESCRIPTION OF THE INVENTION

Efforts to improve the growth of CNTs have revealed a number of drawbacks in the conventional CVD approach. The surface area of the catalytic particle for absorbing carbon atoms is limited by the desired geometry and growth of the CNT from the catalytic nano-particle. That is, the growing CNT covers most of the catalyst. To grow a SWNT the nano-particle must be very small, approximately 1-10 nm in diameter. The presence of the growing CNT further reduces the available surface area. Furthermore,

the absorption process itself causes the surface of the catalytic nano-particle to become encrusted with amorphous carbon and graphite which slows and eventually stops absorption of feedstock carbon and growth of the CNT. The effectiveness of the scrubber gas to clean the surface of the nano-particle is limited because the scrubber gas tends to attack the CNT necessitating a lower concentration of scrubber gas. The conventional process cannot be sustained indefinitely, which places a limit on the length of CNT growth. Likewise the growth rate in the conventional process is limited by the absorption rate and a viscous force produced by the process gases that opposes the extrusion force. Sustainability and growth rate will be important to commercialization of CNTs. In theory, the CNT structure is formed of pure carbon atoms. However, in the conventional process CNT growth in the presence of the impurities in the process gases can introduce contaminants into the CNT structure of 2% or more. Furthermore, the high-pressure noxious gas environment is not hospitable to in-situ annealing of defects using electron guns or in-situ observation of CNT growth using electron gun microscopes or optical sensors.

As we have discovered, many of these deficiencies are attributable to the noxious gases present in any CVD process and the fact that in conventional CVD , the catalytic surface at which absorption of carbon feedstock takes place and at which growth of the CNTs occurs are one and the same. The desired conditions for absorption of reactive carbon atoms into the catalytic material and for growth of CNTs in a CVD process are quite different.

The present invention addresses these deficiencies with a system and method for growing nanotubes using an ion implantation process that facilitates sustained growth of high quality nanotubes from an element selected from among Carbon (C), Germanium (Ge), Boron (B), Boron-Nitride (BN), Boron-Carbide (BC), $B_iC_jN_k$ where i, j and k are any non-negative integers, Silicon (Si) and Silicon-Carbide (SiC). Without loss of generality, in the exemplary case of carbon nanotubes (CNTs), a catalyst (an alloy of atoms such as Fe, Co and Ni atoms) is placed on or in a membrane that physically and possibly environmentally separates an implantation chamber from a growth chamber. The combination of catalyst and membrane may be referred to as the "catalytic transmembrane". Carbon ions are implanted into the catalytic material either directly or indirectly to grow a CNT on an opposing surface directly exposed to the growth

chamber. Because ion implantation is performed in a vacuum, the environment is not hostile to the growth process and the chambers do not have to be environmentally separated.

Ion implantation via the membrane provides for greater flexibility to separate and independently control the implantation and growth processes. Specifically ion implantation eliminates the noxious gases and overcomes any encrusting problem in order to sustain growth; sufficiently high-energy ions penetrate through any encrustation. Use of the membrane to separate implantation from growth also prevents the ion beam from damaging the CNTs. Growth rates via direct implantation are expected to be considerably slower than CVD but sustainable and may be increased by indirect implantation via "knock on" or "sputtering" processes that amplify the number of carbon ions transferred into the catalyst. Ion implantation is a more precise and controllable process than CVD that facilitates closer spacing of CNTs in an array and control of CNT length. Furthermore, the ion implantation system is conducive to the introduction of diagnostic equipment such as electron guns and optical sensors in-situ to control defects in the growing CNT and observe the growth of the CNT as well as the membrane surface exposed to the implantation chamber. In-situ observation of CNT growth is particularly important to further the science of CNT growth.

As shown in Figures 4a-4b, the method of ion implantation uses a membrane **50** that physically and possibly environmentally separates a chamber **51** into an implantation region or chamber **52** (held at vacuum by a vacuum pump **53**) from a growth region or chamber **54.** A catalyst **56** (a 'nano-particle') including atoms **57** supported on or in membrane **50** provides an implantation surface **58** to receive carbon ions **62** with sufficient energy to reach, penetrate and stop in the catalyst and a growth surface **62** directly exposed to the growth region to grow carbon nanotubes **63**. The catalyst or nano-particle is typically a single 3D particle containing an alloy of many atoms such as Fe, Co and Ni but could be multiple nano-particles of varying geometry and configurations. Note, the illustrations are not to scale; the membrane diameter is typically in the tens of millimeters while the nano-particle is at most tens of nanometers. In this embodiment, the membrane is supported along a portion of the walls of chamber **51** (not shown) to physically separate the implantation and growth chambers, one on either side of the membrane, but does not span the entire chamber to form an environmental seal between

the two chambers. Consequently, the growth chamber is held at the same vacuum. The membrane could physically span the entire chamber and still not environmentally separate the two chambers if the membrane does not provide a seal. The key is that the membrane provides a region or chamber for performing ion implantation on one side and a region or chamber for growing nanotubes on the other.

In one embodiment shown in Figure 4a, source **64** emits carbon ions in a carbon ion beam or an ionized hydrocarbon H_xC_y beam that are implanted directly through membrane into catalyst **56.** A second source **75** of dopant ions such as B or N can be provided to dope the CNT by replacing carbon atoms in the lattice with a dopant atom. The beam preferably implants the dopant ions into the catalyst but may be directed at the CNT. Doped CNTs can be used as nanodiodes and other nanoelectronic devices.

In another embodiment shown in Figure 4b, source **64** directs an ion beam **65** onto a carbon-containing layer **66** such as graphite on the topside of the membrane. The knock-on layer may be formed from naturally occurring carbon that includes approximately 99% C12, 1 % C13 and ≈0% C14 isotopes, a manufactured carbon including any specified isotope composition, or a filtered source of a substantially pure isotope. Through a "knock-on" process, each ion knocks multiple carbon ions **62** forward through the membrane into catalyst **56** providing gain. In this embodiment, ion beam **65** may be ionized carbon or some other ionized particle, heavier or lighter than carbon. The particle may be an ionized element such as Carbon, Argon or a heavy ion such as Kr, an ionized molecule such as H_2O or an ionized hydrocarbon H_xC_y as long as the particle can knock Carbon ions out of layer **66** with sufficient energy to penetrate and stop in the catalyst. The catalyst may be formed in the membrane to expose the implantation surface to the ion beam so that it is not required to penetrate through the membrane. The growth surface must be exposed to the growth chamber but the implantation surface may or may not be directly exposed to the ion beam in the implantation chamber. Unlike the thermal diffusion processes of CVD, the ion beam may penetrate through to the catalyst. The catalyst must still be hot so the thermal diffusion processes will extrude the CNT out of the particles surface. For intense ion beams this heat may be supplied by the beam but for lower beam intensities it must be supplied by an external heater. Once the injected carbon ions **62** slow down within the catalyst they recombine with electrons to form additional neutral carbon atoms **57** needed to initiate

and sustain growth of the CNTs **63**.

The viability of ion implantation through a membrane **300** into a catalyst **302** for a rudimentary design shown in Figure 5a is confirmed by the plot **304** of the number of carbon ions versus implantation depth shown in Figure 5b. In this example, a 5 nm sphere of Fe **302** is placed on the backside of an 8 nm Si membrane **300**. This thickness is determined by the initial energy of the ion. A wide range is acceptable depending on the thickness of an anti-sputtering layer and a graphite enhancement carbon layer (not included in this simple example). It can run from at least 100 eV to 100 keV. This membrane can be Al_2O_3, Si, SiO_2 or any nonreactive material compatible with the catalyst. A graphite knock-on layer perhaps 5 nm to 100 nm is formed on the membrane. In this simulation, a 2 keV Carbon ion beam **305** is directed onto the membrane. As shown, a majority of the carbon ions are implanted within the 5nm depth inside the sphere. A fair portion of the carbon ions are backscattered and absorbed in the Silicon membrane and some of the carbon ions pass through the structure entirely. The ion bombardment scatters Si ions **306** that are substantially reabsorbed in the Si membrane. Similarly Fe ions **308** are scattered but substantially reabsorbed in the catalyst. These results demonstrate that ion implantation through a membrane with a knock-on process to amplify the carbon implantation is feasible to initiate CNT growth.

Another embodiment of a system for ion implantation synthesis of CNTs is illustrated in Figure 6. Membrane **50** including an insulating layer **71**, suitably Si or SiO_2, knock-on layer **66** and an anti-sputtering layer **73** separates implantation chamber **52** from growth chamber **54**. A gasket **68** holds membrane **50** in place and environmentally seals the implantation and growth chambers from each other and the external environment. As described in Figure 4, sealing the two chambers is not essential. It provides an additional degree of freedom to control the environment in the growth chamber. As shown in Figure 7, in one embodiment gasket **68** includes a soft gold ring **69** on opposite sides and along the periphery of the membrane and conflat (CF) vacuum flanges, knife edge (304 SS) **70** on opposing faces of the implantation and growth chambers **52**, **54**. The CF vacuum flanges **70** engage the soft gold rings **69** to form the requisite seals. Other gasket configurations are possible as well. This allows the environments, namely the gas compositions and pressure, to be independently controllable. Given the 'thinness' of the membrane the differential pressure cannot be

allowed to get too high. The membranes currently being tested are specified to withstand a differential pressure of up to 1 atmosphere (760 Torr). In many applications separately controllable environments may not be desirable; hence the gasket is not required.

An implantation environmental control system includes a pump system including a vacuum pump **72** to control the pressure of the implantation chamber and possibly an energy source **74** to heat the catalytic material. If the energy of the ion beam is sufficiently high, the beam will self-heat the catalytic material such that a separate energy source is not required. A number of electrical ports **82** are provided to accommodate pressure sensors, thermocouples and the like to monitor conditions inside both chambers.

Because the CNT is not grown inside implantation chamber **52,** the ion implantation process can be tailored for more efficient implantation and growth control. Specifically, the use of "knock-on" processes is facilitated by implanting ions from one side of the catalyst to grow CNTs on the other side. The implantation surface is not obstructed by the growth of the CNT. The ion beam will not attack the CNT itself. Furthermore, since ion implantation is performed in a vacuum, the environment is hospitable to the introduction of diagnostic equipment in the implanation chamber to study the membrane and implantation surface.

A growth environmental control system includes a pump system **90** including a vacuum and/or pressure pump to control the pressure of growth chamber **54** and possibly one or more gas feeds **92** to introduce a gas **94** such as an inert gas or possibly functionalizing gases for attaching doping materials to CNTs to modify or enhance their mechanical, electrical, optical, or chemical properties for further processing into electronic or sensor devices. Eliminating the hot noxious gases associated with conventional CVD processes, particularly the carbon-containing growth gas, from the growth chamber has several benefits. First, these gases tend to attack and contaminate the CNT as it grows. Second, electron guns **96** and **98** can be used in-situ to selectively fix and create defects in the CNT as it grows. Electron gun **96** can be used to anneal defects in the NT structure to provide missing carbon atoms. Electron gun **98** can be used, for example, to rotate pairs of common atoms to move the bonds and change the bond structure of the CNT. Lastly, the environment facilitates in-situ observation of the growth process using, for example, an electron microscope **100** and optical equipment

102 for Raman spectroscopy, fluorescent spectroscopy or other appropriate measurements. The electron guns and observation equipment are suitably located outside the chamber and routed through ports in the chamber.

The growth chamber may be operated in a vacuum or gases may be introduced and the pressure controlled to be nearer atmospheric pressure. Pure vacuum is 0 Torr, less than 10^{-6} is considered to be ultra-high vacuum and less than 10^{-2} Torr a good vacuum. The implantation chamber is maintained at "vacuum" which is to be considered at least a good vacuum and preferably ultra-high vacuum for ion implantation. Vacuum conditions may provide an optimal environment for carbon growth and for use of the electron guns. Alternately, an inert gas can be introduced into the growth chamber.

For simplicity of explanation, the membrane has been described as supporting a single catalyst or nano-particle. For purposes of scientific research and some commercial applications it may be desirable to grow a single CNT. In other cases, it may be desirable to grow an array of CNTs and in some cases a very large array, perhaps upwards to billions of separate NTs in a single structure. The membrane is well suited for either single CNTs or arrays of CNTs. The array of catalysts can be fabricated on or in the membrane use using standard processing techniques. This allows for control over the geometry of the nano-particle and particularly the geometry of the absorption and growth surfaces.

In one embodiment as shown in Figure 8 membrane **50** includes a relatively thick substrate **110** formed of a materially such as Si, SiO_2, or Al_2O_3 that is chemically inactive to the nanotube material. The substrate should be sufficiently strong to handle any pressure gradients between the chambers and exhibit thermal expansion properties close to the catalytic material. Substrate **110** is patterned and a catalyst **112** is deposited to form an array. A spacer layer **113** separates a knock on layer **114** (e.g. Graphite) from the catalyst material. An anti-sputtering layer **116** (e.g. Ti, Mo, etc.) is deposited over the knock-on layer. A source directs an ion beam **118** through the anti-sputtering layer onto knock-on layer **114**. Through a "knock-on" process, each ion knocks multiple carbon ions **119** forward through the membrane into catalyst **112** thereby providing gain. The implanted carbon ions become neutral carbon atoms and grow CNTS **120**. Carbon ions that are knocked backward from layer **114** are captured by the anti-sputtering layer **116.** In this example, membrane **50** is placed in a vacuum chamber

122. The membrane physically divides the chamber into an ion implantation chamber on one side and a growth chamber on the other but both chambers are held at vacuum in the same environment. Other membrane configurations that provide the requisite functionality of separating and possibly sealing the implantation and growth chambers and providing different catalytic surfaces for implantation and growth are contemplated by the current invention.

As described above, an energy source is used to heat the catalytic material to maintain the temperature needed for diffusion through the catalytic material.As shown in Figures 9a and 9b, provision of an electrical current **126** through a resistive heater strip **128** patterned around the individual nano-particles **112** on substrate **110** can maintain the membrane at a constant temperature . The integrated heater strip may be more effective at maintaining the entire array of nano-particles at the desired temperature. One of the electron guns in the growth chamber can locally heat the growth region so that growth is stimulated.

In another embodiment shown in Figure 10, a catalyst **130** is embedded in membrane **132** so that a portion **134** of catalyst surface is directly exposed to the implanation chamber and a different portion **136** of catalyst surface is directly exposed to the growth chamber. A carbon ion beam **138** is directed onto portion **134** to directly implant carbon ions **140** into catalyst **130** to grow CNTs **142** on the portion **136** of the catalyst surface exposed to the growth chamber. Note, portion **134** could be covered by a non-carbon containing layer and still achieve direct implantation without knock-on processes. In this example, membrane **132** is placed in a vacuum chamber **144**. The membrane physically divides the chamber into an ion implantation chamber on one side and a growth chamber on the other but both chambers are held at vacuum in the same environment.

In another embodiment depicted in Figures 11a and 11b, a catalyst **150** and a knock-on material **152** are formed on opposite sides of a membrane **154** separated by an air gap **156**. Ions **158** from a source strike knock-on material **152** ejecting carbon ions **160** that reach, penetrate and stop in catalyst **150.** A pair of CNTs **162** and **164** grow in opposite directions from the catalyst. When CNT **164** reaches the knock-on material **152** the growth process serves to "lift-off" catalyst **150** from the membrane.

In another embodiment illustrated in Figures 12a-12c, an ion beam sputters

carbon ions from a target that back scatter onto a catalyst or catalysts. As shown in Figure 12a, an ion beam **170** is directed at a target **172** comprised of carbon-containing atoms such as Graphite to "sputter" carbon ions **174** from the target. The sputtered carbon ions **174** are back scattered onto the backside of a membrane **176** formed with an array of catalysts **178**. The carbon ions are implanted in the catalysts causing CNTs **180** to grow on the front side of the membrane. In this example, membrane **176** is placed in a vacuum chamber **180**. The membrane physically divides the chamber into an ion implantation chamber on one side and a growth chamber on the other but both chambers are held at vacuum in the same environment. In an alternate geometry, ion beam **170** is directed through an aperture **400** (a thin layer **402** or a hole) in a membrane **404** onto target **172** comprising a gold layer **406** and a graphite layer **408** on a silicon substrate **410**. The sputtered carbon ions **174** are backscattered onto catalysts **178** on the front side of membrane **404**. Thin layer **402** may be a knock on layer to enhance the carbon flux. The thickness of the graphite and gold layers as well as the ion energy of the beam can be adjusted to achieve the required implant energy for different catalysts thicknesses. This structure can repeat laterally to grow a larger array. In another geometry, beam **170** is directed through an aperture **420** in a substrate **422** onto a target **172** comprising a gold layer **406** and a graphite layer **408** on a silicon substrate **410** at an angle to the beam. The sputtered carbon ions **174** are back scattered onto a catalysts **178** on a side wall **424** shown here after lift-off growth of the CNT **426** has begun. In this geometry, the CNT is not directly exposed to the ion beam.

In another embodiment illustrated in Figure 13, a continuous layer **190** of catalytic material is formed on the backside of a patterned membrane **192** in vacuum chamber **193**. A knock-on layer **194** is separated from the catalytic layer by a spacer layer **196**. Patterned membrane **192** exposes defined portions of the catalyst layer to the growth environment. Ions **198** from a source strike knock-on layer **194** ejecting carbon ions **199** that reach, penetrate and stop in catalyst layer **190** causing CNTs **200** to grow on the exposed portions of the catalyst surface.

In another embodiment illustrated in Figure 14, a hybrid CVD-ion implantation process is used to grow CNTs. Even with the use of knock-on processes, CNT growth via ion implantation may be slower than conventional CVD. The use of a membrane **202**

to both separate and environmentally seal an implantation chamber **204** from a feedstock/growth chamber **206** facilitates a hybrid growth process. A catalyst **208** is placed on the underside of membrane **202** exposed to the feedstock/growth chamber.

A feedstock system includes gas feeds **210** to introduce process gases into the feedstock/growth chamber **206**, a pump system **212** including a vacuum and/or pressure pump to control the pressure of the chamber, and an energy source to heat the gases and/or catalytic material to separate carbon atoms **214** from the growth gas molecules **216** for absorption into the catalytic material. The process gas typically includes a mixture of a carbon-containing growth gas **218**, typically a hydrocarbon C_xH_y such as Ethylene (C_2H_4), Methane (CH_4), Acetylene (C_2H_2) or Ethanol (C_2H_5OH) or possibly a non-hydrocarbon such as carbon-monoxide (CO), a buffer gas **220** such as an inert gas, e.g. Argon (Ar), to control pressure inside the chamber and prevent released hydrogen atoms from exploding, and possibly a scrubber gas **222** such as H_2O or O_2 to periodically clean the surface of the catalyst. In some applications the buffer and or scrubber gases may not be required. The carbon atoms **214** are absorbed into catalyst **208** to grow CNTs **224** in the feedstock/growth chamber. Even with the scrubber gas, over time the catalyst becomes encrusted with amorphous carbon and graphite which slows and eventually stops absorption of feedstock carbon and growth of the CNT

At this point, the CVD process is suspended and the ion implantation process is inititated. A vacuum pump **230** maintains a vacuum in the implanation chamber so that a source **232** can direct an ion beam **234** onto membrane **202** to implant carbon ions into catalyst **208** to sustain CNT growth albeit at a slower growth rate. The carbon ions can be implanted either directly or via knock-on processes. This approach combines the high initial growth rate of a CVD process with the sustainability of an ion implantation process. Notice that if a crust of carbon builds up on the catalytic particle, the ion energy can be increased to penetrate through the crust into the catalyst. Carbon build up would normaly stop growth for the standard CVD method. This can be a real advantage over CVD growth.

In another embodiment depicted in Figures 15, a membrane **250** is constructed to provide a closed cavity **252**. A catalyst **254** is placed inside the cavity and a knock-on material **256** is suitably placed outside the cavity opposite the catalyst. Ions **258** from a source strike knock-on material **256** ejecting carbon ions **260** that reach, penetrate and

stop in catalyst **254** causing a CNT **262** to grow within the closed cavity.

Although the description of the invention has focused on the growth of carbon nanotubes the approach is viable for growing nanotubes from other materials such as Germanium (Ge), Boron (B), Boron-Nitride (BN), Boron-Carbide (BC), $B_iC_jN_k$, Silicon (Si) or Silicon-Carbon (SiC). The interest in and development of carbon nanotube technology is well beyond that of other materials, hence the focus on carbon nanotubes. However, the approach of using a catalytic membrane to separate the implantation and growth chambers is just as applicable for growing nanotubes from these other discovered or yet to be discovered materials.

While several illustrative embodiments of the invention have been shown and described, numerous variations and alternate embodiments will occur to those skilled in the art. Such variations and alternate embodiments are contemplated, and can be made without departing from the spirit and scope of the invention as defined in the appended claims.

WE CLAIM:

1. An apparatus for growing nanotubes from an element selected from among Carbon, Germanium, Boron, Boron-Nitride, Boron-Carbide, $B_iC_jN_k$, Silicon and Silicon-Carbide, comprising:

a chamber;

a membrane physically separating said chamber into an implantation region and a growth region;

one or more catalysts supported on the membrane, each said catalyst having a first portion of catalyst surface towards the implantation region and a different second portion of catalyst surface directly exposed to the growth region;

a pump for holding at least said implantation region at vacuum; and

a source configured to direct ions through the implantation region onto the membrane to implant element ions through the first portion of catalyst surface into the catalyst to grow element nanotubes on the second portion of catalyst surface in the growth region.

2. The apparatus of claim 1, wherein the source emits element ions that are directly implanted through the first portion of catalyst surface into the catalyst.

3. The apparatus of claim 1, wherein said membrane comprises an element containing layer between the catalyst and the implantation region and separated from the catalyst, said source emitting ions into said element-containing layer that releases a larger number of element ions that are implanted through the first portion of catalyst surface into the catalyst.

4. The apparatus of claim 3, wherein said catalyst is selected from iron (Fe), cobalt (Co), or nickel (Ni) and said element-containing layer is Graphite.

5. The apparatus of claim 3, wherein said source emits element ions.

6. The apparatus of claim 3, wherein said source emits ions of a different element or

molecule than the element grown into said nanotube.

7. The apparatus of claim 6, wherein said different element or molecule has a higher molecular weight than said element grown into said nanotube.

8. The apparatus of claim 3, wherein the catalyst is separated by open space from the element-containing layer.

9. The apparatus of claim 3, wherein the element-containing layer releases the element ions forward into the catalyst through knock-on processes.

10. The apparatus of claim 3, wherein the element-containing layer back scatters the element ions into the catalyst through a sputtering process.

11. The apparatus of claim 1, further comprising:

a dopant source configured to direct dopant ions into the catalyst to replace element atoms in the nanotube lattice.

12. The apparatus of claim 1, wherein the membrane physically separates but does not environmentally seal the growth and implantation regions from each other so that said

pump holds both said implantation and growth regions at vacuum.

13. The apparatus of claim 1, wherein the membrane physically separates and seals the growth and implantation regions from each other, wherein said pump holds only said implantation region at vacuum, further comprising:

a second pump to control the pressure of the growth region; and

one or more gas feeds to introduce gases into the growth region.

14. The apparatus of claim 13, wherein said gas feeds introduce an element-containing gas into the growth region such that neutral element atoms are absorbed at said second different portion of catalyst surface to initiate nanotube growth via a CVD

process, said source emitting ions to implant element ions into said first portion of catalyst surface to sustain nanotube growth via the ion implantation process.

15. The apparatus of claim 1, further comprising:

a first piece of diagnostic equipment in the implantation region to characterize surface properties of the membrane; and

a second piece of diagnostic equipment in said growth region to characterize properties of the nanotube.

16. The apparatus of claim 1, wherein the geometry of the first portion of the catalyst surface is configured for efficient implantation of element ions into the catalyst and the geometry of the second different portions of the catalyst surface is configured to grow carbon nanotubes with a specified geometry.

17. The apparatus of claim 1, wherein said membrane supports an array of catalysts to grow an array of carbon nanotubes in said growth region.

18. An apparatus for growing carbon nanotubes (CNTs), comprising:

a chamber;

a membrane physically separating said chamber into an implantation region and a growth region;

a plurality of catalysts supported on the membrane, each said catalyst having a first portion of catalyst surface towards the implantation region and a different second portion of catalyst surface directly exposed to the growth region;

a carbon-containing layer supported on the membrane towards the implantation region and separated from the first portion of catalyst surface;

a pump for holding at least said implantation region at vacuum; and

a source configured to direct ions through the implantation region onto the carbon-containing layer causing the layer to release a larger number of carbon ions through knock-on processes forward to implant those carbons ions through the first portion of catalyst surface into the catalyst to grow carbon nanotubes on the second portion of catalyst surface in the growth region.

19. A method for growing nanotubes from an element selected from among Carbon, Germanium, Boron, Boron-Nitride, Boron-Carbide, $B_iC_jN_k$, Silicon and Silicon-Carbide, comprising:

placing a membrane in a chamber to physically separate an implantation region from a growth region, said membrane supporting one or more catalysts each having a first portion of catalyst surface towards the implantation region and a different second portion of catalyst surface directly exposed to the growth region;

pumping the implantation region to hold it at vacuum; and

emitting a beam of ions through the implantation region onto the membrane to implant element ions through the first portion of catalyst surface into the catalyst to grow nanotubes on the second portion of catalyst surface in the growth region.

20. The method of claim 19, wherein the beam includes element ions that are directly implanted through the first portion of catalyst surface into the catalyst.

21. The method of claim 19, further comprising:

placing an element-containing layer between the catalyst and the implantation region and separated from the catalyst, said beam of ions striking said element-containing layer to release a larger number of element ions that are implanted through the first portion of catalyst surface into the catalyst.

22. The method of claim 21, wherein the beam includes element ions.

23. The method of claim 21, wherein the beam includes ions of a different element or molecule than the element grown into said nanotube.

24. The method of claim 19, wherein the membrane physically separates and seals the growth and implantation regions from each other, further comprising:

introducing an element-containing growth gas into the growth region such that neutral element ions are absorbed at said second different portion of catalyst surface to initiate growth via a CVD process, said beam of ions being used to implant element ions

into said first portion of catalyst surface to sustain nanotube growth via the ion implantation process.

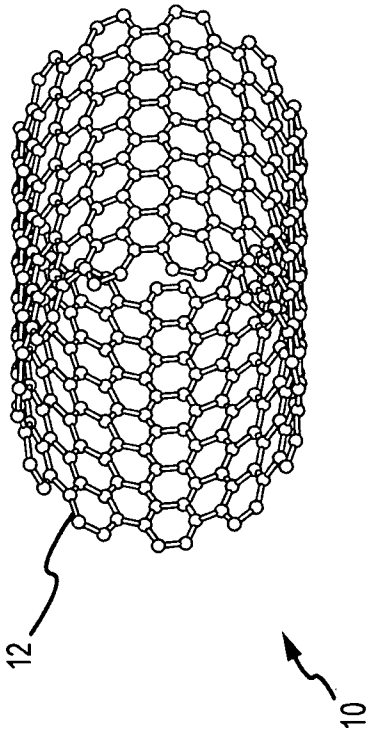

FIG.1
(PRIOR ART)

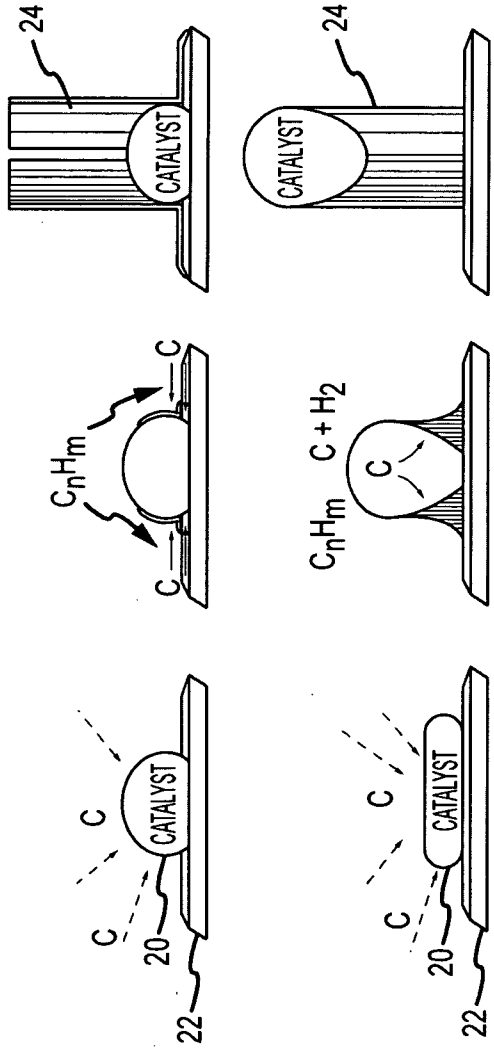

FIG.2a
(PRIOR ART)

FIG.2b
(PRIOR ART)

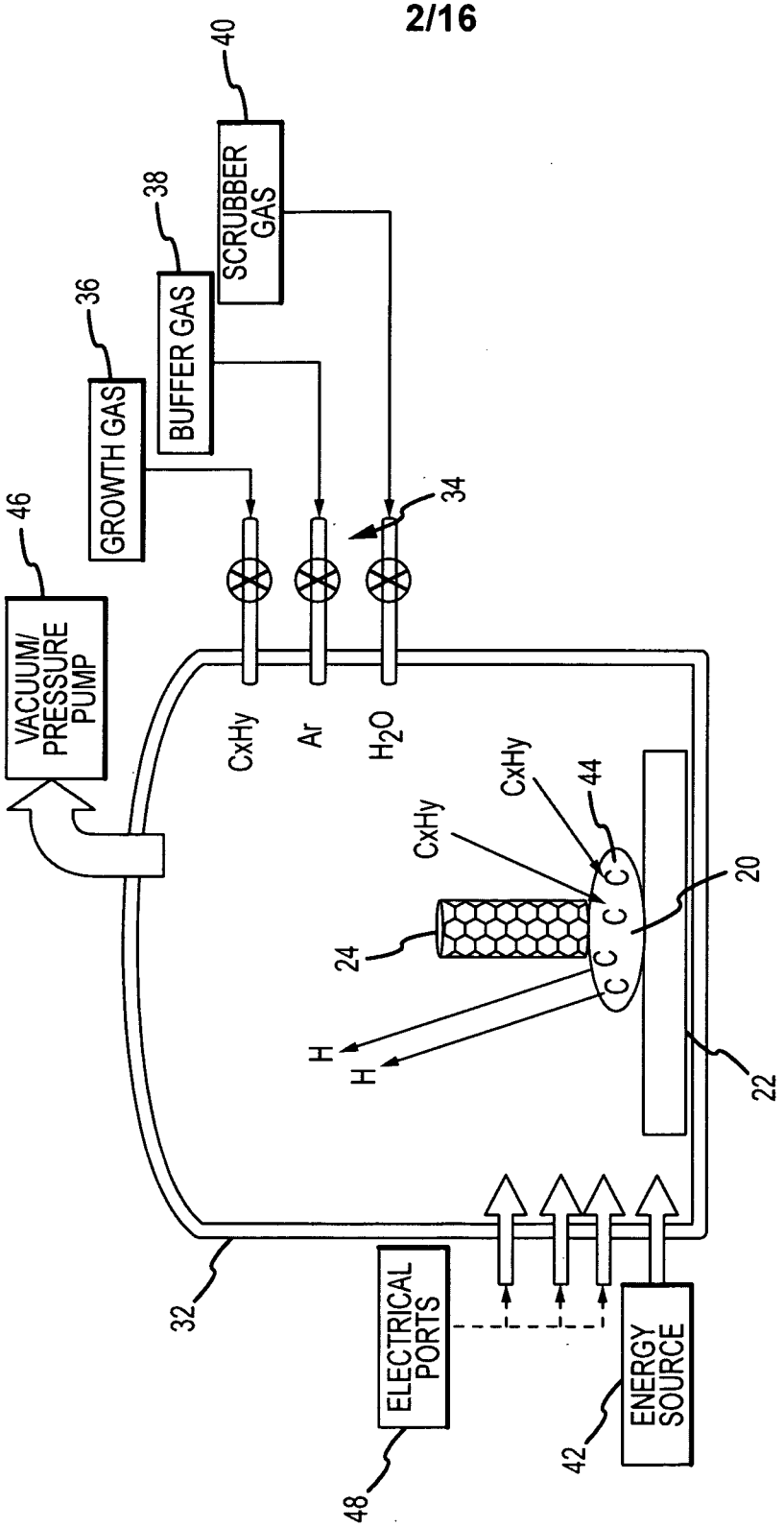

FIG.3
(PRIOR ART)

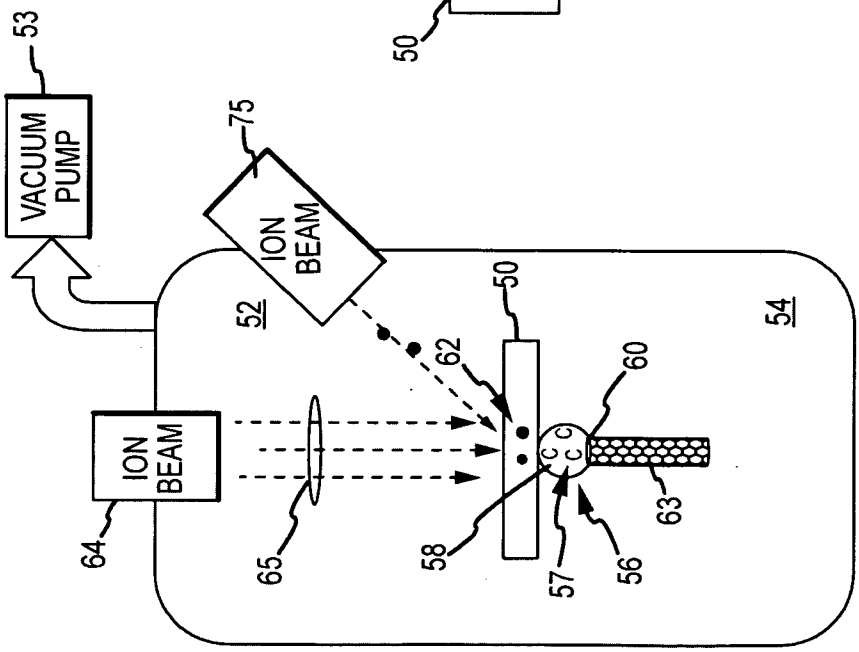
53
VACUUM PUMP
75
ION BEAM
52
50
54
62
60
ION BEAM
64
65
58
57
56
63

FIG.4a

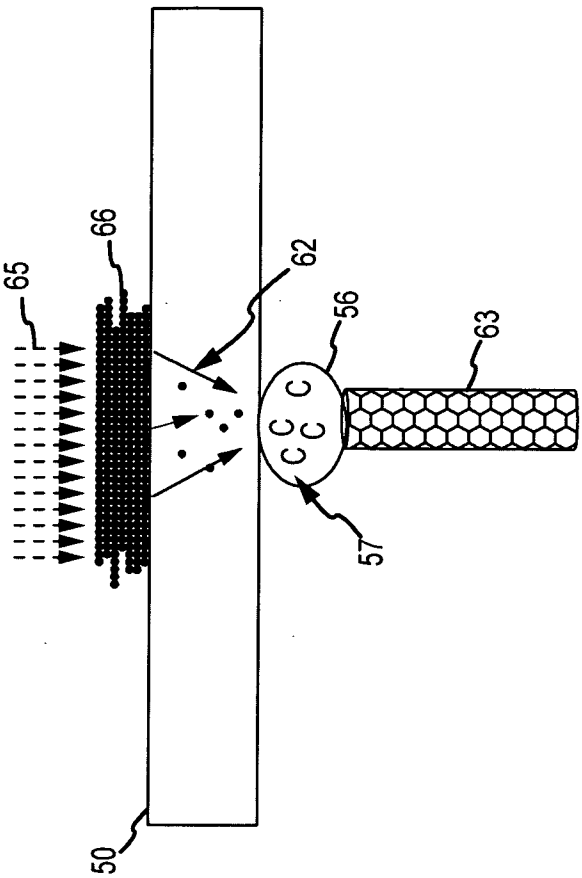
66
65
62
56
63
50
57

FIG.4b

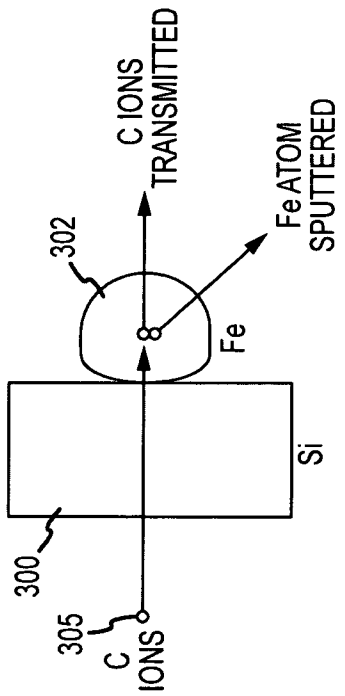
C IONS TRANSMITTED
Fe ATOM SPUTTERED
302
Fe
Si
300
305
C IONS

FIG.5a

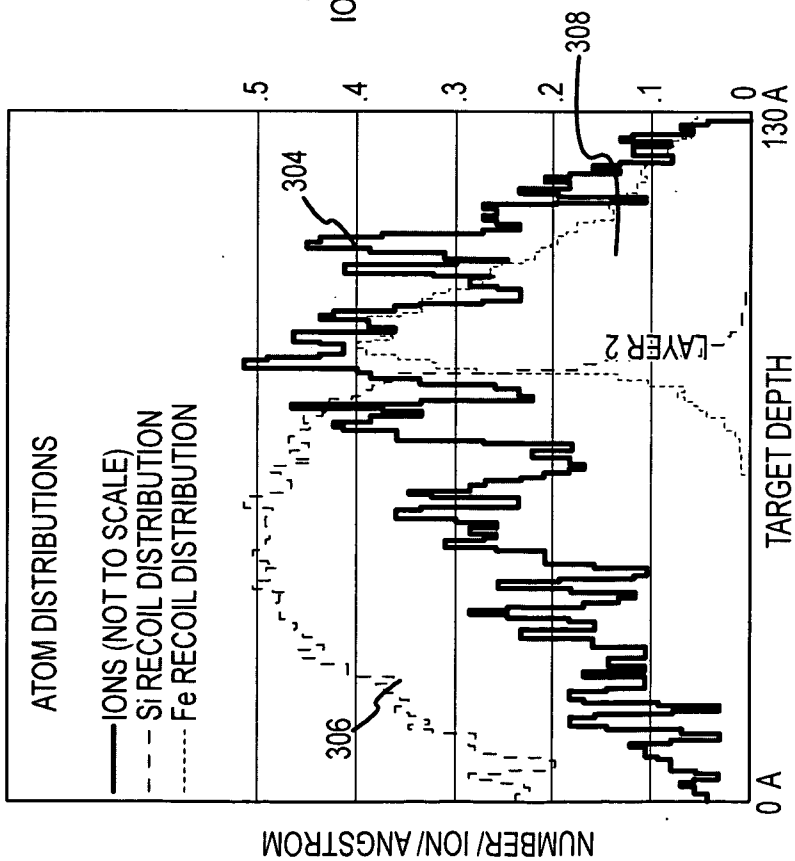
ATOM DISTRIBUTIONS
IONS (NOT TO SCALE)
Si RECOIL DISTRIBUTION
Fe RECOIL DISTRIBUTION
304
306
308
LAYER 2
.5
.4
.3
.2
.1
0
0 A
130 A
TARGET DEPTH
NUMBER/ ION/ ANGSTROM

FIG.5b

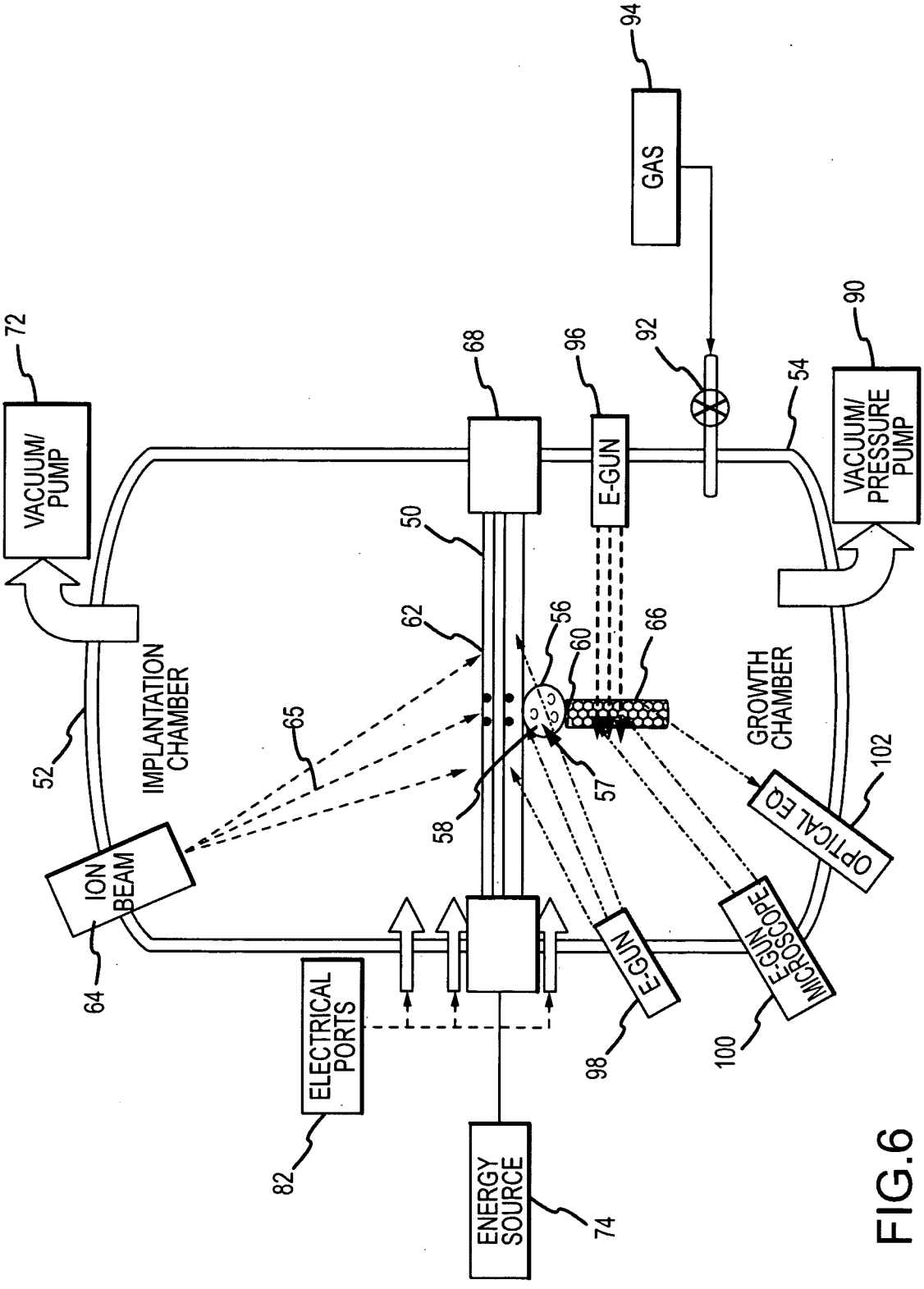
94
GAS
72
VACUUM/ PUMP
68
96
E-GUN
92
54
90
VACUUM/ PRESSURE PUMP
50
62
56
60
66
IMPLANTATION CHAMBER
GROWTH CHAMBER
52
65
57
58
102
OPTICAL EQ
ION BEAM
64
E-GUN
E-GUN MICROSCOPE
ELECTRICAL PORTS
98
100
82
ENERGY SOURCE
74

FIG.6

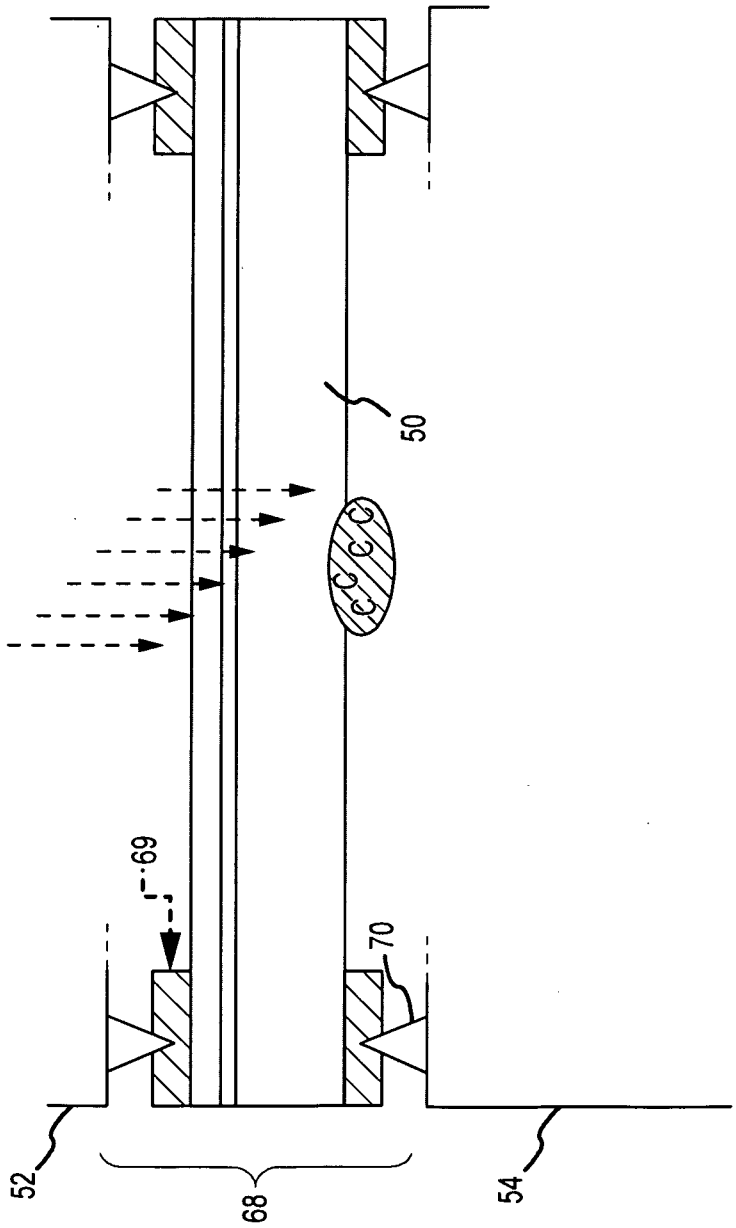

FIG.7

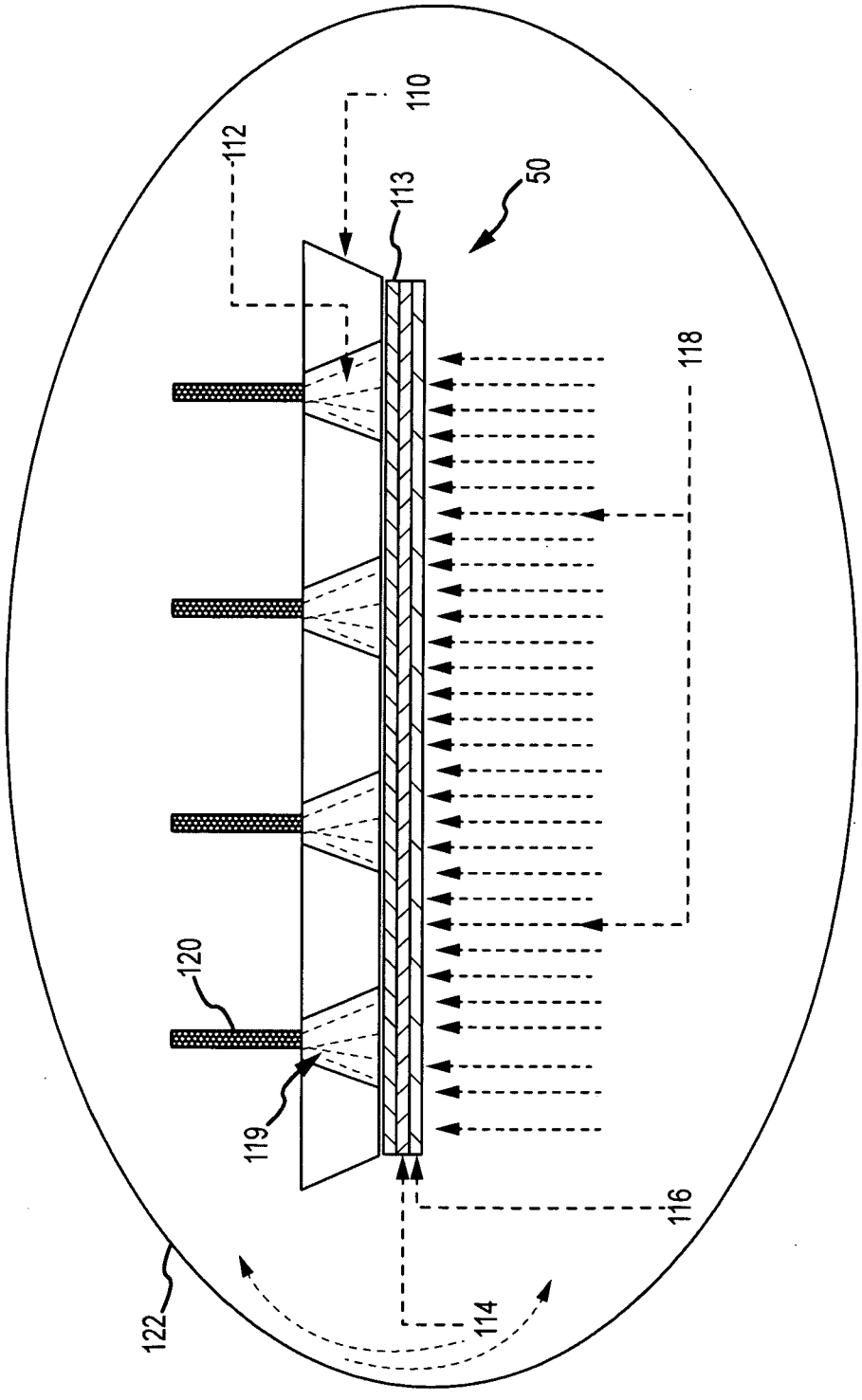

FIG.8

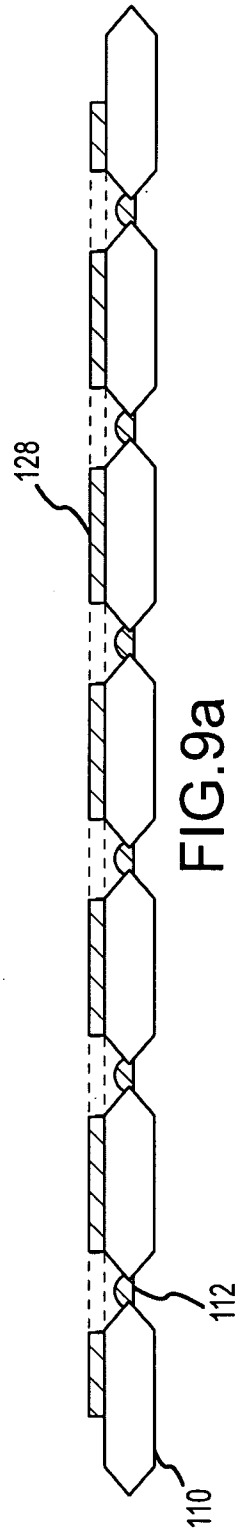

FIG.9a

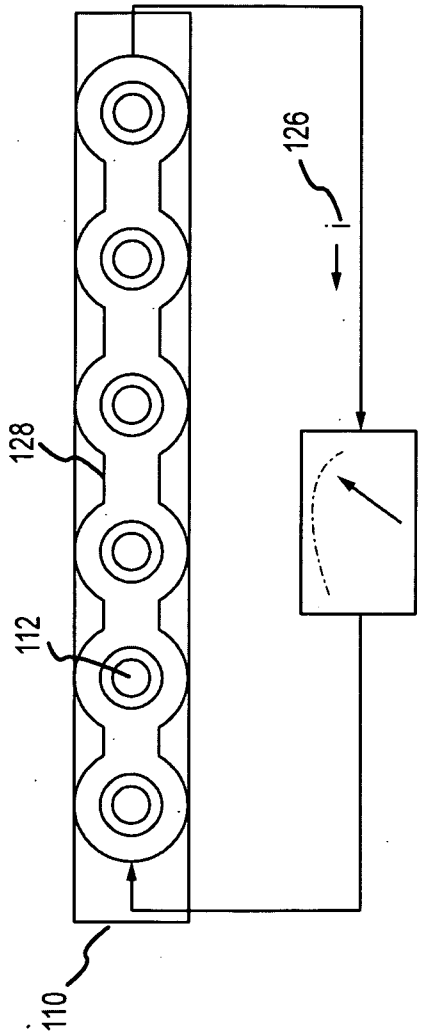

FIG.9b

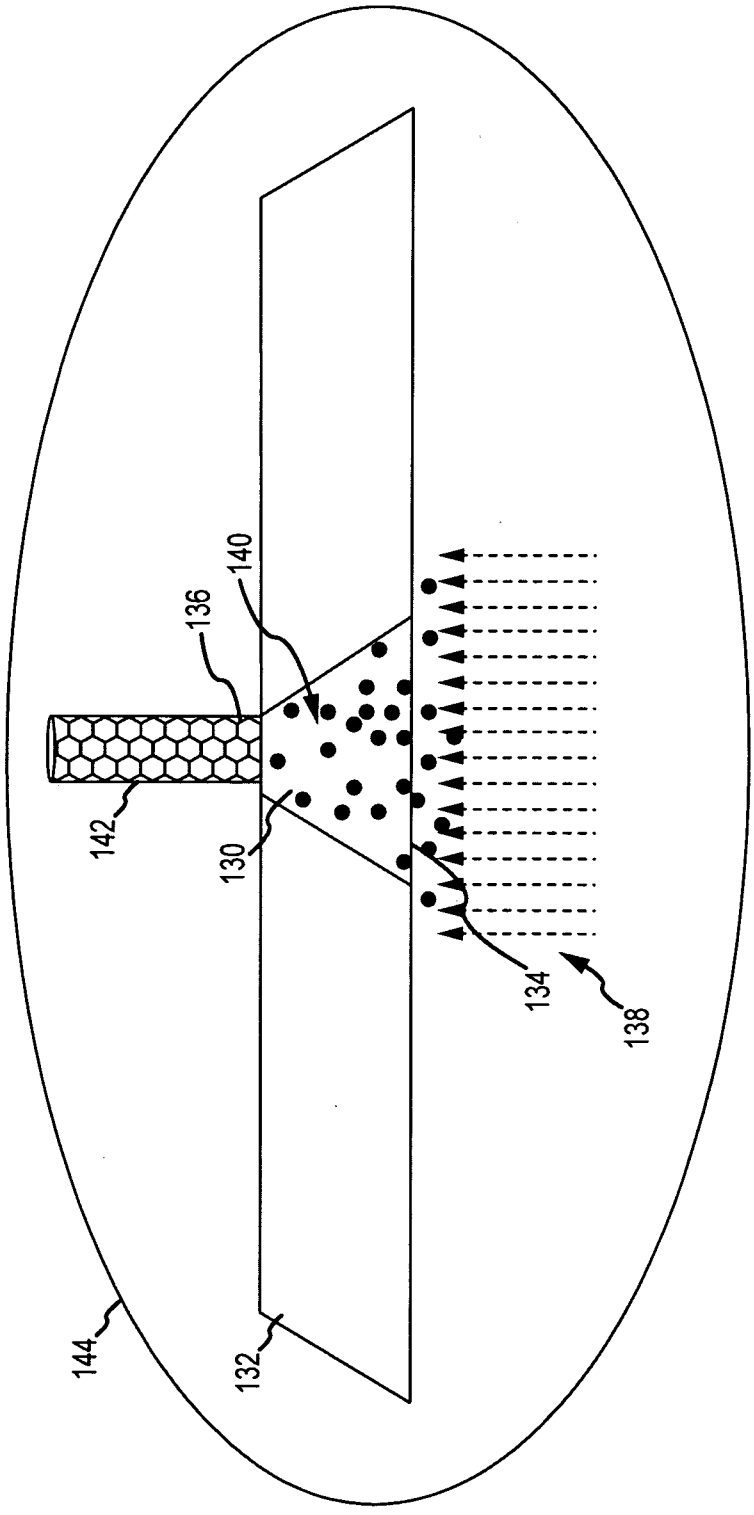

FIG.10

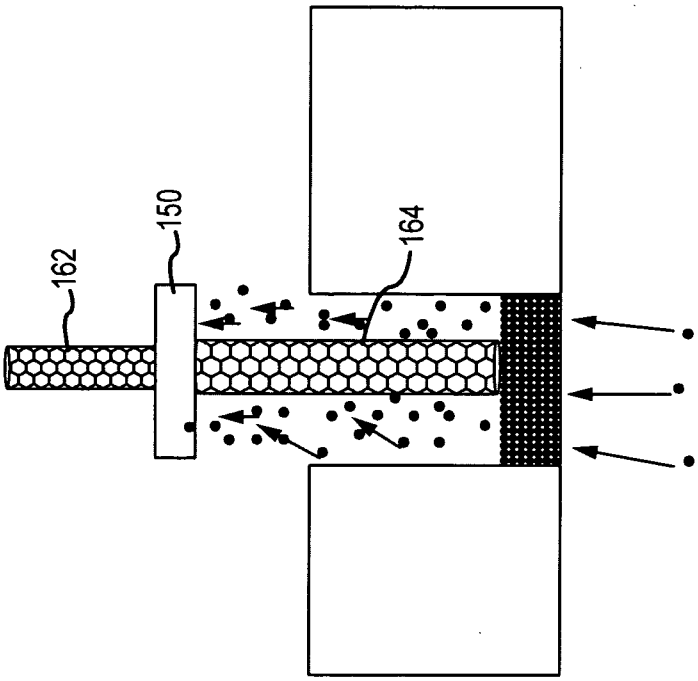

FIG.11b

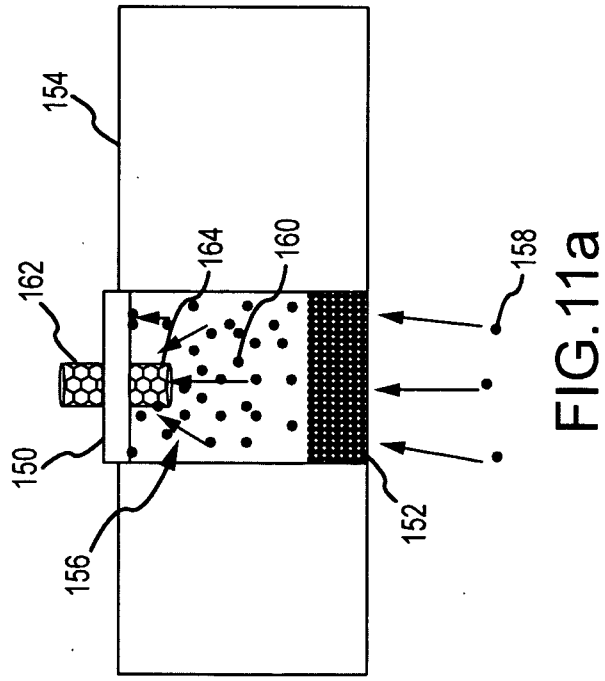

FIG.11a

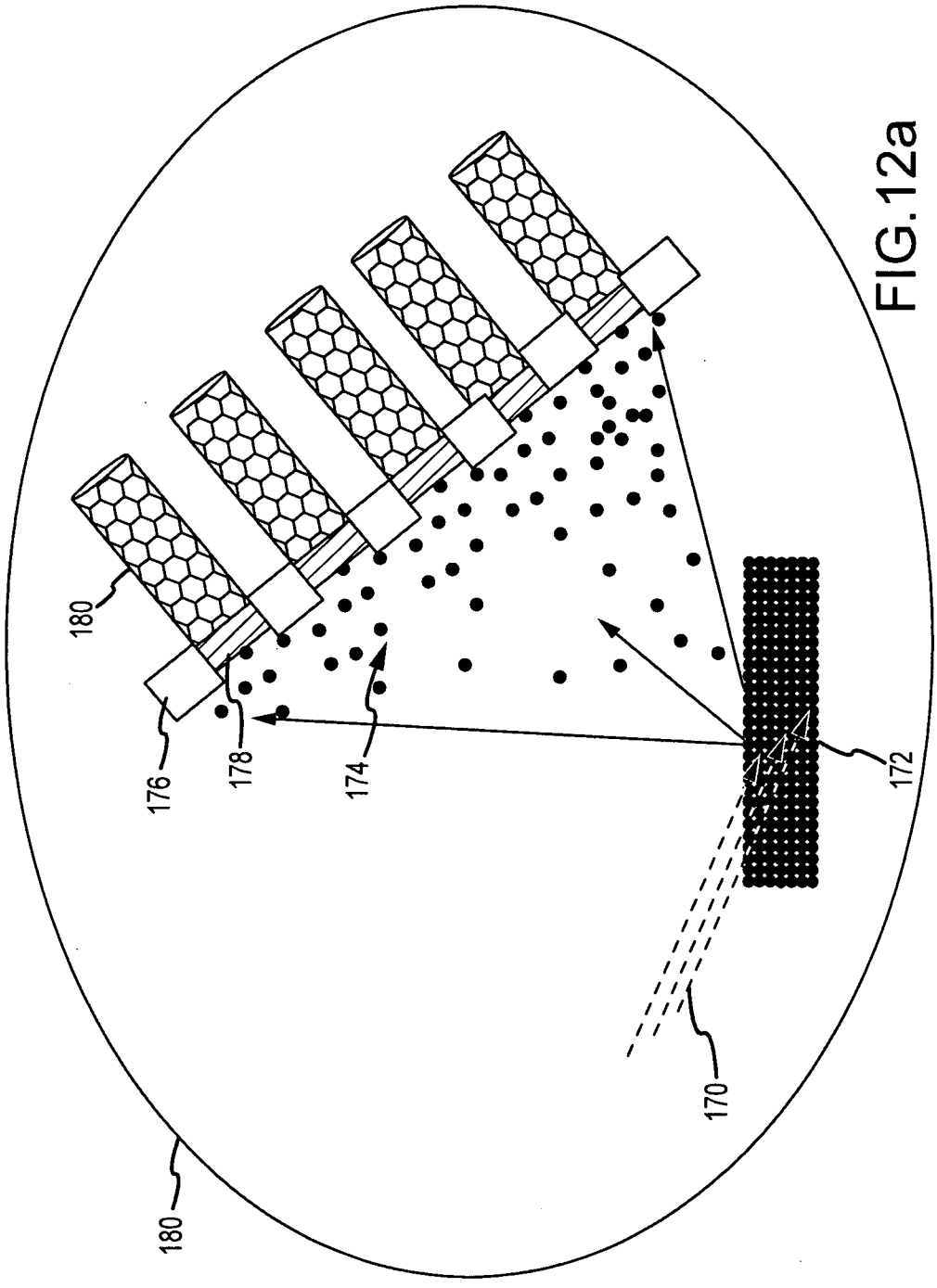

FIG.12a

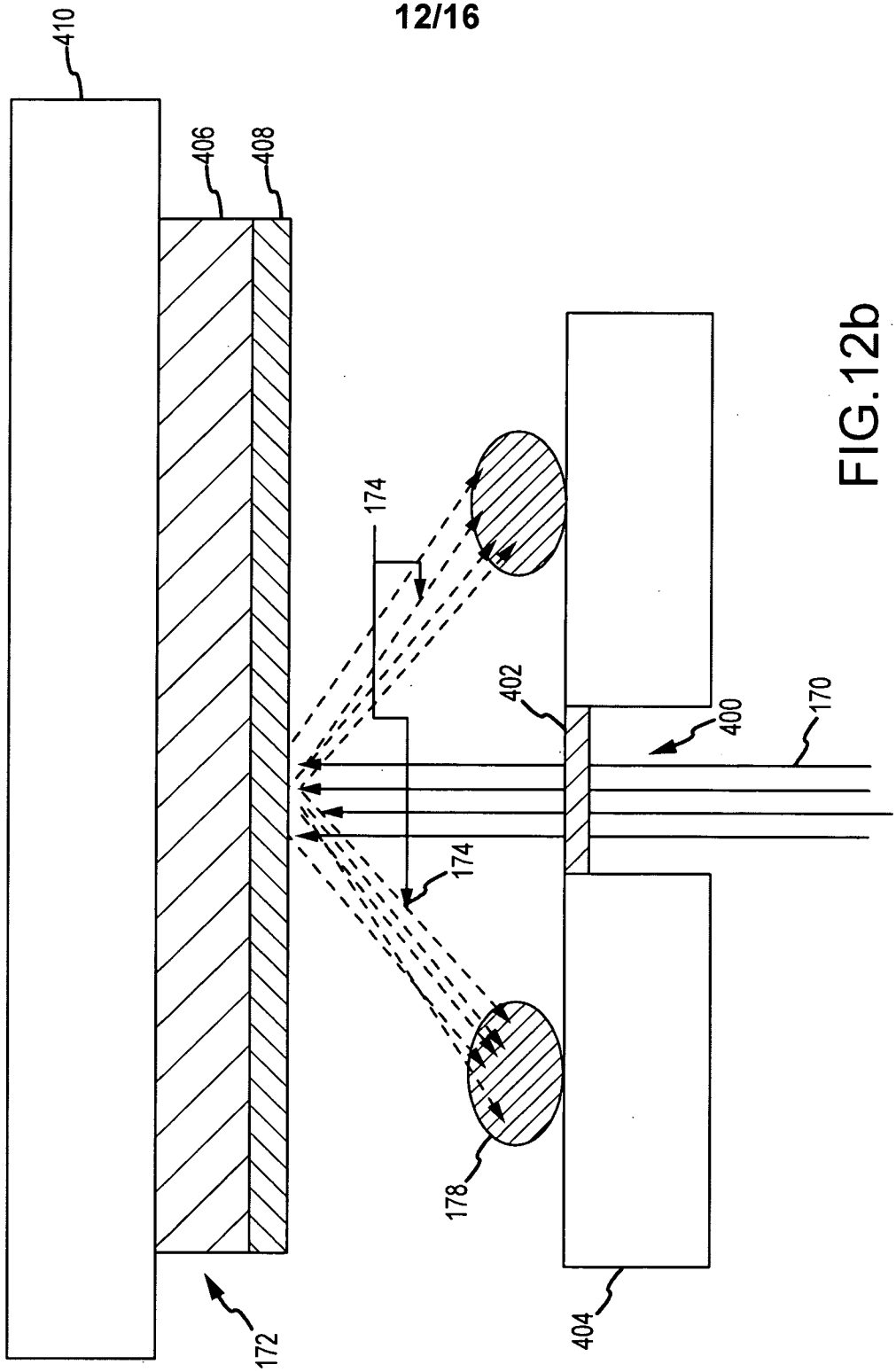

FIG.12b

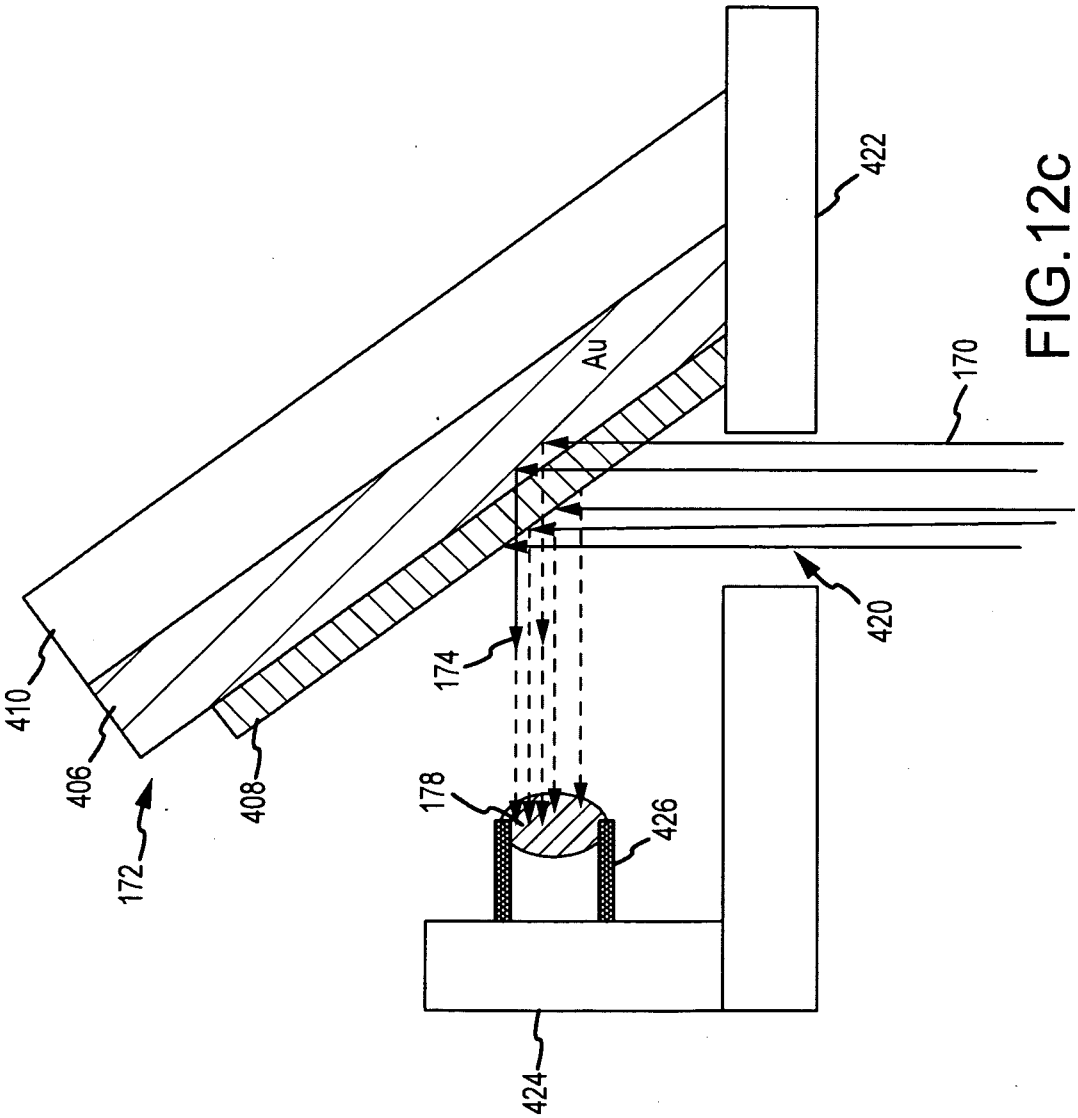

FIG.12c

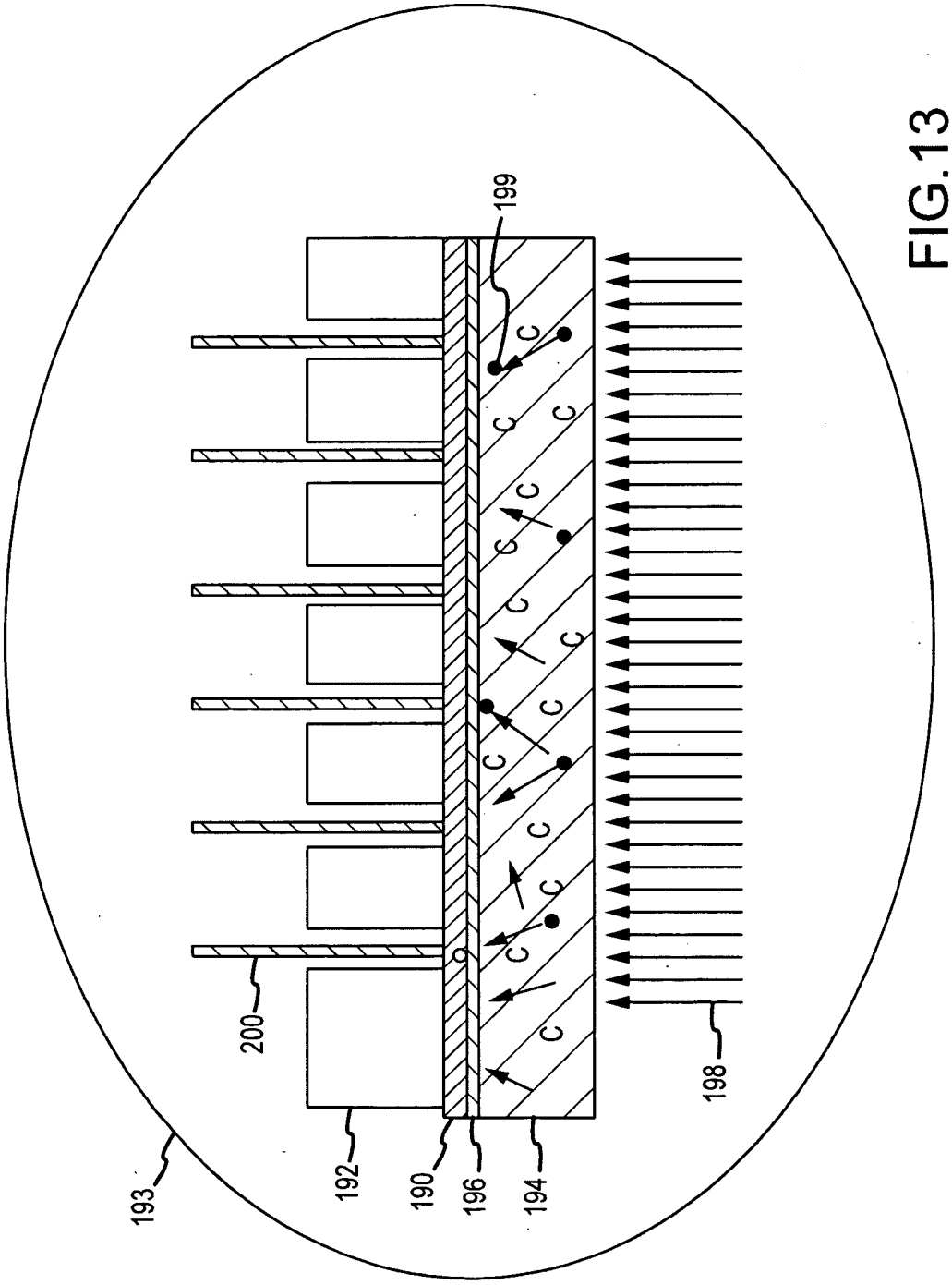

FIG.13

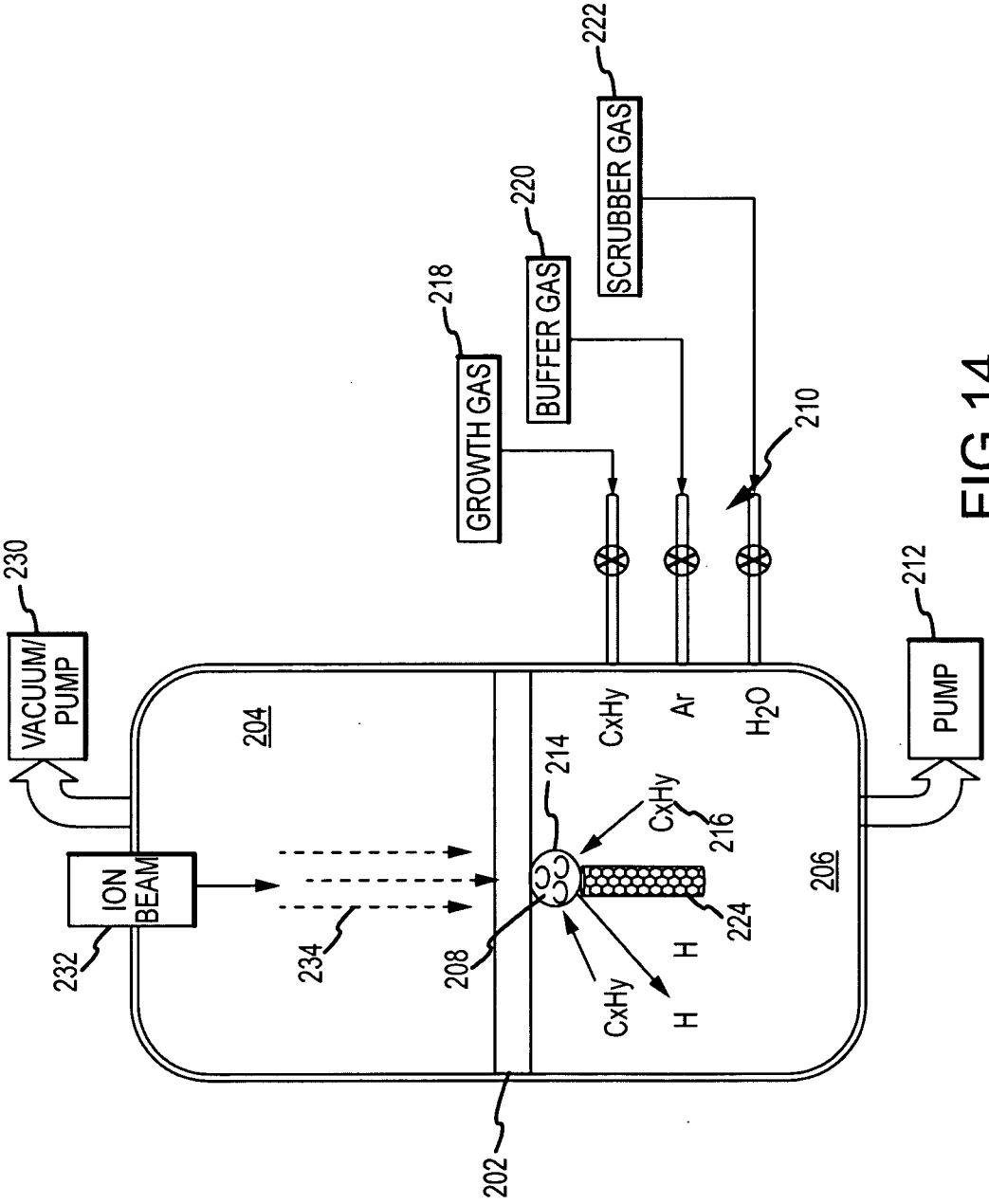
222
SCRUBBER GAS
220
BUFFER GAS
218
GROWTH GAS
210
230
VACUUM/ PUMP
212
PUMP
204
CxHy
Ar
H2O
214
CxHy
216
ION BEAM
206
232
234
208
224
CxHy
H
H
202

FIG.14

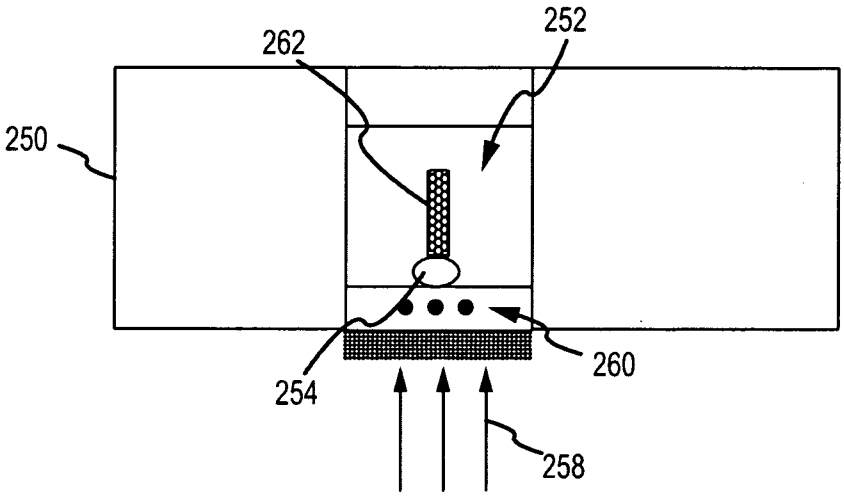

FIG.15