

MICROWAVE REACTOR FOR DEPOSITION OR TREATMENT OF CARBON COMPOUNDS

BACKGROUND

5 Technical Field:

The disclosure concerns a chamber or reactor for processing a workpiece such as a semiconductor wafer using microwave power.

10 Background Discussion

Processing of a workpiece such as a semiconductor wafer can be carried out using a form of electromagnetic energy, such as RF power or microwave power, for example. The power may be employed, for example, to generate a plasma, for carrying out a plasma-based process such as plasma enhanced chemical vapor deposition (PECVD) or plasma enhanced reactive ion etching (PERIE).

15 Two carbon-based films, namely diamond and graphene, have mechanical and electrical properties that are desirable for many applications.

Diamond films can have extreme hardness, high thermal conductivity, good optical transparency and high electrical resistivity. These properties are useful in applications such as optical coatings. In addition, a diamond film can also be used as a hard mask material in the semiconductor industry due to its superior etch selectivity compared with other amorphous carbon films deposited by traditional PECVD. The etch selectivity of diamond can be two or three times higher than other amorphous carbon films due to a high sp³ carbon percentage. This high etch selectivity is desirable for a high aspect ratio etch in order to maintain good pattern integrity during high ion energy bombardment etch. This is likely to become more critical as feature sizes continue to shrink for next generation devices.

20 A monolayer of graphene, in which a single atomic layer of carbon atoms are arranged in a hexagonal lattice, has exotic properties and a wide spectrum of potential applications. The high specific surface area of graphene indicates that graphene is likely able to store more energy than other carbonaceous materials. In addition, delocalized electrons in a graphene sheet that travel in high speed with intrinsic mobility of $\sim 2 - 2.5 \times 10^5$ cm²/vs, help to transport current efficiently. Due to its thin thickness and high electron mobility, graphene can be used to replace the traditional metal barrier layers for next generation semiconductor devices because the resistance of metal lines gets higher as their

thickness and dimension continues to shrink. Graphene also demonstrates high optical transparency, which can be used in flexible electronics, for example in smart watch applications. Chemical vapor deposition (CVD) has been used to grow both diamond and graphene films.

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SUMMARY

In one aspect, a plasma reactor for processing a workpiece includes a chamber having a dielectric window, a workpiece support to hold a workpiece in the chamber, a rotary coupling including a stationary stage configured to be coupled to a microwave source and a rotatable stage having an axis of rotation, a microwave antenna overlying the dielectric window of the chamber, a rotary actuator to rotate the microwave antenna, and a process gas distributor including a gas distribution ring surrounding the workpiece support. The microwave antenna includes at least one conduit coupled to the rotatable stage. The gas distribution ring including a cylindrical chamber liner separating a circular conduit from the chamber and a plurality of apertures extending radially through the liner to connect the conduit to the chamber.

In another aspect, a plasma reactor for processing a workpiece includes a chamber having a dielectric window, a workpiece support to hold a workpiece in the chamber, a rotary coupling including a stationary stage configured to be coupled to a microwave source and a rotatable stage having an axis of rotation, a microwave antenna overlying the dielectric window of the chamber, a rotary actuator to rotate the microwave antenna, a first gas supply to provide a hydrocarbon gas, a second gas supply to provide an inert gas, a gas distributor to deliver the hydrocarbon gas and the inert gas to the chamber, a vacuum pump coupled to the chamber to evacuate the chamber, and a controller configured to operate the microwave source, gas distributor and vacuum pump to deposit a carbon allotrope on the workpiece.

High quality graphene films are normally synthesized by high temperature chemical vapor deposition (CVD) with metal catalysts. However, the growth temperature is 800-1100° C, which is much higher than the thermal budget of most semiconductor devices. Moreover, a transfer process from metal substrates to targeted substrates is needed in order to incorporate the graphene into electronic devices. In this disclosure, microwave surface wave plasma provides high density of active radicals, which facilitates graphene nucleation and growth at much lower temperature (e.g., less than 800° C) without using metal

catalysts. The direct growth on arbitrary substrates at lower temperature can be a significant advantage for a variety of applications.

Some implementations may provide one or more of the following advantages. Microwave plasma processing can provide low temperature deposition because of its high radical density and low energy. Microwave plasma processing can provide not only high density of hydrocarbon species for fast deposition, but also high density of hydrogen radicals, which can etch away amorphous carbon phase at much lower process temperature. As a result, fast deposition of high quality films can be achieved at reduced process temperatures. Therefore, microwave plasma-based deposition, can yield high quality diamond and graphene films on both dielectric and metal substrates suitable for high-volume manufacturing.

The details of one or more implementations are set forth in the accompanying drawings and the description below. Other potential features, aspects, and advantages will become apparent from the description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is schematic cross-sectional side view of a processing reactor.

FIG. 1B is a schematic enlarged view of a microwave antenna from the reactor of FIG. 1A.

FIG. 2 is a schematic cross-sectional plan taken along line 2-2 of FIG. 1B.

FIG. 3 is a schematic plan view of the embodiment of the microwave antenna.

FIG. 4 is a schematic cross-sectional perspective view of the microwave antenna.

FIGS. 5A and 5B are schematic side views of a gas distribution plate.

FIGS. 6A and 6B are a schematic plan views of a gas distribution ring.

Like reference numbers and designations in the various drawings indicate like elements.

It is contemplated that elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation. It is to be noted, however, that the drawings illustrate only exemplary embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

DETAILED DESCRIPTION

Although diamond and graphene films have been deposited by CVD growth, such processes require high growth temperatures, typically 800-1000° C. Unfortunately, such temperatures are not compatible with current integration process flows in the semiconductor industry because the metal lines and low k films on device wafers can not tolerate the high temperature. In addition, graphene deposited by high temperature CVD needs to be transferred off of a thick metal foil on which it is deposited.

In addition, the quality of carbon compound materials can be improved by processing with extremely high density but non-equilibrium plasmas. A microwave reactor can provide both the low temperature and the high density, non-equilibrium plasma needed for high quality diamond and graphene films.

However, even with a rotating source to compensate for non-uniformity in the microwave emission caused by the chamber and slot layout, some microwave reactors do not meet the stringent uniformity required for distribution across the workpiece of deposition rate or etch rate. The minimum uniformity may correspond to a process rate variation across a 300 mm diameter workpiece of less than 1%.

Unfortunately, for some reactors or processes, a showerhead can not be used to deposition that inside the showerhead. However, the pumping liner can be used for skew of the pumping port flow. Process uniformity can further be controlled by adjusting the pedestal position and process pressure.

Referring now to FIGS. 1A and 1B, a workpiece processing reactor 100 includes a chamber 101 containing a workpiece support 102. The chamber 101 is enclosed by a side wall 104 formed of a material that is opaque to microwaves, e.g., a conductor, and a ceiling 106 formed of a microwave transparent material, e.g., a dielectric material. In one embodiment, the ceiling 106 may be implemented as a dielectric window 108 formed in the shape of a disk. The dielectric window 108 can fluidically seal the region above the window with the microwave supply assembly 110 from the chamber 101. In some implementations, the dielectric window 108 includes perforations. For example, the gas distribution plate 142 can form part of the window 108 (in which case the perforations extend partially into the window).

The workpiece support 102 can be a pedestal with a top surface 102a to support a workpiece 10 inside the chamber 101. In some implementations, a temperature control system 103 can control the temperature of the pedestal. For example, the temperature control system 103 can include a resistive heater 103a embedded in or placed on the

surface of the workpiece support 102 and a power source 103b electrically coupled to the heater 103a. Alternatively or in addition, coolant channels 103c can be formed in the pedestal, and coolant from a coolant supply 103d can flow, e.g., be pumped, through the channels 103c.

5 In some implementations, the workpiece support 102 is coupled to a motor and is rotatable inside the chamber 101 by the motor. In some implementations, the vertical position of the workpiece support 102 is adjustable, e.g., by a vertical actuator.

A vacuum pump 105 is coupled to the chamber 101, e.g., by a passage with an opening in a region below the pedestal 102, to evacuate the chamber 101. Examples of
10 vacuum pumps include an exhaust pump with throttle valve or isolation valve, dry pump and turbo pump.

A microwave supply assembly 110 supplies microwave radiation to the chamber 100. The microwave supply assembly 110 includes a rotating microwave antenna 114 that overlies the dielectric window 108. The antenna 114 can rotate while the window 108
15 remains stationary; the antenna 114 could be slightly separated from the window 108 or in sliding contact with the window 108. The microwave antenna 114 is enclosed by a conductive shield 122 that includes a cylindrical side wall 124 and a disk-shaped cap 126. In an implementation depicted in FIG. 4, the microwave antenna 114 is disk-shaped.

As shown in FIG. 1A, the microwave antenna 114 is fed by an axial waveguide 116.
20 The axial waveguide 116 is coupled through an overlying rotary microwave coupling 118 to a stationary microwave feed 120. A remote microwave source or generator 132 is coupled to the rotary coupling 118 by the microwave feed 120.

The rotary coupling 118 includes a stationary stage 118-1 and a rotatable stage 118-2. The stationary stage 118-1 is stationary relative to the chamber 100 and is connected to
25 the microwave feed 120. The rotatable stage 118-2 is connected to the axial waveguide 116 and has an axis of rotation coinciding with an axis of symmetry 114a of the microwave antenna 114. The rotary microwave coupling 118 permits microwave energy to flow from the stationary stage 118-1 to the rotatable stage 118-2 with negligible loss or leakage. As one possible example, a slip-ring RF seal (not shown) may be placed at the interface
30 between the stationary and rotatable stages 118-1 and 118-2. The antenna 114, rotary coupling 118 and axial waveguide 116 can provide the microwave supply assembly 110.

A rotatory actuator 130 is stationary relative to the chamber 101 and includes a motor 130-1. In some implementations, the rotatory actuator 130 includes a drive shaft 130-2 that drives a belt 130-3. The belt 130-3 is wound around a rotatable portion of the

microwave supply assembly 110, so that driving the belt 130-3 rotates the antenna 114. For example, the belt 130-3 can be wound around and drive the rotatable stage 118-2. The belt 130-2 can be a toothed belt, and can engaged toothed outer surfaces of the drive shaft from the motor 130-1 and the rotatable stage 118-2. In other implementations, the toothed
5 outer surface of the drive gear 130-2 directly engages a driven gear formed on the rotatable assembly 118-2. For example, the driven gear can be implemented as a circular array of teeth on the bottom surface of the rotatable stage 118-2.

The workpiece processing reactor 100 includes a process gas distributor 140.

In some implementations, the process gas distributor 140 includes a gas distribution
10 plate (GDP) 142 disposed beneath or forming the ceiling 106. The gas distribution plate 142 has an array of gas injection orifices 144 extending axially through it. The gas distribution plate 142 receives process gas from a process gas supply 146. The gas distribution plate may be formed of quartz.

Referring to FIG. 5A, in some implementations, the gas distribution plate 142 is a
15 dual channel showerhead configured to supply two different process gasses. For example, the gas distribution plate can include a lower plate 170 through which a plurality of axial apertures 170a and 170b are formed. The gas distribution plate can also include a middle plate 172 through which a plurality of axial apertures 172a are formed. The middle plate 172 extends over the lower plate 170, and the gap between the lower plate 170 and the
20 middle plate 172 provides a lower plenum 174 into which a first process gas can flow from a first process gas supply 146a. This first process gas can then flow through a first plurality of apertures 170a into the chamber 101.

An upper plate 176 can extends over the middle plate 170, and the gap between the middle plate 172 and the upper plate 176 provides an upper plenum 176 into which a
25 second process gas can flow from a second process gas supply 146b. The upper plate can be provided by the dielectric window 108, e.g., a quartz window.

Either the lower plate 170 or the middle plate 172, or both, can include annular
projections 170c that extend axially from the main body of respective plate through the lower plenum 174. A plurality of apertures 170d are formed through the annular
30 projections 170c, and the apertures 170b, 170d, 172a are aligned such that the second process gas can then flow from the upper plenum 178 through the apertures into the chamber 101. As such, the first and second processes gasses do not mix until inside the chamber 101.

Referring to FIG. 5B, in some implementations, the lower plenum 174, the upper plenum 178, or both are connected to a pump 179 that draws the first or second process gas through the respective plenum 174 or 178. This generates a cross-flow of gas through the plenum; a portion of the gas will escape through the apertures into the chamber 101.

5 The process gas distributor 140 can also include a gas distribution ring 150 that surrounds the workpiece support 102. Referring to FIGS. 1A and 6A, the gas distribution ring 150 can include a channel 152 having an inner wall 154 that provides a liner for the chamber 101. The gas distribution ring 150 receives process gas from the process gas supply 146. A plurality of apertures 156, e.g., six to one-hundred apertures, are formed
10 radially through the inner wall 154. The apertures 156 can be arranged with uniform angular spacing around the axis of symmetry 114a, thus providing angularly uniform gas flow into the chamber 101. In some implementations, the apertures 156 all have the same size and shape. In some implementations, the apertures 156 are positioned below a plane defined by the top surface 102a of the workpiece support 102 on which the workpiece will
15 rest. In some implementations, no gas distribution plate is used; the process gas distributor 140 only injects gas from the side walls of the chamber 140. The gas distribution ring 150 and liner can be made from aluminum (e.g., anodized aluminum) or a ceramic material.

Referring to FIG. 6B, in some implementations, the gas distribution ring 150 is divided into two radial arcs 150a, 150b. A first channel 152a in the first radial arc 150a is
20 connected to the process gas source 146. A second channel 152b in the second arc 150b is connected to a vacuum pump 158. The first channel 152a and the second channel 152b can be separated by a barrier 152c. Thus the process gas must exit from the first channel 152a into the chamber 101 before being drawn into the second channel 152b. The two radial
25 arcs 150a, 150b can have substantially the same arc length, and are positioned on opposite sides of the axis of symmetry 114a.

The apertures 156 can be positioned slightly above a plane defined by the top surface 102a of the workpiece support 102 on which the workpiece will rest. The process gas emerges from the apertures 156a in the first radial arc 150a and is drawn into the apertures 156b in the second radial arc 150b, thus creating a cross-flow of the process gas across the
30 workpiece 10 on the workpiece support 102.

The microwave antenna 114 is depicted in detail in FIGS. 1B through 4, and includes an antenna floor 160, an antenna ceiling 162, and a pair parallel spiral waveguide side walls 164, 166 extending between the floor 160 and the ceiling 162. The pair of parallel spiral waveguide side walls 164, 166 form a pair of parallel spiral waveguide

cavities 168, 169. In the illustrated embodiment, the pair of parallel spiral waveguide cavities 168, 169 form spirals of Archimedes, in which the radius of each spiral increases with the angle of rotation.

Small slots 175, or openings through the antenna floor 160, serve as microwave radiation ports and are disposed at locations periodically spaced along the length of each spiral waveguide cavity 168, 169. The slots 175 may be of any suitable shape and have an opening size, in one embodiment, a small fraction (e.g., one tenth or less) of a wavelength of the microwave generator 132. In one embodiment, the distance S between neighboring slots 175 along the length of each spiral conduit 168, 169 is a fraction (e.g., about one-half) of a wavelength of the microwave source 132. Microwave energy radiates through the slots 175 into the chamber 100.

A pair of feed openings 180, 182 in the ceiling 162 are disposed on opposing sides of the axis of symmetry 114a and provide respective paths for microwave energy to be fed into respective peripheral (radially outward) open ends 168a, 169a of the spiral waveguide cavities 168, 169. The peripheral open ends 168a, 169a are displaced from one another by an angle of 180 degrees along the periphery of the microwave antenna 114. Likewise, the pair of feed openings 180, 182 are displaced from one another by an angle of 180 degrees along the periphery of the microwave antenna 114.

A distributor waveguide 200 depicted in FIGS. 3 and 4 overlies the ceiling 162 and distributes microwave energy from the axial waveguide 116 to the pair of feed openings 180, 182. The distributor waveguide 200 includes a waveguide top 202 overlying and facing the ceiling 162 and a pair of slanted end walls 204, 206 extending between the waveguide top 202 and the ceiling 162. The pair of slanted end walls 204, 206 reflect microwave energy flowing radially within the distributor waveguide 200 to flow axially into the feed openings 180, 182 respectively. A first slanted reflector surface 184 in registration with the feed opening 180 is disposed at an angle (e.g., 45 degrees) relative to the axis of symmetry 114a. A second slanted reflector surface 186 in registration with the feed opening 182 is disposed at an angle (e.g., 45 degrees) relative to the axis of symmetry 114a. The first and second slanted reflector surfaces 184, 186 reflect microwave energy flowing axially from the feed openings 180, 182 to flow azimuthally through the spiral waveguide cavities 168, 169 respectively. In one embodiment, the length of each of the slanted surfaces 184, 186, 204, 206 along the direction of wave propagation is one-quarter wavelength of the microwave generator 132. The slanted surfaces 184, 186, 204, 206 may be referred to as reflective surfaces.

Referring to FIG. 3, the distributor waveguide 200 has a length L corresponding to the diameter of the chamber 100, and a width W of several inches, in one embodiment. Axial flat side walls 200-1, 200-2 along the length L enclose the interior of the distributor waveguide 200. The height of the side walls 200-1, 200-2 corresponds to the distance
5 between the ceiling 162 and the waveguide top 202. In one embodiment, this distance may be on the order one or a few inches. Optionally, plural microwave stub tuners 300 are placed at periodic locations along the length of the distributor waveguide 200.

An advantage of the embodiments of FIGS. 1B-4 is that microwave energy is uniformly distributed along the lengths of each spiral waveguide cavity 168, 169, so as to
10 radiate in uniformly distributed intervals corresponding to the periodic locations of the slots 175. A further advantage is that power distribution among the pair of spiral waveguide cavities 168, 169 can be balanced by adjustment of the plural stub tuners 300.

Deposition of Diamond or Graphene

15 The plasma reactor 100 can be employed to perform deposition of a carbon compound, for example a carbon allotrope, e.g., diamond or graphene. In one example, the workpiece 111 includes a patterned dielectric layer (e.g., silicon oxide) onto which a film of the carbon allotrope is to be deposited. For example, a possible application is to use a thin graphene layer to replace the tungsten layer in bitlines because the resistance of thin
20 metal layer increases significantly as metal thickness drops, whereas a thin graphene layer can still show high electrical mobility.

In a process for deposition of the carbon allotrope, a feedstock gas is supplied to the chamber 100 by a process gas distributor 140. The feedstock gas includes at least a hydrocarbon compound, e.g., CH_4 , C_2H_2 , C_2H_4 , or C_3H_6 , etc.

25 An inert gas, e.g., argon or helium, can also be supplied to the chamber 100. The inert gas can be used to dilute the feedstock gas; this can increase plasma density. The gas supply 146 can establish a total pressure (feedstock and inert gas) of 20mTorr to 20Torr. The ratio of inert gas to feedstock gas can range from 1:20 to 20:1, e.g., 20:1 to 1:1.

30 The inert gas can be mixed with the feedstock gas before being delivered into the chamber 100, or the inert gas could be delivered by separate nozzles and mix in the chamber. In some implementations, the inert gas is supplied through the gas distribution plate 142 and the feedstock gas is supplied through the gas distribution ring 150. In some implementations, the inert gas is supplied through the gas distribution ring 150 and the feedstock gas is supplied through the gas distribution plate 150.

The microwave source 132 supplies microwave power at a frequency of 915 MHz to 2.45 GHz, e.g., 2.45 GHz. The microwave source 132 can apply 2 kW to 15 kW, e.g., 15 kW, of continuous power, or 8 kW to 50 kW, e.g., 50 kW, of pulsing power. The pulses of the pulsing power have a frequency of 10 Hz to 2500 Hz and duty cycle of 10% to 100%,
5 e.g., 50%.

Application of the microwave power at appropriate frequency and power will ignite plasma in the chamber 100. The mere presence of the plasma will generate some carbon ions and radicals (as well as ions and radicals of the inert gas), which can be deposited on the workpiece to grow the layer of carbon compound. A microwave plasma can generate a
10 high density of hydrogen radicals, which can etch away loose connected hydrocarbons and sp² carbon to favor of high percentage of sp³ diamond phase growth. For diamond growth, diamond seeds can be prepared on surface before the deposition process in order to facilitate growth from seeds.

Without being limited to any particular theory, a microwave plasma generates a high
15 density of hydrogen radicals, which can etch away any amorphous carbon phase material, leaving a higher quality carbon allotrope at a lower process temperature.

This deposition process can be carried out with the workpiece at a relatively low temperature, e.g., 25-800° C. Consequently, the pedestal 102 supporting the workpiece 10 need not to be heated. In some implementations, the pedestal 102 is cooled, e.g., by the
20 coolant flowing through passages 103c. In some implementations, a coolant gas, e.g., helium, can flow between the pedestal 102 and the backside of the workpiece 10 to improve heat transfer between the workpiece 10 and the pedestal 102. The workpiece 10 can be electrostatically clamped to the pedestal 102, e.g., by application of a chucking voltage to an electrode embedded in the pedestal.

25 The deposition process can proceed, e.g., for 15-1800 seconds.

While particular implementations have been described, other and further implementations may be devised without departing from the basic scope of this disclosure. For example

- Rather than a single workpiece support, the chamber 101 can include
30 multiple supports so that multiple workpieces can be processed simultaneously.
- Although the reactor is described as including a gas distribution plate, in some implementations the gas distribution plate is omitted; process gas can be supplied solely through the gas distribution ring 150.

- Instead of being incorporated into the ceiling, the gas distribution plate could hang below the ceiling as a separate showerhead.

The scope of the invention is determined by the claims that follow.

CLAIMS

1. A plasma reactor for processing a workpiece comprising:
 - a chamber having a dielectric window;
 - a workpiece support to hold a workpiece in the chamber;
 - a rotary coupling comprising a stationary stage configured to be coupled to a microwave source and a rotatable stage having an axis of rotation;
 - a microwave antenna overlying the dielectric window of the chamber, the microwave antenna including at least one conduit coupled to the rotatable stage;
 - a rotary actuator to rotate the microwave antenna;
 - a process gas supply; and
 - a process gas distributor including a gas distribution ring surrounding the workpiece support, the gas distribution ring including a cylindrical chamber liner, the cylindrical chamber liner forming a portion of a chamber wall separated from the workpiece support by a gap and separating a circular conduit from the chamber, the gas distribution ring including a plurality of apertures extending radially through the cylindrical chamber liner to connect the circular conduit to the chamber, wherein
 - the circular conduit comprises a first arc coupled to the process gas supply, a second arc coupled to a vacuum pump, and a barrier preventing direct fluid flow between the first arc and second arc such that process gas flows through the first arc into the chamber and out of the chamber through the second arc, and wherein
 - the plurality of the apertures are positioned in the cylindrical chamber liner radially outward of the workpiece support and open into the chamber below a plane defined by a top surface of the workpiece support.
2. The plasma reactor of claim 1, wherein the plurality of apertures are distributed with uniform angular spacing around the cylindrical chamber liner.
3. The plasma reactor of claim 1, wherein the first arc and the second arc have substantially the same arc length.
4. The plasma reactor of claim 1, comprising a gas distribution plate on a ceiling of the chamber.

5. The plasma reactor of claim 4, wherein the dielectric window provides the gas distribution plate.

6. The plasma reactor of claim 1, wherein the gas distribution ring has between six and one-hundred apertures.