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(54) **INTEGRATED CLUSTER TOOL FOR SELECTIVE AREA DEPOSITION**

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C23C 16/02 (2006.01)
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(Continued)

(52) **U.S. Cl.**
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None
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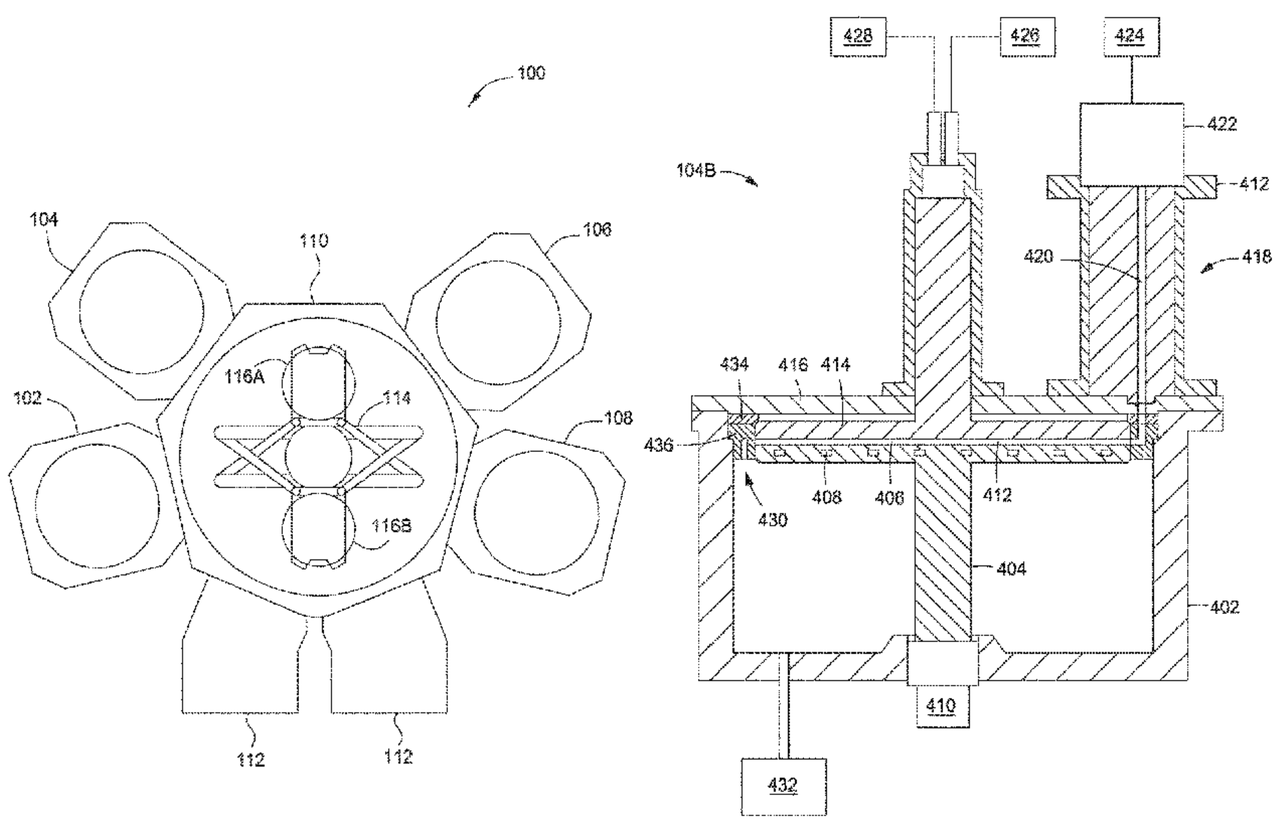
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(57) **ABSTRACT**

Embodiments described herein relate to apparatus and methods for processing a substrate. In one embodiment, a cluster tool apparatus is provided having a transfer chamber and a pre-clean chamber, a self-assembled monolayer (SAM) deposition chamber, an atomic layer deposition (ALD) chamber, and a post-processing chamber disposed about the transfer chamber. A substrate may be processed by the cluster tool and transferred between the pre-clean chamber, the SAM deposition chamber, the ALD chamber, and the post-processing chamber. Transfer of the substrate between each of the chambers may be facilitated by the transfer chamber which houses a transfer robot.

21 Claims, 8 Drawing Sheets



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C23C 16/54	(2006.01)
C23C 16/56	(2006.01)
H01L 21/02	(2006.01)
H01J 37/32	(2006.01)
H01L 21/677	(2006.01)
H01L 21/8234	(2006.01)

(52) **U.S. Cl.**

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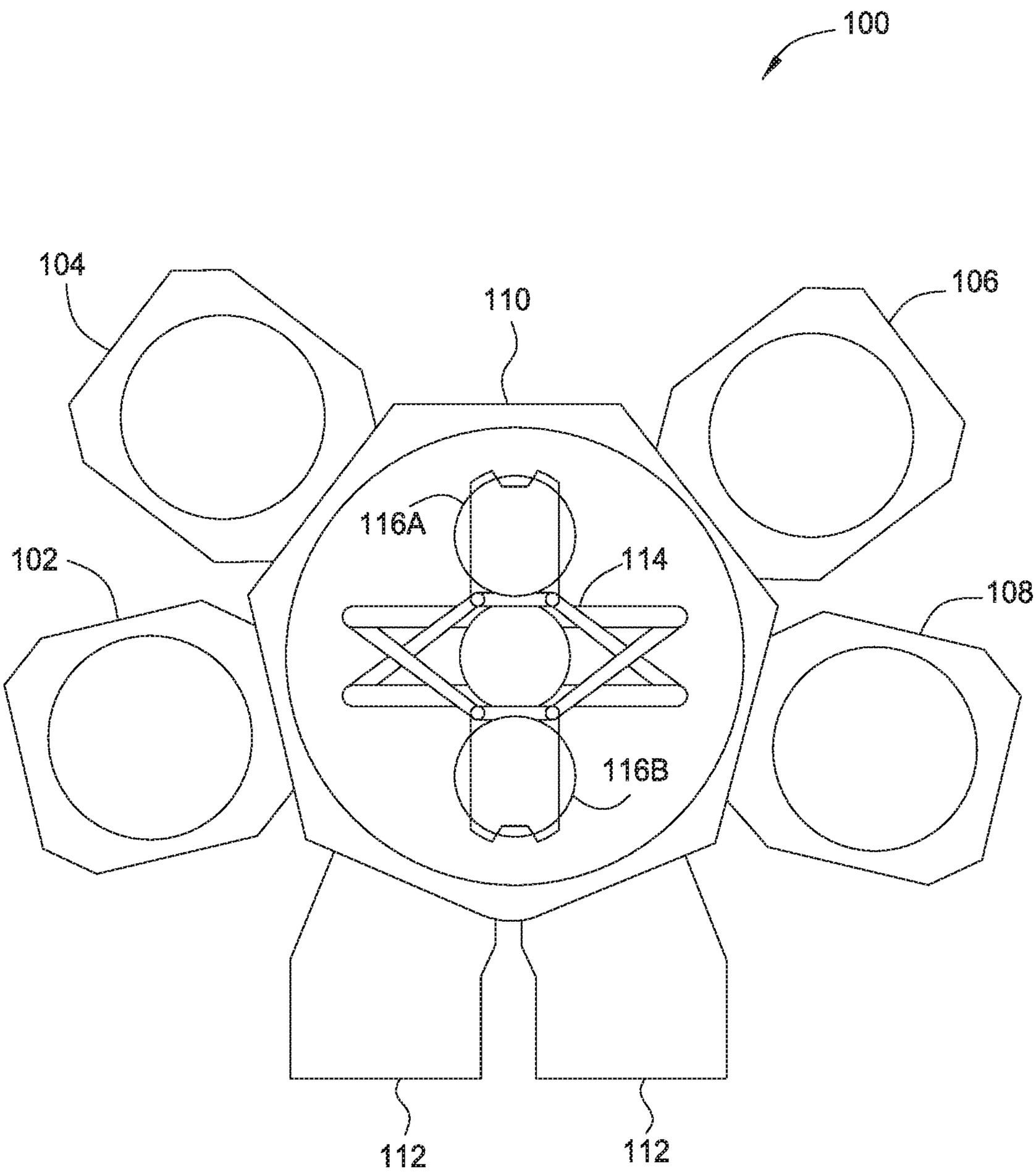


FIG. 1

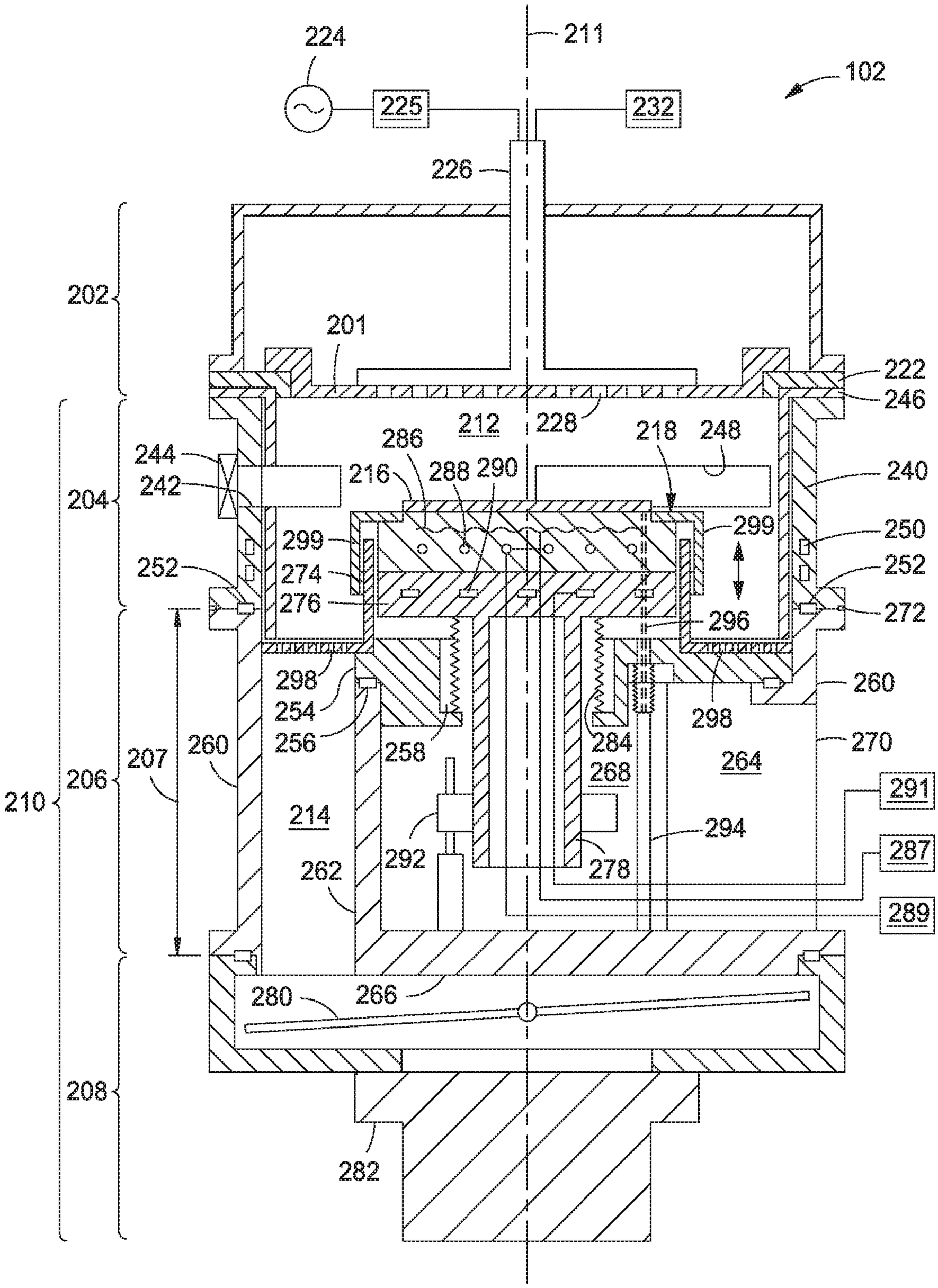

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FIG. 2

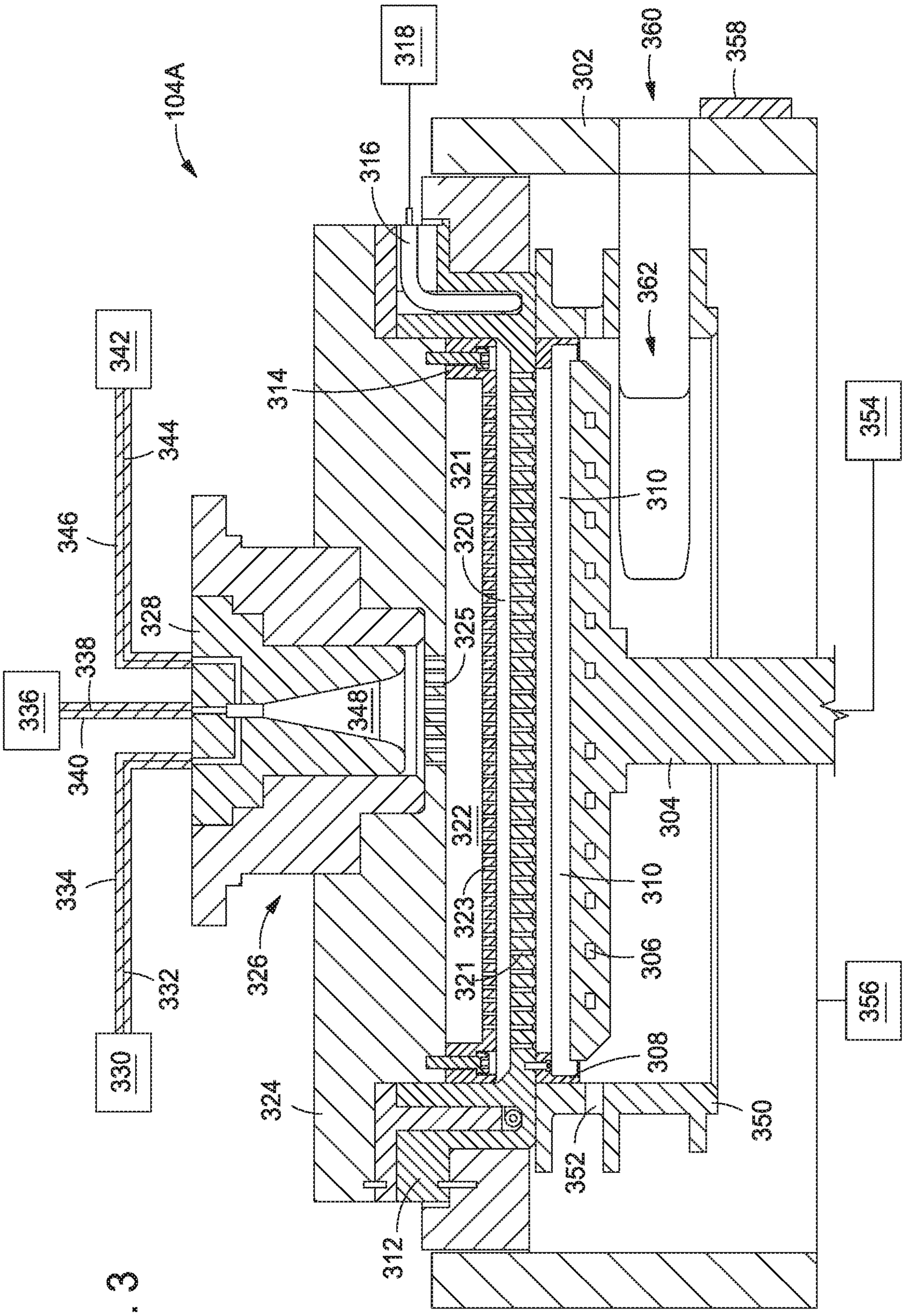

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FIG. 3

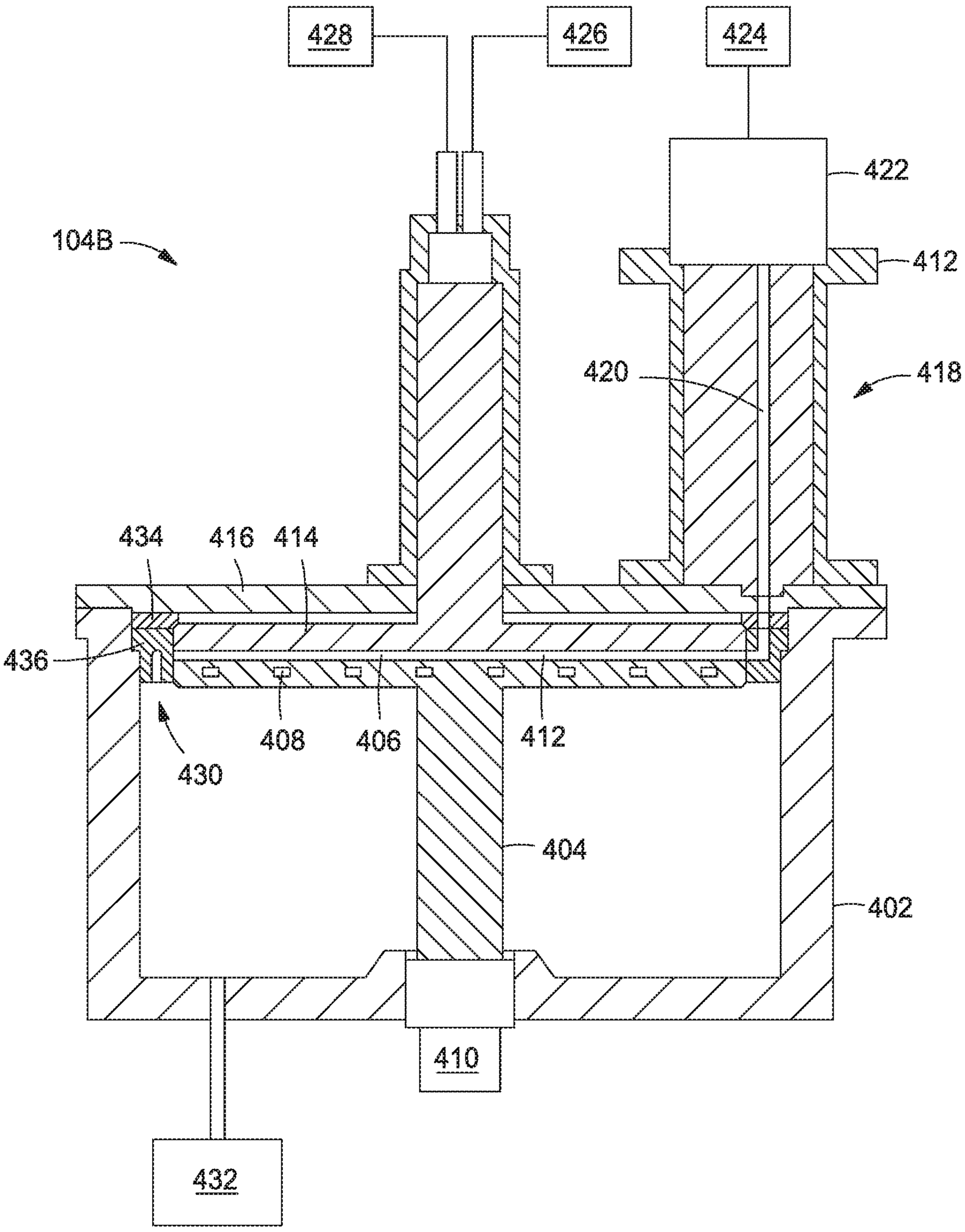

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FIG. 4

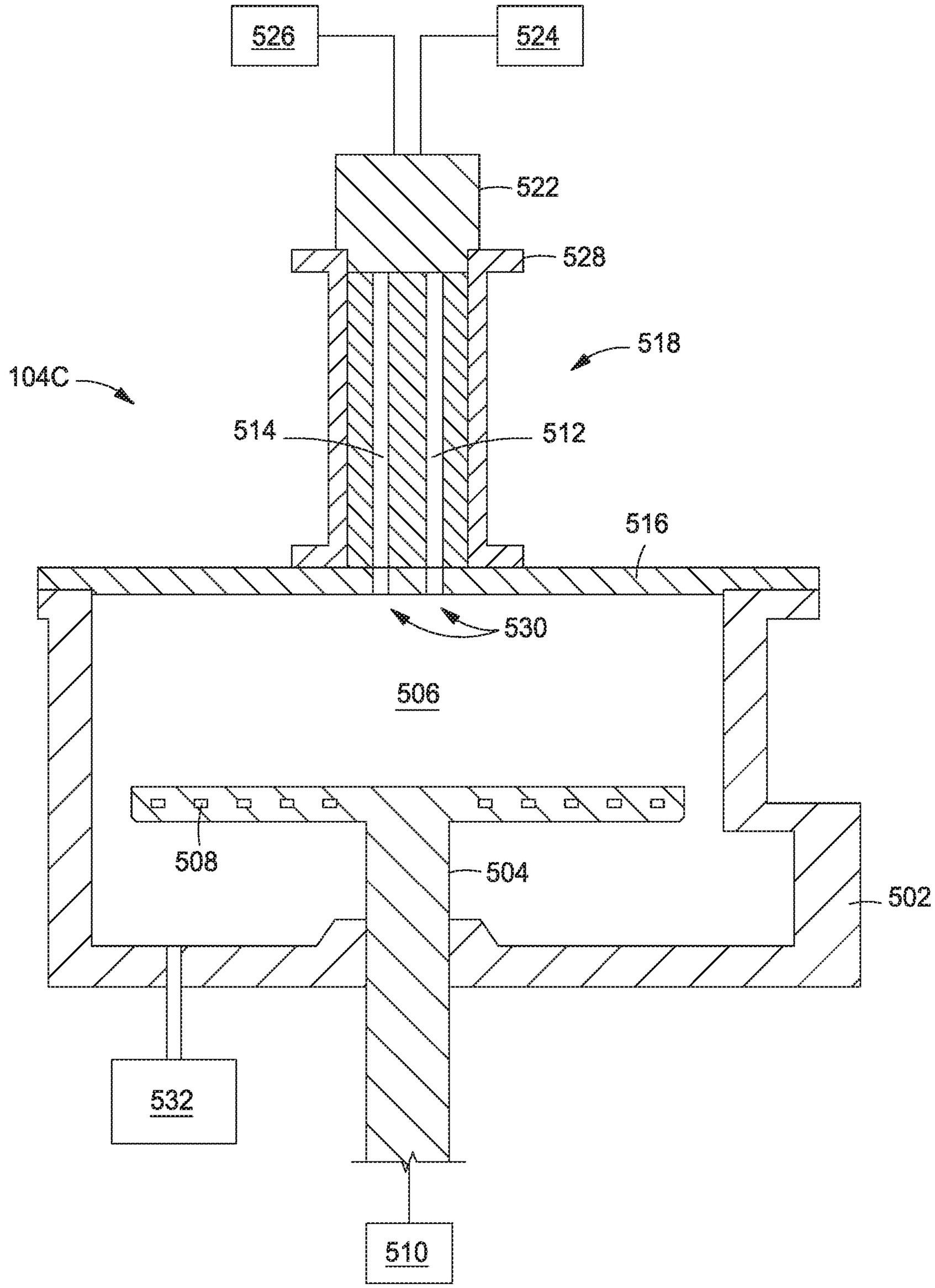


FIG. 5

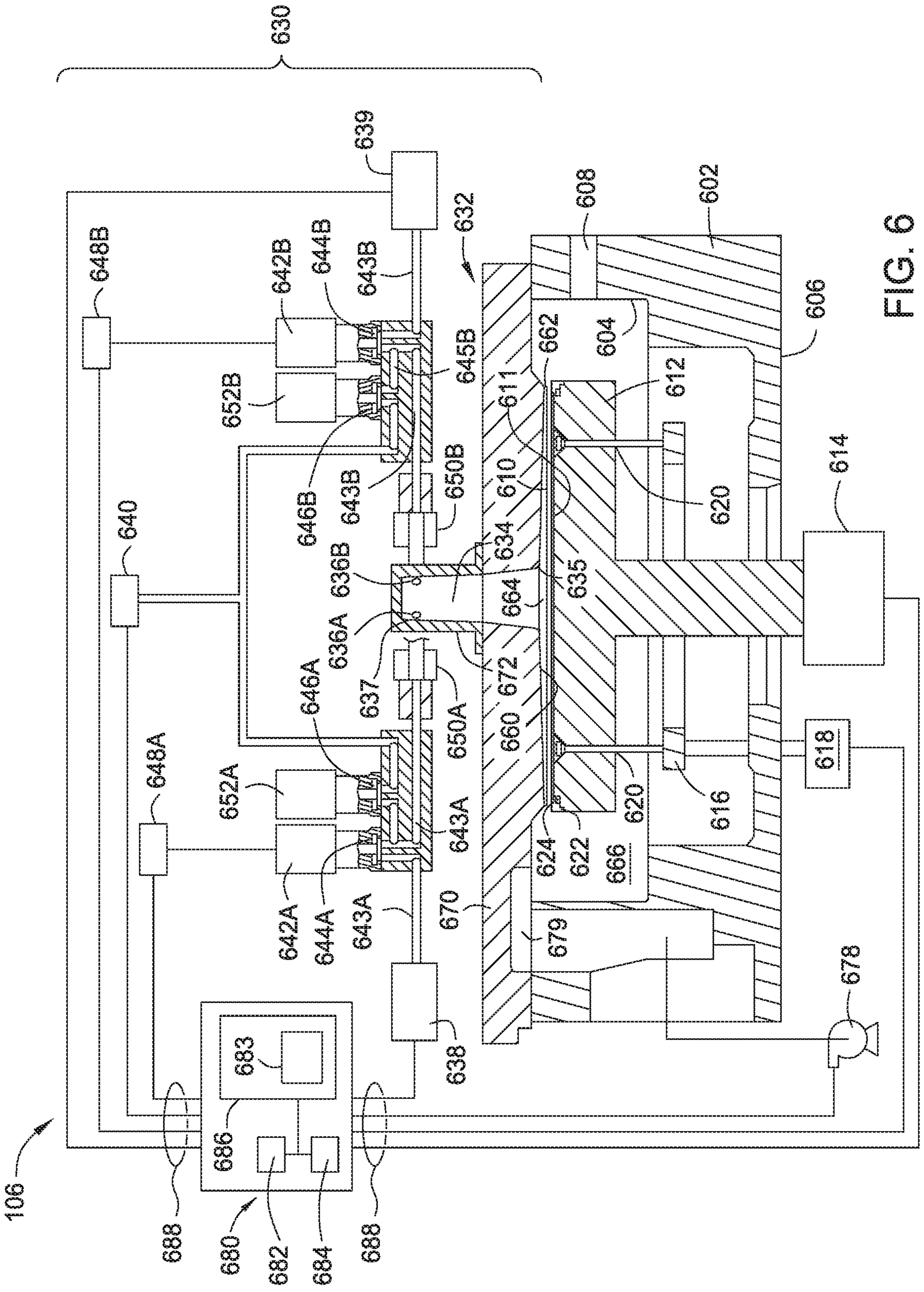

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FIG. 6

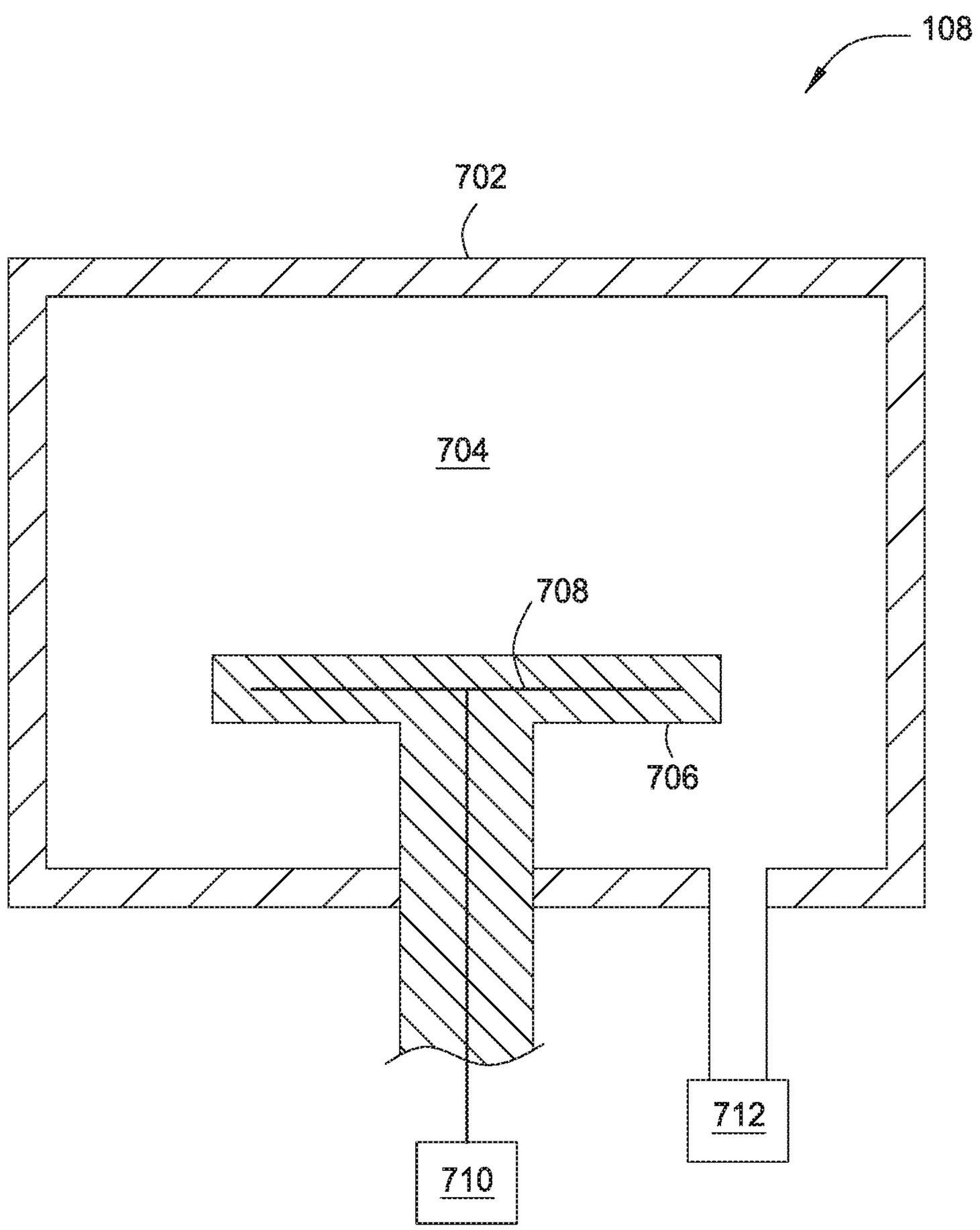


FIG. 7

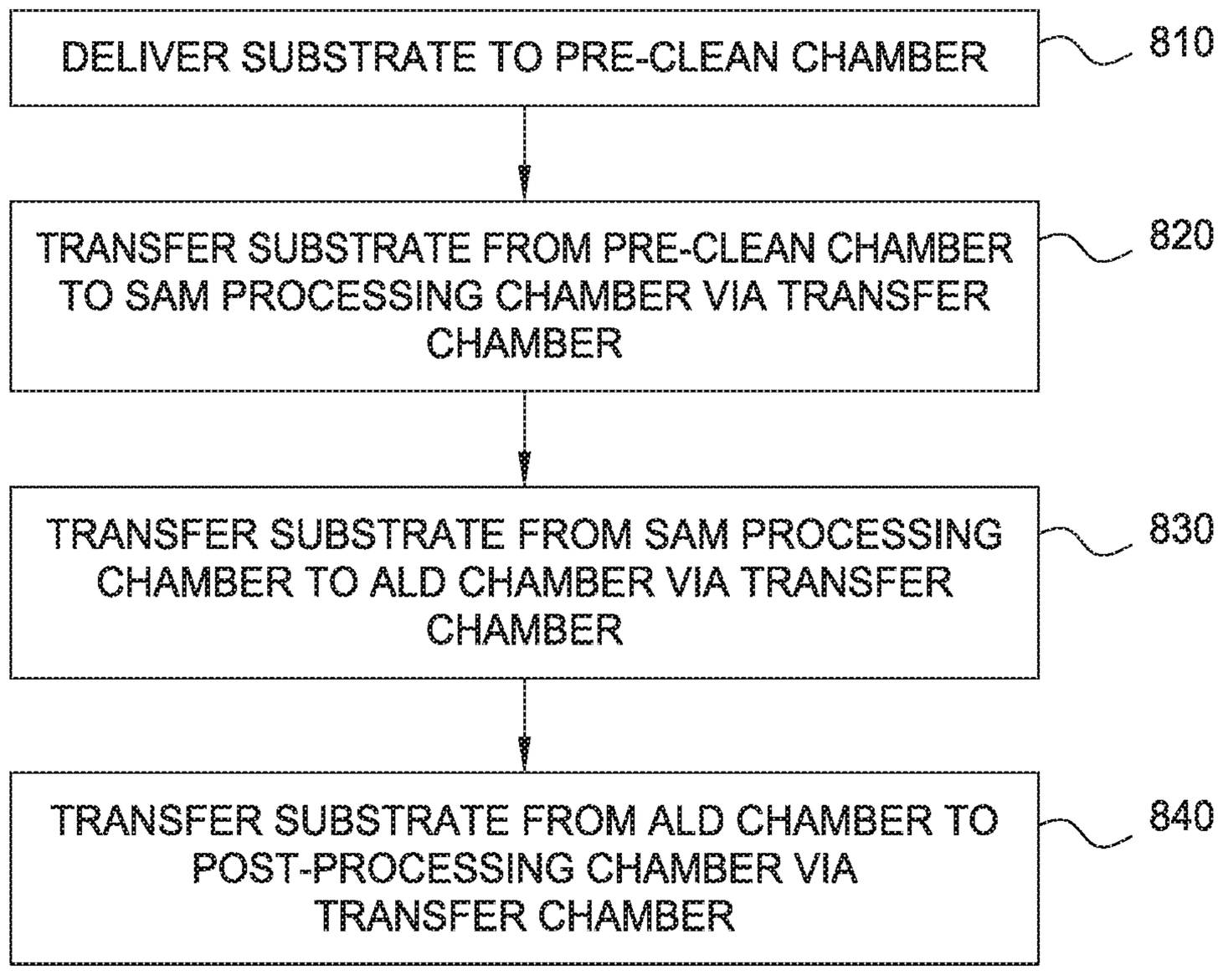

DELIVER SUBSTRATE TO PRE-CLEAN CHAMBER
810
TRANSFER SUBSTRATE FROM PRE-CLEAN CHAMBER TO SAM PROCESSING CHAMBER VIA TRANSFER CHAMBER
820
TRANSFER SUBSTRATE FROM SAM PROCESSING CHAMBER TO ALD CHAMBER VIA TRANSFER CHAMBER
830
TRANSFER SUBSTRATE FROM ALD CHAMBER TO POST-PROCESSING CHAMBER VIA TRANSFER CHAMBER
840

FIG. 8

INTEGRATED CLUSTER TOOL FOR SELECTIVE AREA DEPOSITION

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application of U.S. patent application Ser. No. 15/173,356, filed Jun. 3, 2016, which is incorporated by reference herein.

BACKGROUND

Field

Embodiments of the present disclosure generally relate to apparatus for processing substrates. More specifically, embodiments described herein relate to an integrated cluster tool for selective area deposition.

Description of the Related Art

Reliably producing sub-half micron and smaller features is one of the key technology challenges for next generation very large scale integration (VLSI) and ultra large scale integration (ULSI) of semiconductor devices. However, as the limits of circuit technology are pushed, the shrinking dimensions of VLSI and ULSI technology have placed additional demands on processing capabilities.

As circuit densities increase for next generation devices, the widths of interconnects, such as vias, trenches, contacts, gate structures and other features, as well as the dielectric materials therebetween, decrease to 45 nm and 32 nm dimensions and beyond. In order to enable the fabrication of next generation devices and structures, three dimensional (3D) stacking of features in semiconductor chips is often utilized. In particular, fin field effect transistors (FinFETs) are often utilized to form three dimensional (3D) structures in semiconductor chips. By arranging transistors in three dimensions instead of conventional two dimensions, multiple transistors may be placed in the integrated circuits (ICs) very close to each other. As circuit densities and stacking increase, the ability to selectively deposit subsequent materials on previously deposited materials gains importance.

Self-assembled monolayers (SAMs) may be utilized as a masking material to improve subsequent material deposition selectivity. SAMs are generally surface chemistry dependent and can be formed preferentially on various materials. However, current apparatus for depositing SAMs often suffers from slow deposition rates which undesirably decreases throughput. In addition, SAM apparatus integration with pre and post processing apparatus which provides suitable throughput is lacking in the industry.

Thus, what is needed in the art are improved substrate processing apparatus and methods.

SUMMARY

In one embodiment, a substrate processing apparatus is provided. The apparatus includes a platform having a centrally disposed transfer chamber and a first process chamber coupled to the transfer chamber. The first process chamber is configured to perform an etching process. A second process chamber is coupled to the transfer chamber and the second process chamber is configured to perform a self-assembled monolayer treatment process. A third process chamber is coupled to the transfer chamber and the third process chamber is configured to perform an atomic layer deposition process. A fourth process chamber is coupled to the transfer chamber and the fourth process chamber is configured to perform an anneal process.

In another embodiment, a substrate processing apparatus is provided. The apparatus includes a platform having a centrally disposed transfer chamber and a first process chamber coupled to the transfer chamber. The first process chamber is configured to perform an etching process. A second process chamber is coupled to the transfer chamber adjacent the first process chamber and the second process chamber is configured to perform a self-assembled monolayer treatment process. A third process chamber is coupled to the transfer chamber adjacent the second process chamber and the third process chamber is configured to perform an atomic layer deposition process. A fourth process chamber is coupled to the transfer chamber adjacent the third process chamber and the fourth process chamber is configured to perform an anneal process.

In yet another embodiment, a substrate processing method is provided. The method includes transferring a substrate to a first process chamber and performing an etching process on the substrate in the first process chamber. The substrate is transferred from the first process chamber to a second process chamber via a transfer chamber and a self-assembled monolayer treatment process is performed on the substrate in the second process chamber. The substrate is transferred from the second process chamber to a third process chamber via the transfer chamber and an atomic layer deposition process is performed on the substrate in the third process chamber. The substrate is transferred from the third process chamber to a fourth process chamber via the transfer chamber and an anneal process is performed on the substrate in the fourth process chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only exemplary embodiments and are therefore not to be considered limiting of its scope, may admit to other equally effective embodiments.

FIG. **1** illustrates a schematic, plan view of a cluster tool apparatus according to one embodiment described herein.

FIG. **2** illustrates a schematic, cross-sectional view of a process chamber according to one embodiment described herein.

FIG. **3** illustrates a schematic, cross-sectional view of a process chamber according to one embodiment described herein.

FIG. **4** illustrates a schematic, cross-sectional view of a process chamber according to one embodiment described herein.

FIG. **5** illustrates a schematic, cross-sectional view of a process chamber according to one embodiment described herein.

FIG. **6** illustrates a schematic, cross-sectional view of a process chamber according to one embodiment described herein.

FIG. **7** illustrates a schematic, cross-sectional view of a process chamber according to one embodiment described herein.

FIG. **8** illustrates operations of a method for processing a substrate according to one embodiment described herein.

To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation.

DETAILED DESCRIPTION

Embodiments described herein relate to apparatus and methods for processing a substrate. In one embodiment, a cluster tool apparatus is provided having a transfer chamber and a pre-clean chamber, a self-assembled monolayer (SAM) deposition chamber, an atomic layer deposition (ALD) chamber, and a post-processing chamber disposed about the transfer chamber. A substrate may be processed by the cluster tool and transferred between the pre-clean chamber, the SAM deposition chamber, the ALD chamber, and the post-processing chamber. Transfer of the substrate between each of the chambers may be facilitated by the transfer chamber which houses a transfer robot.

As utilized herein, "self-assembled monolayer" (SAM) generally refers to a layer of molecules that are attached (e.g., by a chemical bond) to a surface and that have adopted a preferred orientation with respect to that surface and even with respect to each other. The SAM typically includes an organized layer of amphiphilic molecules in which one end of the molecule, the "head group" shows a specific, reversible affinity for a substrate. Selection of the head group will depend on the application of the SAM, with the type of SAM compounds based on the substrate utilized. Generally, the head group is connected to an alkyl chain in which a tail or "terminal end" can be functionalized, for example, to vary wetting and interfacial properties. The molecules that form the SAM will selectively attach to one material over another material (e.g., metal vs. dielectric) and if of sufficient density, can successfully operation subsequent deposition allowing for selective deposition on materials not coated with the SAM.

FIG. **1** illustrates a schematic, plan view of a cluster tool apparatus **100** according to one embodiment described herein. Examples of suitable apparatus which may be utilized in accordance with the embodiments described herein include the CENTURA® and ENDURA® platforms, both of which are available from Applied Materials, Inc., Santa Clara, Calif. It is contemplated that other suitably configured apparatus from other manufacturers may also be advantageously utilized in accordance with the embodiments described herein. In addition, the PRODUCER® platform, also available from Applied Materials, Inc., Santa Clara, Calif., having dual-chamber capability may be advantageously employed according to the embodiments described herein. In embodiments utilizing the PRODUCER® platform, load lock chambers with bake or anneal capability may be employed as post processing chambers in accordance with the embodiments described hereinafter.

Generally, the apparatus **100** includes a plurality of process chambers **102**, **104**, **106**, **108**, a transfer chamber **110**, and load lock chambers **112**. Each of the process chambers **102**, **104**, **106**, **108** are coupled to the transfer chamber **110**. In one embodiment, the process chamber **104** is disposed adjacent the process chamber **102**. In one embodiment, the process chamber **106** is disposed adjacent the process chamber **104**. In one embodiment, the process chamber **108** is disposed adjacent the process chamber **106**. Each process chamber represents, and may be used for, a different stage or phase of substrate processing. In one embodiment, the process chamber **102** is a pre-clean chamber. The process chamber **102** prepares surfaces of a substrate being processed for subsequent processing. In various examples, the process chamber **102** may remove substrate defects which result from air exposure, remove native oxide layers, and/or remove sacrificial layers disposed on a surface of the substrate to be treated by SAM or ALD processing. In another example, the process chamber **102** is utilized for substrate surface functionalization. In this example, surface terminal groups may be modified to enable, assist, or prevent the formation of a SAM on the substrate, depending upon the desired implementation.

Specific examples of surface treatment which may be performed by the process chamber **102** include metal oxide removal via plasma treatment, surface hydroxyl functionalization using H_2/O_2 plasma treatment or water vapor exposure, and/or oxide removal using a SICONI® process or a FRONTIER process. The SICONI® process and FRONTIER process are available from Applied Materials, Inc., Santa Clara, Calif. It is contemplated that other similar treatment processes may be utilized in accordance with the embodiments described herein. More specifically, the process chamber **102** is utilized to enable selective area SAM adsorption. For example, an octadecyltrichlorosilane (ODTCS) SAM may bond to a dielectric or metal oxide material preferentially to a metal or Si—H terminated surface, assuming desirable conditions are present. The process chamber **102** is utilized to remove the metal oxide or native oxide to form an exposed metal surface of Si—H terminated surface which generally prohibits SAM adsorption.

In another embodiment, the process chamber **102** may be utilized as a post-process chamber. The process chamber **102**, which is described in greater detail with regard to FIG. **2**, includes a heated pedestal which is utilized to perform a bake or anneal process. The bake or anneal process may be utilized after the substrate has been processed by other chambers of the apparatus **100**.

In one embodiment, the process chamber **104** is a SAM deposition chamber. The process chamber **104** is configured to enable vapor phase SAM molecules to selectively adsorb to one material of a substrate preferentially to another material of the substrate. The selective adsorption is generally controlled by the reactivity of the SAM molecule headgroup and the surface termination characteristics/functional groups disposed on the substrate surface. For example, a substrate having exposed SiO_2 and Cu materials which are exposed to the same SAM treatment process will result in the SAM molecules selective to metals bonding to the Cu preferentially and substantially no adsorption on the SiO_2 material. The resulting SAM material has a high water contact angle (i.e. greater than about 105°) which indicates the formation of a dense SAM. Thus, the process chamber **104** is utilized to perform SAM deposition processes.

In one embodiment, the process chamber **106** is an ALD chamber. The process chamber **106** is configured to enable deposition on surfaces of the substrate not covered by the SAM materials. For example, ALD materials generally do not form on surfaces which have a water contact angle greater than about 105°, such as greater than about 110°. Accordingly, the ALD process may be selectively deposited on a desired material of the substrate by utilizing the SAM material to improve the selectivity of deposition.

In one embodiment, the process chamber **108** is a post-process chamber, such as an anneal or bake chamber. In another embodiment, the process chamber **108** is a plasma processing chamber. In one example, the process chamber **108** enables SAM material removal from the substrate by

thermal desorption or exposure to a plasma, such as an oxygen and/or hydrogen containing plasma. Alternatively or in combination, the process chamber **108** may be utilized for ALD clean up processes. For example, for an imperfect SAM treatment, some ALD nucleation may occur on defect sites of the substrate which are not covered by SAM materials. The process chamber **108** may be utilized to perform an etch process to etch exposed ALD materials which results in removal of the ALD films grown on the defect sites while only removing a small amount of material from the intended ALD growth location.

The transfer chamber **110**, which enables transfer of the substrate between the process chambers **102**, **104**, **106**, **108**, houses a transfer robot **114** therein. The transfer robot **114** may be a single blade robot or a dual blade robot as illustrated. The dual blade robot **114** has a pair of substrate transport blades **116**A, **116**B attached to distal ends of a pair of extendable arms. The blades **116**A, **116**B are used to support and carry individual substrates between the chambers **102**, **104**, **106**, **108**. The transfer chamber **110** is also maintained under vacuum or an otherwise reduced oxygen environment. Air exposure of the substrate between SAM treatment and ALD treatment is potentially detrimental to the effectiveness of the SAM material for ALD blocking and transferring the substrate between the process chamber **104** and the process chamber **106** in-situ provides for improved processing performance, such as higher deposition selectivity. In addition, it may be desirable to perform cyclic SAM and ALD processes, thus, the transfer chamber enables efficient transfer of substrates between the process chambers **104**, **106** while also improving the processing performance by preventing exposure of the substrate to an ambient air environment.

FIG. **2** illustrates a schematic, cross-sectional view of the process chamber **102** according to one embodiment described herein. The process chamber **102** may be a plasma etch chamber, a plasma treatment chamber, a bake chamber, an anneal chamber, or other suitable vacuum processing chamber.

The process chamber **102** may be assembled from multiple modules. The modular design enables the process chamber **102** to meet various process requirements. As shown in FIG. **2**, the process chamber **102** includes a source module **202**, a process module **204**, a flow module **206**, and an exhaust module **208**. The source module **202**, the process module **204** and the flow module **206** collectively enclose a process region **212**. The process module **204**, the flow module **206**, and the exhaust module **208** may be considered collectively as a chamber module **210** in certain embodiments.

During operation, a substrate **216** may be positioned on a substrate support assembly **218** and exposed to a process environment, such as plasma generated in the process region **212**. Exemplary processes which may be performed in the process chamber **102** include etching, plasma treatment processes, and baking or annealing processes. Vacuum may be maintained in the process region **212** by suction from the exhaust module **208** through evacuation channels **214** defined by the flow module **206**.

The process region **212** and the evacuation channels **214** are substantially symmetrically about a central axis **211** to provide symmetrical electrical current, gas flow, and thermal flow to establish uniform process conditions.

In one embodiment, the source module **202** is a capacitively coupled plasma source configured to generate one or more plasmas, at least one of which may be considered a remote plasma and one of which may be considered a direct plasma. The source module **202** may include a plate stack **201**, which may function as an electrode (i.e. anode), isolated from and supported by the process module **204** by an isolator **222**. The plate stack **201** may include various showerheads, diffusers, and screen/blocker plates arranged in a stacked orientation. The plate stack **201** may be connected to a gas source **232** through a gas inlet tube **226**. The plate stack **201** and the gas inlet tube **226** may be all fabricated from a radio frequency (RF) conductive material, such as aluminum or stainless steel. The plate stack **201** may be coupled to a RF power source **224** via the conductive gas inlet tube **226**. An RF matching network **225** may also be coupled to the RF power source **224**. The conductive gas inlet tube **226** may be coaxial with the central axis **211** of the process chamber **102** so that both RF power and processing gases are symmetrically provided.

Even though a capacitive plasma source is described above, the source module **202** may be any suitable gas/plasma source according to a process requirement. For example, the source module **202** may be an inductive coupled plasma source, a remote plasma source, or a microwave plasma source.

The process module **204** is coupled to the source module **202**. The process module **204** may include a chamber body **240** enclosing the process region **212**. The chamber body **240** may be fabricated from a conductive material resistive to processing environments, such as aluminum or stainless steel. The substrate support assembly **218** may be centrally disposed within the chamber body **240** and positioned to support the substrate **216** in the process region **212** symmetrically about the central axis **211**.

A slit valve opening **242** is formed through the chamber body **240** to allow passages of the substrate **216**. A slit valve **244** is disposed outside the chamber body **240** to selectively open and close the slit valve opening **242**.

In one embodiment, an upper liner assembly **246** is disposed within an upper portion of the chamber body **240** shielding the chamber body **240** from the process environment. The upper liner assembly **246** includes an opening **248** corresponding to the slit valve opening **242** formed in the chamber body **240**. In one embodiment, the upper liner assembly **246** includes two or more openings **248** formed symmetrically about the central axis **211** to compensate for the asymmetry of the chamber body **240** caused by the slit valve opening **242**, thus creating symmetry in the process region **212** within the process chamber **102**. For example, the upper liner assembly **246** is a cylindrical wall having three identical openings **248** formed 120 degrees apart from one another. The upper liner assembly **246** may be constructed from a conductive, process compatible material, such as aluminum, stainless steel, and/or yttria (e.g., yttria coated aluminum).

In one embodiment, cooling channels **250** are formed in the chamber body **240** to provide temperature control to the chamber body **240** and the upper liner assembly **246** to enhance the thermal symmetry within the process chamber **102** and symmetry of the plasma provided in the process region **212**.

The flow module **206** is attached to the process module **204**. The flow module **206** provides flow paths between the process region **212** defined in the process module **204** and the exhaust module **208**. The flow module **206** also provides an interface between the substrate support assembly **218** and the atmospheric environment exterior to the process chamber **102**.

The flow module **206** has a height **207**. The height **207** is selected according to amount of vertical movement or

degree of variable volume dictated by the process requirements. Accordingly, when building a process chamber for a particular process, a flow module with a suitable height may be selected to meet the process requirements. The flow module may be swapped for another flow module with a different height when configuring the process chamber for a different process.

The flow module **206** includes an outer wall **260**, an inner wall **262**, two or more pairs of radial walls **264** connecting between the inner wall **262** and the outer wall **260**, and a bottom wall **266** attached to the inner wall **262** and the two or more pairs of radial walls **264**. The outer wall **260** includes two or more through holes **270** formed between each pair of radial walls **264**. A chassis **254** is sealably disposed over the inner wall **262** and the two or more pairs of radial walls **264**. The through holes **270** connect an atmosphere volume **268** defined by the inner wall **262** with the exterior environment, thus accommodating utility connections, such as electrical connections, gas connections, and cooling fluid connections. The chassis **254** includes a central opening **258** for receiving the substrate support assembly **218**.

The outer wall **260** of the flow module **206** is shaped to match the chamber body **240** of the process module **204**. In one embodiment, the outer wall **260** includes a flange which corresponds to a flange on the chamber body **240**. A plurality of bolts may be used to secure the flanges to couple the flow module **206** to the process module **204**. In one embodiment, a seal **252** is disposed between the flange of the chamber body **240** and the flange of the outer wall **260** to form a vacuum seal therebetween. The seal **252** may be an o-ring or other type of seal. In one embodiment, a RF grounding gasket **272** is disposed between the flow module **206** and the process module **204** to provide a solid contact therebetween for a uniform and symmetric RF ground return path.

The inner wall **262**, bottom wall **266**, radial walls **264** and the chassis **254** divide the volume inside the outer wall **260** into the evacuation channels **214** and the atmosphere volume **268**. The evacuation channels **214** connect with the process region **212** of the process module **204**. A seal **256** is disposed in the grooves **254***b*, **264***b* to provide vacuum seal between the evacuation channels **214** and the atmosphere volume **268**. The seal **256** may be an o-ring or other type of seal, such as an elastomeric seal.

The outer wall **260** and the inner wall **262** may be cylindrical walls concentrically arranged. When assembled, a central axis of the outer wall **260** and the inner wall **262** coincides with the central axis **211** of the process chamber **102**. The two or more pairs of radial walls **264** are arranged between the inner wall **262** and the outer wall **260** to divide the space therebetween into the evacuation channels **214** and through holes **270**. In one embodiment, the two or more pairs of radial walls **264** are arranged so that the evacuation channels **214** are symmetrical about the central axis **211**. The flow module **206** includes three pairs of radial walls **264** disposed at 120 degrees apart from one another forming three evacuation channels **214** symmetrical to the central axis **211**. The symmetrical arrangement of the evacuation channels **214** promotes symmetrical removal of gases from the process region **212**, resulting in symmetrical flow of gases across the substrate **216**. In addition, the symmetrical positioning of the evacuation channels **214** and radial walls **264** promotes symmetry in the thermal distribution and electrical conductance in the process chamber **102**.

The exhaust module **208** includes a symmetric flow valve **280** and a vacuum pump **282** attached to the symmetric flow valve **280**. The vacuum pump **282** may be a symmetric turbo molecular pump in certain embodiments. The symmetric flow valve **280** connects to the evacuation channels **214** to provide symmetric and uniform flow in the process chamber **102**.

The substrate support assembly **218** is positioned along the central axis **211** to position the substrate **216** symmetrically about the central axis **211**. The substrate support assembly **218** is supported by the chassis **254**. The substrate support assembly **218** includes a support plate **274**, a base plate **276** that are disposed in the process region **212**, and a hollow shaft **278** disposed through the central opening **258** of the chassis **254**. A bellows **284** connects between the base plate **276** and the chassis **254** and surrounds the hollow shaft **278**. The bellows **284** allows the substrate support assembly **218** to move vertically along the central axis **211** and provides vacuum seal between the atmosphere volume **268** in the flow module **206** and the process region **212** in the process module **204**.

The support plate **274** may be an electrostatic chuck (ESC) having a chucking electrode **286**. The chucking electrode **286** may be a monopolar 4-zone ESC, a bipolar 4-zone ESC, or a high temperature ESC. It is contemplated that the bipolar ESC may not require exposure to plasma for RF grounding during de-chucking of the substrate **216**. The 4-zone ESCs may utilize four concentric heating zones (i.e. a heating element **288**) to modulate center to edge heating profiles of substrates disposed on the chucking electrode **286** during processing to provide for improved temperature uniformity. The high temperature ESC may be suitable for utilization with temperatures up to about 600° C. In one embodiment, temperatures generated by the chucking electrode **286** may be suitable for sublimation of byproducts of substrate layers etched to maintain high material selectivity.

The support plate **274** may also include the heating element **288** for heating the substrate **216** during processing. The base plate **276** includes cooling channels **290** formed therein. The chucking electrode **286** may be connected to a bias power source **287** through the hollow shaft **278**, the atmosphere volume **268**, and one of the through holes **270**. The heating element **288** is connected to a heating power source **289** through the hollow shaft **278**, the atmosphere volume **268**, and one of the through holes **270**. The cooling channels **290** are connected to a cooling fluid source **291** through the hollow shaft **278**, the atmosphere volume **268**, and one of the through holes **170**. In one embodiment, the support plate **274** is configured to heat the substrate **216** to a temperature greater than the vaporization temperature of a SAM material disposed on the substrate **216**.

In one embodiment, an actuator assembly **292** is coupled to the hollow shaft **278** to move the substrate support assembly **218** vertically. The actuator assembly **292** may enable the substrate support assembly **218** to move within the process region **212** and change a processing position of the substrate **216**. For example, the actuator assembly **292** positions the substrate support assembly **218** a distance of between about 0.5 inches and about 6 inches from the plate stack **201**. The reduced distance between the plate stack **201** and the substrate support assembly **218**, when compared to conventional plasma processing apparatus, provides an increased capactively coupled plasma (CCP) generation window in a low pressure regime, such as less than 20 mTorr, for example about 1 mTorr. Accordingly, a gap between the RF electrode (i.e. the plate stack **201**) and RF ground may be increased to enable low pressure CCP discharge by reducing the breakdown voltage of the CCP. In embodiments generating a CCP, the substrate support assembly **218** may also function as an electrode (i.e. cath-

ode) or ground via the grounding gasket **272**, depending upon the desired implementation. The actuator assembly **292** is disposed in the atmosphere volume **268**. Lift pin actuators **294** are disposed in the atmosphere volume **268** to move lift pins **296**.

A plasma screen **298** is disposed between the process region **212** and the evacuation channels **214** to confine the plasma within the process region **212**. A substrate support liner **299** is disposed around the substrate support assembly **218** to shield the substrate support assembly **218** from the process chemistry.

During operation, one or more processing gases from the gas source **232** may enter the process region **212** through the plate stack **201**. Suitable process gases for utilization in a low pressure regime include H_2, He, Ar, O_2, NF_3, NH_3, N_2, N_2O, H_2O, SiF_4, SiH_4, $SiCl_4$, and various fluorocarbon precursors. An RF power may be applied between the plate stack **201** and the substrate support assembly **218** to ignite and maintain a direct plasma (ion generation) in the process region **212**. The RF power may also be applied to the plate stack **201** via the gas inlet tube **226** and a remote plasma (radical generation) may be generated within the plate stack **201**. Synchronized or step RF pulsing may be utilized to control the ion energy and radical density. A zero DC bias may be utilized and may provide for reduced ion bombardment which may enable reduced particle generation. Multiple RF frequencies (i.e. 400 kHz, 2 MHz, 13.56 MHz, 27 MHz, 40 MHz, 60 MHz) may be utilized to modulate plasma density and ion energy. Tailored waveform and phase angle modulation may be utilized to control ion energy distribution. It is contemplated that the RF power source **224** and RF matching network **225** may be configured to operation at powers as low as about 5 W while maintaining stable plasma discharge.

The substrate **216** disposed on the substrate support assembly **218** may be processed by both the direct plasma and the remote plasma. For example, the direct plasma generated in the process region **212** is utilized to modify materials on the surface of the substrate **216** by exposing the material to ions. Radicals generated from the remote plasma in the plate stack **201** are extracted from the remote plasma to remove the modified materials with high selectivity to a non-modified material on the substrate **216**. Accordingly, a highly selective material removal process may be achieved.

The one or more processing gases utilized to form the plasmas may be continuously supplied to the process region **212** or the plate stack **201** and the vacuum pump **282** operates through the symmetric flow valve **280** and the flow module **206** to generate a symmetric and uniform plasma profile adjacent the substrate **216**. By defining the process region **212** and the evacuation channels **214** in separate modules, embodiments of the present disclosure provide uniform and symmetric process environment with simplified chamber structure, thus, reducing fabrication costs and enabling damage free plasma etching processes with high degrees of material selectivity.

FIG. **3** illustrates a schematic, cross-sectional view of the process chamber **104** according to one embodiment described herein. Embodiments of FIG. **3** illustrate one implementation of a process chamber **104**A. The process chamber **104**A includes a chamber body **302** which defines a process volume **310**. A substrate support **304** is disposed in the process volume **310** and a showerhead **312** is disposed opposite the substrate support **304**. A pumping liner **350** is coupled to the chamber body **302** and is disposed radially outward of the substrate support **304**. A lid plate **324** is coupled to the showerhead **312** and supported by the chamber body **302**. A backing plate **314** is disposed between the showerhead **312** and the lid plate **324**. An injection assembly **326** is coupled to the lid plate **324** and the injection assembly may be in fluid communication with the process volume **310**.

The chamber body **302** may be manufactured from a material suitable to withstand temperatures of up to about 300° C. For example, the chamber body **302** may be formed from aluminum, alloys thereof, stainless steel, and other suitable metallic materials. A slit valve opening **360** is formed in the chamber body **302** to allow for ingress and egress of a substrate to and from the process volume **310**. A slit valve door **358** is coupled to the chamber body **302** and may be moveable to seal and unseal the slit valve opening **360**. In one embodiment, the slit valve door **358** is formed from the same materials as the chamber body **302**. Alternatively, the slit valve door **358** may be formed from materials different form the chamber body **302**.

The substrate support **304** may be moveably disposed within the process volume **310**. As illustrated, the substrate support **304** is disposed in an elevated processing position. The substrate support **304** may be lowered such that a substrate supporting surface of the substrate support **304** is coplanar with or below the slit valve opening **360** to allow for positioning of a substrate on the substrate support **304**. The substrate support may be formed from a material suitable for operation at elevated processing temperatures and may be a metallic material, a ceramic material, or combinations thereof. For example, the pedestal may be formed from aluminum, aluminum alloys, stainless steel, or ceramic materials, such as aluminum oxide or aluminum nitride.

The substrate support **304** has a heating member **306** disposed therein and the heating member **306** is coupled to a power source **354**. The power source **354** may also provide power for raising and lowering the substrate support **304** within the process volume **310**. The heating member **306** is a resistive heater or the like and may be disposed within the substrate support **304** in any desirable orientation. For example, the heating member **306** is formed in the substrate support **304** in a spiral orientation or other suitable orientation configured to heat the substrate support uniformly, such as a tortured path orientation. In one embodiment, the heating member **306** is configured to heat the substrate support **304** to a temperature between about 100° C. and about 300° C.

The pumping liner **350** is sized to surround the substrate support **304** and the process volume **310**. Similar to the substrate support **304**, the pumping liner **350** may be formed from metallic materials, ceramic materials, or combinations thereof. For example, the pedestal may be formed from aluminum, aluminum alloys, stainless steel, or ceramic materials, such as aluminum oxide or aluminum nitride. The pumping liner **350** has an opening **362** formed therein to allow for ingress and egress of a substrate into the process volume **310**. The opening **362** is positioned substantially co-planar with the slit valve opening **360**. A plurality of holes **352** are formed along an inner diameter of the pumping liner **350**. The plurality of holes **352** provide for evacuation of gases and other materials from the process volume **310** to an exhaust **356**. Accordingly, the process volume **310** is in fluid communication with the exhaust **356** via the holes **352** of the pumping liner **350**.

The showerhead **312**, which is disposed opposite the substrate support **304**, is coupled directly or indirectly to and supported by the chamber body **302**. The showerhead **312** may be formed from materials similar to the materials

utilized for the substrate support **304** and the pumping liner **350**. The showerhead **312** has a plurality of first passages **321** formed therein which extend from the process volume **310** to a first plenum **320** formed between the showerhead **312** and the backing plate **314**. The first passages **321** enable fluid communication and the transfer of vapor from the first plenum **320** to the process volume **310**.

A showerhead liner **308** is also disposed in the process volume **310**. The showerhead liner **308** may be formed from the same or similar materials as the showerhead **312** and the showerhead liner may be coupled to the showerhead **312**. In one embodiment, the showerhead liner **308** is a ring-like body. The showerhead liner **308** has an inner diameter which is substantially similar to an outer diameter of the substrate support **304**. The inner diameter of the showerhead liner **308** may also be sized such that the innermost surface of the showerhead liner **308** is radially outward of the first passages **321** in order to not interfere with vapor delivery to the process volume **310**. The showerhead liner **308** occupies physical space within the process volume **310** and reduces the volume of the process volume **310**, thereby reducing the amount of SAM precursor needed to form SAM molecules on a substrate. Thus, efficiency of a SAM formation process may be increased.

The showerhead **312** also has a heater **316** disposed therein. The heater **316** is a resistive heater of the like and may be disposed within the showerhead **312** radially outward of the first passages **321**. In one embodiment, the heater **316** is disposed within the showerhead **312** in a circumferential orientation which substantially surrounds the first passages **321**. The heater **316** may be coupled to a power source **318** to enable resistive heating of the showerhead **312**. In one embodiment, the showerhead **312** is configured to be heated to a temperature between about 150° C. and about 250° C.

The backing plate **314**, which is disposed between the showerhead and the lid plate **324**, and partially defines the first plenum **320**, has a second plurality of passages **323** disposed therein. A second plenum **322** is formed between the backing plate **314** and the lid plate **324**. The passages **323** enable the second plenum **322** to be in fluid communication with the first plenum **320**. A third plurality of passages **325** is formed in the lid plate **324** between the second plenum **322** and the injection assembly **326**.

The injection assembly **326** is configured to deliver vaporized materials to the process volume **310**. In operation, vaporized materials, such as SAM precursors and/or co-reactant precursors, are delivered from the injection assembly **326** through the third plurality of passages **325** to the second plenum **322**. The vaporized materials travel through the second plurality of passages **323** of the backing plate **314** to the first plenum **320** and through the first plurality of passages **321** of the showerhead **312** to the process volume **310**. After processing of a substrate, the vaporized materials and other effluent are removed from the process volume **310** through the holes **352** of the pumping liner **350** via the exhaust **356**.

The injection assembly **326** includes a housing **327** coupled to the lid plate **324** and an injector **328** coupled to the housing **327**. The injector **328** is disposed within the housing **327** and the injector **328** includes a third plenum **348**. In one embodiment, the third plenum **348** is funnel shaped. The shape of the third plenum **348** may be configured to facilitate and encourage mixing of vaporized materials prior to delivery to the process volume **310**. Although the third plenum **348** is illustrated as a funnel shape, other shapes which facilitate mixing of vaporized materials are contemplated.

A first ampoule **330** is coupled to the injection assembly **326** via a first conduit **332**. More specifically, the first ampoule **330** is in fluid communication with the third plenum **348** of the injector **328** via the first conduit **332**. The first conduit **332** extends from the first ampoule **330** to the third plenum **348**. A first heater jacket **334** surrounds the first conduit **332** on portions of the first conduit **332** disposed beyond the injector **328**. In one embodiment, the first heater jacket **334** is resistively heated to maintain a temperature of the first conduit **332** between about 50° C. and about 250° C.

The first ampoule **330** is configured to vaporize and deliver SAM precursors to the process volume **310**. Suitable examples of SAM precursors include phosphonic acid materials, such as butylphosphonic acid, hexylphosphonic acid, octylphosphonic acid, dodecylphosphonic acid, and octadecylphosphonic acid. In another embodiment, the SAM precursors may be thiol materials, such as dodecanethiol and octadecanethiol. In another embodiment, the SAM precursors may be silylamine materials, such as tris(dimethylamino)octylsilane and tris(dimethylamino)octadecylsilane. In another embodiment, the SAM precursors may be chlorosilane materials, such as dodecyltrichlorosilane and octadecyltrichlorosilane. In another embodiment, the SAM precursors may be oxysilane materials, such as octadecylthiethoxysilane and octadecyltrimethylsilane. In another embodiment, the SAM precursors may have a fluorinated R group, such as (1,1,2,2-perfluorodecyl)trichlorosilane, trichloro(1,1,2,2-perflrorooctyl)silane, (trideca-fluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane, (tridecafluoro-1,1,2,2-tetrahydro-octyl) triethoxysilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl) methyldichlorosilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane, and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane, among others.

A second ampoule **336** is coupled to the injection assembly **326** via a second conduit **338**. More specifically, the second ampoule **336** is in fluid communication with the third plenum **348** of the injector **328** via the second conduit **338**. The second conduit **338** extends from the second ampoule **336** to the third plenum **348**. A second heater jacket **340** surrounds the second conduit **338** on portions of the second conduit **338** disposed beyond the injector **328**. In one embodiment, the second heater jacket **340** is resistively heated to maintain a temperature of the second conduit **338** between about 50° C. and about 250° C.

The second ampoule **336** is configured to vaporize and deliver co-reactant precursors to the process volume **310**. Suitable examples of co-reactant precursors include hydroxyl moiety materials, such as ambient air, water solution or vapor, hydrogen peroxide solution or vapor, organic alcohol solutions or vapors, such as methanol, isopropanol, ethanol, and diols, among others. Hydrogen gas and oxygen gas may also be utilized in combination to form hydroxyl moieties. It is contemplated that other non-hydroxyl moiety precursors may also be utilized in accordance with the embodiments described herein. Non-hydroxyl moiety precursors may include nitrogen gas, (di)isocyanates, hydrogen sulfide, and ammonia, among others.

In one embodiment, a cleaning gas source **342** is coupled to the injection assembly **326** via a third conduit **344**. More specifically, the cleaning gas source **342** is in fluid communication with the third plenum **348** of the injector **328** via the third conduit **344**. The third conduit **344** extends from the

cleaning gas source **342** to the third plenum **348**. A third heater jacket **346** may optionally surround the third conduit **344** on portions of the third conduit **344** disposed beyond the injector **328**. In one embodiment, the third heater jacket **346** is resistively heated to maintain a temperature of the third conduit **344** between about 50° C. and about 250° C. Gases provided by the cleaning gas source **342** may include chlorine containing materials, fluorine containing materials, and other materials suitable for cleaning components of the process chamber **104**A.

In another embodiment, the cleaning gas source **342** is a remote plasma source. In this embodiment, the remote plasma source may energize cleaning gas to generate radicals and/or ions and the deliver the plasma products to the process volume **310**. In one embodiment, the remote plasma source is optional.

In another embodiment, the cleaning gas source **342** is a carrier gas source. A carrier gas may be utilized to facilitate delivery of vapor phase SAM precursors and the carrier gas, depending on the process volume **310**, may be delivered at a flow rate suitable to facilitate transport of the SAM precursors from the third plenum **348**, through the third passages **325**, through the second plenum **322** and the second passages **323**, and through the first plenum **320** and the first passages **321** to the process volume **310**. Suitable carrier gases include gases, such as noble gases or the like, that are generally inert under SAM adsorption conditions that facilitate delivery of the SAM molecules to surfaces of the substrate.

The heated showerhead **312** and the heated substrate support **304** may heat the process volume **310** to a temperature of between about 50° and about 250° C. The ampoules **330**, **336** and conduits **332**, **338** may be heated to similar temperatures. The showerhead liner **308**, backing plate **314**, lid plate **324**, and injection assembly **326** may also be conductively heated by the showerhead **312**. The temperature of the flow path along which the SAM precursors travel is maintained at an elevated temperature to prevent condensation of the vaporized SAM precursors on the various apparatus. The process volume **310** may also be maintained at a pressure of less than about 600 Torr which may also facilitate maintenance of the vapor state of the SAM precursor and co-reactant precursor.

In an operational embodiment, the SAM precursor is continually flowed through the process volume **310** from the first ampoule **330** to the exhaust **356**. In this embodiment, the pressure of the process volume **310** is maintained in an isobaric state. In another embodiment, the SAM precursor fills the process volume **110** and be maintained in the process volume **110** for a period of time prior to being exhausted from the process volume **310**. In another embodiment, co-reactant precursors are continually flowed to the process volume **310** or provided in a discontinuous manner, such as pulsing. In another embodiment, the SAM precursor and the co-reactant precursor are provided to the process volume **310** in an alternating manner, either continually or statically.

FIG. **4** illustrates a schematic, cross-sectional view of the process chamber **104** according to another embodiment described herein. Embodiments of FIG. **4** illustrate one implementation of a process chamber **104**B. The process chamber **104**B includes a chamber body **402** which defines a process volume **406**. A substrate support **404** is disposed within the process volume **406** and a heater **414** is disposed in the process volume **406** opposite the substrate support **404**. A lid plate **416** is coupled to the chamber body **402** and a vapor generation assembly **418** is coupled to the lid plate **416**.

The chamber body **402** is formed from the same or similar materials as the chamber body **302**. Similarly, the substrate support **404** may be formed from the same or similar materials as the substrate support **304**. The substrate support **404** includes a heating member **408** disposed therein. The heating member **408** is coupled to a power source **410** and be configured to heat the substrate support **404** to temperatures between about 100° C. and about 500° C.

The heater **414**, which is disposed opposite the substrate support **404**, may further define the process volume **406** between the heater **414** and the substrate support **404**. The heater **414** is coupled to a power source **428** and is configured to heat the heater **414** to temperatures between about 100° C. and about 500° C. A temperature of the process volume **406** may be maintained during processing at a temperature of between about 50° C. and about 500° C., such as between about 100° C. and about 250° C. A gas source **426** is also coupled to the heater **414** and the gas source **426** is in fluid communication with the process volume **406**. In one embodiment, the gas source **426** is configured to deliver a co-reactant precursor to the process volume **406**. Alternatively, the gas source **426** is configured to deliver a purge gas, a carrier gas, or a cleaning gas to the process volume **406**, depending on the desired implementation.

The vapor generation assembly **418**, such as a vaporizer, a direct liquid injection vaporizer or the like, is coupled to the lid plate **416**. The vapor generation assembly **418** is coupled to the lid plate **416** radially outward of the process volume **406**. The position of the vapor generation assembly **418**, and injection location of vapor to the process volume **406**, provides for a cross-flow type exposure of a substrate to SAM precursors. The vapor generation assembly **418** includes a vaporizer **422** and an injector **420** extending from the vaporizer **422**. The vaporizer **422** is coupled to a SAM precursor source **524** and receives SAM precursors in liquid form for vaporization. The vaporizer **422** is maintained at a temperature of between about 100° C. and about 500° C. to vaporize the SAM precursor and the temperature of the vaporizer **422** is determine, at least in part, by the vapor pressure of the SAM precursor.

Vaporized SAM precursor exits the vaporizer **422** and travels through the injector **420**. The injector **420** extends from the vaporizer **422** through the vapor generation assembly **418**, which is maintained at an elevated temperature by a heater jacket **412** to maintain the SAM precursor in a vapor state, and to the lid plate **416**.

A manifold **436** is coupled to the chamber body **402** radially outward of the substrate support **404** and the heater **414**. The manifold **436** is formed from the same of similar materials as the substrate support **404** and the heater **414**. The manifold **436** is sized to circumscribe the process volume **406** such that an inner diameter of the manifold **436** is larger than an outer diameter of the substrate support **404** and an outer diameter of the heater **414**. Vapor may flow through the manifold **436** from the injector **420** to an outlet **430** disposed opposite the injector **420**. An exhaust **432** is also coupled to and in fluid communication with the process volume **406**. More specifically, the exhaust **432** is in fluid communication with the process volume **406** via the outlet **430**. Accordingly, process volume effluent may be evacuated from the process volume **406** through the outlet **430** to the exhaust **432**.

A thermal insulator **434** is coupled to the lid plate **416** radially outward of the heater **414**. The thermal insulator **434** is sized similarly to the manifold **436** and may be disposed between the manifold **436** and the lid plate **416**. The thermal

insulator **434** may also be coupled to or in contact with the chamber body **402**. The thermal insulator **434** is formed from a thermally insulative material, such as a ceramic material or the like, configured to reduce or prevent the conduction of heat from the substrate support **404**, the heater **414**, and the manifold **436** from to the lid plate **416**. In one embodiment, the thermal insulator **434** is optional. In this embodiment, an air gap functions as a thermal break between the lid plate **416** and the substrate support **404**, the heater **414**, and the manifold **436**.

FIG. **5** illustrates a schematic, cross-sectional view of the process chamber **104** according to one embodiment described herein. Embodiments of FIG. **5** illustrate one implementation of a process chamber **104**C. The process chamber **104**C includes a chamber body **502** which defines a process volume **506**. A substrate support **504** is disposed within the process volume **506** and a lid plate **516** is coupled to the chamber body **502** opposite the substrate support **504**. A vapor generation assembly **518** is coupled to the lid plate **516**.

The chamber body **502** is formed from the same or similar materials as the chamber body **402**. Similarly, the substrate support **504** is formed from the same or similar materials as the substrate support **404**. The substrate support **504** includes a heating member **508** disposed therein. The heating member **508** is coupled to a power source **510** and is configured to heat the substrate support **504** to temperatures between about 100° C. and about 500° C.

The vapor generation assembly **518**, such as a vaporizer, a direct liquid injection vaporizer or the like, is coupled to the lid plate **516** adjacent a center of the process volume **506**. The position of the vapor generation assembly **518**, and injection location of vapor to the process volume **506**, provides for a top-down type exposure of a substrate to SAM precursors. The vapor generation assembly **518** includes a vaporizer **522** and one or more injectors **512**, **514** extending from the vaporizer **522**. The vaporizer **522** is coupled to a SAM precursor source **524** and receives SAM precursors in liquid form for vaporization. The vaporizer **522** is maintained at a temperature of between about 100° C. and about 500° C. to vaporize the SAM precursor and the temperature of the vaporizer **522** may be determined, at least in part, by the vapor pressure of the SAM precursor.

Vaporized SAM precursors exit the vaporizer **522** and travel through one or both of the injectors **512**, **514**. The injectors **512**, **514** extend from the vaporizer **522** through the vapor generation assembly **518**, which is maintained at an elevated temperature by a heater jacket **528** to maintain the SAM precursor in a vapor state, and to the lid plate **516**. In one embodiment, SAM precursor from the source **524** is introduced to the process volume via the injector **512** through an outlet **530**. A gas source **526** is also in fluid communication with the process volume **506**. The gas source **526** introduces a liquid or gas to the vapor generation assembly **518** and the generated vapor is introduced to the process volume **506** via the injector **514** and the outlet **530**. In one embodiment, the gas source **526** provides a co-reactant precursor. In another embodiment, the gas source **526** provides a purge gas, a carrier gas, or a cleaning gas, depending upon the desired implementation.

The process volume **506** is also in fluid communication with an exhaust **532**. Accordingly, process volume effluent may be evacuated from the process volume **506** via the exhaust **532**. Both process chambers **104**B and **104**C may be maintained at a pressure of less than about 600 Torr. Processes performed in the process chambers **104**B, **104**C may be isobaric or non-isobaric. Similarly, the processes performed in the process chambers **104**B, **104**C may be isothermal or non-isothermal.

FIG. **6** illustrates a schematic, cross-sectional view of the process chamber **106** according to one embodiment described herein. The process chamber **106** includes a gas delivery system **630** adapted for ALD or sequential layer deposition. The process chamber **106** contains a chamber body **602** having sidewalls **604** and a bottom **606**. A slit valve **608** in provides ingress and egress of a substrate **610**, to and from the process chamber **106**.

A substrate support **612** supports the substrate **610** on a substrate receiving surface **611**. The substrate support **612** is mounted to a lift motor **614** to raise and lower the substrate support **612** and the substrate **610** disposed thereon. A lift plate **616** connected to a lift motor **618** is mounted in the process chamber **106** and raises and lowers lift pins **620** movably disposed through substrate support **612**. The lift pins **620** raise and lower the substrate **610** over the surface of substrate support **612**. The substrate support **612** may include a vacuum chuck (not shown), an electrostatic chuck (not shown), or a clamp ring (not shown) for securing the substrate **610** to the substrate support **612** during processing.

The substrate support **612** may be heated to heat the substrate **610** disposed thereon. For example, the substrate support **612** may be heated using an embedded heating element, such as a resistive heater (not shown), or may be heated using radiant heat, such as heating lamps (not shown) disposed above the substrate support **612**. A purge ring **622** may be disposed on the substrate support **612** to define a purge channel **624** which provides a purge gas to a peripheral portion of the substrate **610** to prevent deposition thereon.

A gas delivery system **630** is disposed at an upper portion of the chamber body **602** to provide a gas, such as a process gas and/or a purge gas, to the process chamber **106**. A vacuum system **678** is in communication with a pumping channel **679** to evacuate any desired gases from the process chamber **106** and to help maintain a desired pressure or a desired pressure range inside a pumping zone **666** of the process chamber **106**.

In one embodiment, the gas delivery system **630** contains a chamber lid assembly **632**. The chamber lid assembly **632** includes an expanding channel **634** extending from a central portion of chamber lid assembly **632** and a lower surface **660** extending from the expanding channel **634** to a peripheral portion of the chamber lid assembly **632**. A lower surface **660** is sized and shaped to substantially cover the substrate **610** disposed on the substrate support **612**. The expanding channel **634** has gas inlets **636***a*, **636***b* to provide gas flows from two similar pairs of valves **642***a*/**652***a*, **642***b*/**652***b*, which may be provided together and/or separately.

In one configuration, valve **642***a* and valve **642***b* are coupled to separate reactant gas sources but may also be coupled to the same purge gas source. For example, valve **642***a* is coupled to reactant gas source **638** and valve **642***b* is coupled to reactant gas source **639**, and both valves **642***a*, **642***b* are coupled to purge gas source **640**. Each valve **642***a*, **642***b* includes a delivery line **643***a*, **643***b* having a valve seat assembly **644***a*, **644***b* and each of valves **652***a*, **652***b* includes a purge line **645***a*, **645***b* having a valve seat assembly **646***a*, **646***b*. Delivery line **643***a*, **643***b* is in fluid communication with the reactant gas source **638**, **639** and is in fluid communication with gas inlet **636***a*, **636***b* of the expanding channel **634**. The valve seat assembly **644***a*, **644***b* of delivery line **643***a*, **643***b* controls the flow of the reactant gas from the reactant gas source **638**, **639** to the expanding

channel **634**. Purge line **645***a*, **645***b* is in fluid communication with purge gas source **640** and intersects delivery line **643***a*, **643***b* downstream of valve seat assembly **644***a*, **644***b* of delivery line **643***a*, **643***b*. Valve seat assembly **646***a*, **646***b* of purge line **645***a*, **645***b* controls the flow of the purge gas from purge gas source **640** to the expanding channel **634**. If a carrier gas is used to deliver reactant gases from the reactant gas source **638**, **639**, preferably the same gas is used as a carrier gas and a purge gas (i.e., an argon gas used as a carrier gas and a purge gas).

Each valve seat assembly **644***a*, **644***b*, **646***a*, **646***b* may contain a diaphragm (not shown) and a valve seat (not shown). The diaphragm may be biased open or closed and may be actuated closed or open respectively. The diaphragms may be pneumatically actuated or may be electrically actuated. Pneumatically actuated valves include pneumatically actuated valves available from Fujikin, Inc. and Veriflo Division, Parker Hannifin, Corp. Electrically actuated valves include electrically actuated valves available from Fujikin, Inc. For example, an ALD valve that may be used is the Fujikin Model No. FPR-UDDFAT-21-6.35-PI-ASN or the Fujikin Model No. FPR-NHDT-21-6.35-PA-AYT. Programmable logic controllers **648***a*, **648***b* may be coupled to valves **642***a*, **642***b* to control actuation of the diaphragms of the valve seat assemblies **644***a*, **644***b*, **646***a*, **646***b* of valves **642***a*, **642***b*. Pneumatically actuated valves may provide pulses of gases in time periods as low as about 0.020 seconds. Electrically actuated valves may provide pulses of gases in time periods as low as about 0.005 seconds. An electrically actuated valve typically requires the use of a driver coupled between the valve and the programmable logic controller.

Each valve **642***a*, **642***b* may be a zero dead volume valve to enable flushing of a reactant gas from delivery line **643***a*, **643***b* when valve seat assembly **644***a*, **644***b* is closed. For example, purge line **645***a*, **645***b* may be positioned adjacent valve seat assembly **644***a*, **644***b* of delivery line **643***a*, **643***b*. When valve seat assembly **644***a*, **644***b* is closed, purge line **645***a*, **645***b* may provide a purge gas to flush delivery line **643***a*, **643***b*. In the embodiment shown, purge line **645***a*, **645***b* is positioned slightly spaced from the valve seat assembly **644***a*, **644***b* of delivery line **643***a*, **643***b* so that a purge gas is not directly delivered into valve seat assembly **644***a*, **644***b* when open. A zero dead volume valve as used herein is defined as a valve which has negligible dead volume (i.e., not necessary zero dead volume).

Each valve pair **642***a*/**652***a*, **642***b*/**652***b* may be adapted to provide a combined gas flow and/or separate gas flows of the reactant gas and the purge gas. In reference to valve pair **642***a*/**652***a*, one example of a combined gas flow of the reactant gas and the purge gas includes a continuous flow of a purge gas from purge gas source **640** through purge line **645***a* and pulses of a reactant gas from reactant gas source **638** through delivery line **643***a*. The continuous flow of the purge gas may be provided by leaving the diaphragm of valve seat assembly **646***a* of the purge line **645***a* open. The pulses of the reactant gas from reactant gas source **638** may be provided by opening and closing the diaphragm of valve seat assembly **644***a* of delivery line **643***a*. In reference to valve pair **642***a*/**652***a*, one example of separate gas flows of the reactant gas and the purge gas includes pulses of a purge gas from purge gas source **640** through purge line **645***a* and pulses of a reactant gas from reactant gas source **638** through delivery line **643***a*. The pulses of the purge gas may be provided by opening and closing the diaphragm of valve seat assembly **646***a* of purge line **645***a*. The pulses of the reactant gas from reactant gas source **638** may be provided by opening and closing the diaphragm of valve seat assembly **644***a* of delivery line **643***a*.

Delivery lines **643***a*, **643***b* of valves **642***a*, **642***b* may be coupled to gas inlets **636***a*, **636***b* through gas conduits **650***a*, **650***b*. Gas conduits **650***i*, **650***b* may be integrated or may be separate from valves **642***a*, **642***b*. In one aspect, valves **642***a*, **642***b* are coupled in close proximity to expanding channel **634** to reduce any unnecessary volume of delivery line **643***a*, **643***b* and gas conduits **650***a*, **650***b* between valves **642***a*, **642***b* and gas inlets **636***a*, **636***b*.

The expanding channel **634** contains a channel which has an inner diameter which increases from an upper portion **637** to a lower portion **635** of expanding channel **634** adjacent lower surface **660** of chamber lid assembly **632**. In one embodiment, expanding channel **234** may be shaped as a truncated cone (including shapes resembling a truncated cone). Whether a gas is provided toward the walls of expanding channel **634** or directly downward towards substrate **610**, the velocity of the gas flow decreases as the gas flow travels through expanding channel **634** due to the expansion of the gas. The reduction of the velocity of the gas flow helps reduce the likelihood the gas flow will blow off reactants adsorbed on the surface of substrate **610**.

Not wishing to be bound by theory, it is believed that the diameter of expanding channel **634**, which is gradually increasing from upper portion **637** to lower portion **635** of expanding channel **634**, allows less of an adiabatic expansion of a gas through expanding channel **634** which helps to control the temperature of the gas. For instance, a sudden adiabatic expansion of a gas delivered through gas inlet **636***a*, **636***b* into expanding channel **634** may result in a drop in the temperature of the gas which may cause condensation of the gas and formation of droplets. On the other hand, a gradually expanding channel **634** is believed to provide less of an adiabatic expansion of a gas. Therefore, more heat may be transferred to or from the gas, and, thus, the temperature of the gas may be more easily controlled by controlling the surrounding temperature of the gas (i.e., controlling the temperature of chamber lid assembly **632**). The gradually expanding channel **634** may contain one or more tapered inner surfaces, such as a tapered straight surface, a concave surface, a convex surface, or combinations thereof or may contain sections of one or more tapered inner surfaces (i.e., a portion tapered and a portion non-tapered).

In one embodiment, gas inlets **636***a*, **636***b* are located adjacent upper portion **637** of expanding channel **634**. In other embodiments, one or more gas inlets **636***a*, **636***b* may be located along the length of expanding channel **634** between upper portion **637** and lower portion **635**.

At least a portion of lower surface **660** of chamber lid assembly **632** may be tapered from expanding channel **634** to a peripheral portion of chamber lid assembly **632** to help provide an improved velocity profile of a gas flow from expanding channel **634** across the surface of substrate **610** (i.e., from the center of the substrate to the edge of the substrate). Lower surface **660** may contain one or more tapered surfaces, such as a straight surface, a concave surface, a convex surface, or combinations thereof. In one embodiment, lower surface **660** is tapered in the shape of a funnel.

A choke **662** may be located at a peripheral portion of chamber lid assembly **632** adjacent the periphery of substrate **610**. Choke **662**, when chamber lid assembly **632** is assembled to form a processing zone around substrate **610**, contains any member restricting the flow of gas therethrough at an area adjacent the periphery of substrate **610**. In one

embodiment, the spacing between choke **662** and substrate support **612** is between about 0.04 inches and about 2.0 inches, and preferably between 0.04 inches and about 0.2 inches. The spacing may vary depending on the gases being delivered and the process conditions during deposition. Choke **662** helps provide a more uniform pressure distribution within the volume or reaction zone **664** defined between chamber lid assembly **632** and substrate **610** by isolating reaction zone **664** from the non-uniform pressure distribution of pumping zone **666**.

In one aspect, since reaction zone **664** is isolated from pumping zone **666**, a reactant gas or purge gas needs only adequately fill reaction zone **664** to ensure sufficient exposure of substrate **610** to the reactant gas or purge gas. Process chamber **106** sequentially introduces reactants to the surface of substrate **610** to provide absorption of alternating thin layers of the reactants onto the surface of substrate **610**. As a consequence, atomic layer deposition does not require a flow of a reactant which reaches the surface of substrate **610** simultaneously. Instead, a flow of a reactant needs to be provided in an amount which is sufficient to adsorb a thin layer of the reactant on the surface of substrate **610**.

Chamber lid assembly **632** may include cooling elements and/or heating elements depending on the particular gas being delivered therethrough. Controlling the temperature of chamber lid assembly **632** may be used to prevent gas decomposition, deposition, or condensation on chamber lid assembly **632**. For example, water channels (not shown) may be formed in chamber lid assembly **632** to cool chamber lid assembly **632**. In another example, heating elements (not shown) may be embedded or may surround components of chamber lid assembly **632** to heat chamber lid assembly **632**. In one embodiment, components of chamber lid assembly **632** may be individually heated or cooled. For example, chamber lid assembly **632** may contain lid plate **670** and lid cap **672** in which lid plate **670** and lid cap **672** form expanding channel **634**. Lid cap **672** may be maintained at one temperature range and lid plate **670** may be maintained at another temperature range. For example, lid cap **672** may be heated by being wrapped in heater tape or by using another heating device to prevent condensation of reactant gases and lid plate **670** may be maintained at ambient temperature. In another example, lid cap **672** may be heated and lid plate **670** may be cooled with water channels formed therethrough to prevent thermal decomposition of reactant gases on lid plate **670**.

Chamber lid assembly **632** contains components that may be made of stainless steel, aluminum, nickel-plated aluminum, nickel, or other suitable materials compatible with the processing to be performed. In one embodiment, lid cap **672** contains aluminum or stainless steel and lid plate **670** contains aluminum.

Control unit **280**, such as a programmed personal computer, work station computer, or the like, may be coupled to the process chamber **106** to control processing conditions. For example, control unit **680** may be configured to control flow of various process gases and purge gases from gas sources **638**, **639**, and **640** through valves **642***a*, **262***b* during different stages of a substrate process sequence. Illustratively, the control unit **680** contains central processing unit (CPU) **682**, support circuitry **684**, and memory **686** containing associated control software **683**.

The control unit **680** may be one of any form of general purpose computer processor that can be used in an industrial setting for controlling various chambers and sub-processors. The CPU **682** may use any suitable memory **686**, such as random access memory, read only memory, floppy disk drive, hard disk, or any other form of digital storage, local or remote. Various support circuits may be coupled to the CPU **682** for supporting process chamber **106**. The control unit **680** may be coupled to another controller that is located adjacent individual chamber components, such as programmable logic controllers **648***a*, **648***b* of valves **642***a*, **642***b*. Bi-directional communications between the control unit **680** and various other components of process chamber **106** are handled through numerous signal cables collectively referred to as signal buses **688**. In addition to control of process gases and purge gases from gas sources **638**, **639**, **640** and from programmable logic controllers **648***a*, **648***b* of valves **642***a*, **642***b*, control unit **680** may be configured to be responsible for automated control of other activities used in wafer processing-such as wafer transport, temperature control, chamber evacuation, among other activities.

In operation, the substrate **610** is delivered to the process chamber **106** through the slit valve **608** by a robot (not shown), such as the transfer robot **114** (FIG. **1**). Substrate **610** is positioned on substrate support **612** through cooperation of the lift pins **620** and the robot. Substrate support **612** raises substrate **610** into close opposition to lower surface **660** of chamber lid assembly **632**. A first gas flow may be injected into expanding channel **634** of process chamber **106** by valve **642***a* together or separately (i.e., pulses) with a second gas flow injected into process chamber **106** by valve **642***b*. The first gas flow may contain a continuous flow of a purge gas from purge gas source **640** and pulses of a reactant gas from reactant gas source **638** or may contain pulses of a reactant gas from reactant gas source **638** and pulses of a purge gas from purge gas source **640**. The second gas flow may contain a continuous flow of a purge gas from purge gas source **640** and pulses of a reactant gas from reactant gas source **639** or may contain pulses of a reactant gas from reactant gas source **639** and pulses of a purge gas from purge gas source **640**. The gas flow travels through expanding channel **634** as a pattern of vortex flow which provides a sweeping action across the inner surface of expanding channel **634**. The pattern of vortex flow dissipates to a downwardly flow toward the surface of substrate **610**. The velocity of the gas flow reduces as it travels through expanding channel **634**. The gas flow then travels across the surface of substrate **610** and across lower surface **660** of chamber lid assembly **632**. Lower surface **660** of chamber lid assembly **632**, which is downwardly sloping, helps reduce the variation of the velocity of the gas flow across the surface of substrate **610**. The gas flow then travels by choke **662** and into pumping zone **666** of process chamber **106**. Excess gas, by-products, etc. flow into the pumping channel **679** and are then exhausted from process chamber **106** by vacuum system **678**. In one aspect, the gas flow proceeds through expanding channel **634** and between the surface of substrate **610** and lower surface **660** of chamber lid assembly **632** in a laminar manner which aids in uniform exposure of a reactant gas to the surface of substrate **610** and efficient purging of inner surfaces of chamber lid assembly **632**.

FIG. **7** illustrates a schematic, cross-sectional view of the process chamber **108** according to one embodiment described herein. In one embodiment, the process chamber **108** is similar to the process chamber **102**. In this embodiment, the process chamber **108** may be utilized for thermal post-ALD treatment, plasma post-ALD treatment, or a combination thereof. For embodiments utilizing a plasma post-ALD treatment, a plasma etch process may be performed to remove ALD material from undesired locations on the substrate. It is contemplated that the plasma etch process

may be utilized if an imperfect SAM treatment resulted in undesired areas of the substrate remaining exposed during ALD treatment.

In another embodiment, the process chamber **108** is different from the process chamber **102**. A different chamber is illustrated in FIG. **7** having a chamber body **702** defining a process volume **704**. A substrate support **706** is disposed within the process volume **704** and a heater **708**, such as a resistive heater, is disposed within the substrate support **706**. The heater **708** is coupled to a power source **710** and the heater is configured to heat a substrate disposed on the substrate support **706** to a temperature greater than a vaporization temperature of SAM materials disposed on the substrate. Thus, the process chamber **108** volatilizes SAM materials from the substrate and the volatilized materials are exhausted from the process volume **704** via an exhaust.

FIG. **8** illustrates operations of a method **800** for processing a substrate according to one embodiment described herein. At operation **810**, a substrate is delivered to a pre-clean chamber, such as process chamber **102**. A pre-clean process is performed on the substrate and the substrate is transferred from the pre-clean chamber to a SAM processing chamber, such as process chamber **104**, via a transfer chamber (i.e. transfer chamber **110**) at operation **820**.

A SAM material deposition process is performed on the substrate and at operation **830**, the substrate is transferred from the SAM processing chamber to an ALD chamber, such as process chamber **106**, via the transfer chamber. An ALD process is performed on the substrate and the substrate is transferred from the ALD chamber to a post-processing chamber, such as process chamber **108**, via the transfer chamber at operation **840**. Post-processing is performed on the substrate and the substrate may be transferred from the post-processing chamber for subsequent processing.

In summation, the integrated cluster tool apparatus provides for improved in-situ processing and increased throughput when utilizing SAM treatment processes in combination with subsequent deposition processes, such as ALD treatments. Additional process capability, such as pre and post processing of substrates, provides various advantages, such as improved material deposition selectivity, in accordance with embodiments described herein.

While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A substrate processing method, comprising:

transferring a substrate to a first process chamber and performing a surface modification process on a surface of the substrate in the first process chamber, the surface including a first portion comprising metal and a second portion comprising dielectric material;

transferring the substrate from the first process chamber to a second process chamber via a transfer chamber, and disposing the substrate in a process volume of the second process chamber, the second process chamber comprising:

a chamber body;

a substrate support disposed in the chamber body;

a lid plate coupled to the chamber body;

a heater disposed in the chamber body, opposite from the substrate support, wherein the process volume is defined between the substrate support and the heater;

an annular manifold coupled to the chamber body radially outward of the substrate support and the heater, the annular manifold further defining the process volume; and

an injection assembly coupled to the lid plate radially outward of the process volume in fluid communication with the process volume through the annular manifold;

performing a self-assembled monolayer treatment process on the substrate in the second process chamber to form a self-assembled monolayer on the first portion of the substrate where sections of the first portion of the substrate are not covered by the self-assembled monolayer, wherein the self-assembled monolayer treatment process comprises:

vaporizing a liquid in a vaporizer mounted to the lid plate of the second process chamber to generate a vaporized self-assembled monolayer precursor;

directing the vaporized self-assembled monolayer precursor to the process volume of the second process chamber through the lid plate, and then through a thermal insulator, and then into the annular manifold, via the injection assembly, the injection assembly includes an injector surrounded by a heater jacket extending between the vaporizer and the lid plate; and

providing a cross-flow type exposure of the vaporized self-assembled monolayer precursor to the process volume between the substrate support and the heater via the injection assembly in the second process chamber;

transferring the substrate from the second process chamber to a third process chamber via the transfer chamber;

performing an atomic layer deposition process on the substrate in the third process chamber to form an atomic layer on the second portion of the substrate and the sections of the first portion of the substrate not covered by the self-assembled monolayer;

transferring the substrate from the third process chamber to a fourth process chamber via the transfer chamber; and

performing an anneal process on the substrate in the fourth process chamber.

2. The method of claim **1**, wherein the transfer chamber is maintained under vacuum during each of the substrate transfer processes.

3. The method of claim **1**, wherein the anneal process is performed at a temperature greater than a vaporization temperature of a self-assembled monolayer material.

4. The method of claim **1**, wherein the surface modification process is a pre-clean process.

5. The method of claim **4**, wherein the pre-clean process modifies surface terminal groups on the substrate.

6. The method of claim **1**, wherein each of the first process chamber, the second process chamber, the third process chamber, and the fourth process chamber is coupled to the transfer chamber.

7. The method of claim **1**, wherein the metal comprises Cu and the dielectric material comprises SiO_2.

8. The method of claim **1**, further comprising an etch process performed after the atomic layer deposition process, the etch process removing the atomic layer deposited on the sections of the first portion of the substrate that are not covered by the self-assembled monolayer.

9. The method of claim **1**, further comprising:

a vapor generation assembly in fluid communication with the injection assembly and the process volume.

10. A substrate processing method, comprising:
performing a surface modification process on a surface of a substrate in a first process chamber, the surface of the substrate including a first portion comprising metal and a second portion comprising dielectric material, wherein the surface modification process removes defects from the substrate;
transferring the substrate from the first process chamber to a second process chamber via a transfer chamber, and disposing the substrate in a process volume of the second process chamber, the second process chamber comprising:
a chamber body;
a substrate support disposed in the chamber body;
a lid plate coupled to the chamber body;
a heater disposed in the chamber body, opposite from the substrate support, wherein the process volume is defined between the substrate support and the heater;
an annular manifold coupled to the chamber body radially outward of the substrate support and the heater, the annular manifold further defining the process volume; and
an injection assembly coupled to the lid plate radially outward of the process volume in fluid communication with the process volume through the annular manifold;
performing a self-assembled monolayer treatment process on the substrate to form a self-assembled monolayer on the first portion of the substrate where sections of the first portion of the substrate are not covered by the self-assembled monolayer, in the second process chamber, wherein the self-assembled monolayer treatment process comprises:
vaporizing a liquid in a vaporizer mounted to the lid plate of the second process chamber to generate a vaporized self-assembled monolayer precursor;
directing the vaporized self-assembled monolayer precursor to the process volume of the second process chamber through the lid plate, and then through a thermal insulator, and then into the annular manifold, via the injection assembly, the injection assembly includes an injector surrounded by a heater jacket extending between the vaporizer and the lid plate; and
providing a cross-flow type exposure of the vaporized self-assembled monolayer precursor to the process volume between the substrate support and the heater via the injection assembly in the second process chamber;
transferring the substrate from the second process chamber to a third process chamber via the transfer chamber;
performing an atomic layer deposition process on the substrate to form an atomic layer on the second portion of the substrate and the sections of the first portion of the substrate not covered by the self-assembled monolayer, in the third process chamber;
transferring the substrate from the third process chamber to a fourth process chamber via the transfer chamber; and
performing an etch process on the substrate in the fourth process chamber, the etch process removing the atomic layer deposited on the sections of the first portion of the substrate that is not covered by the self-assembled monolayer.

11. The method of claim 10, wherein the transfer chamber is maintained under vacuum during each of the substrate transfer processes.

12. The method of claim 10, further comprising an anneal process performed after the atomic layer deposition process, wherein the anneal process is performed at a temperature greater than a vaporization temperature of a self-assembled monolayer material.

13. The method of claim 10, wherein the surface modification process is a pre-clean process.

14. The method of claim 10, wherein each of the first process chamber, the second process chamber, the third process chamber, and the fourth process chamber is coupled to the transfer chamber.

15. The method of claim 10, wherein the metal comprises Cu and the dielectric material comprises SiO_2.

16. A substrate processing method, comprising:
performing a surface modification process on a substrate in a first process chamber, a surface of the substrate including a first portion comprising metal and a second portion comprising dielectric material, wherein the surface modification process removes defects from the substrate;
transferring the substrate from the first process chamber to a second process chamber via a transfer chamber and disposing the substrate in a process volume of the second process chamber,
the second process chamber comprising:
a chamber body;
a substrate support disposed in the chamber body;
a lid plate coupled to the chamber body;
a heater disposed in the chamber body, opposite from the substrate support, wherein the process volume is defined between the substrate support and the heater;
an annular manifold coupled to the chamber body radially outward of the substrate support and the heater, the annular manifold further defining the process volume; and
an injection assembly coupled to the lid plate radially outward of the process volume in fluid communication with the process volume through the annular manifold;
performing a self-assembled monolayer treatment process on the substrate to form a self-assembled monolayer on the first portion of the substrate where sections of the first portion of the substrate are not covered by the self-assembled monolayer, in the second process chamber, wherein the self-assembled monolayer treatment process comprises:
vaporizing a liquid in a vaporizer mounted to the lid plate of the second process chamber to generate a vaporized self-assembled monolayer precursor;
directing the vaporized self-assembled monolayer precursor to the process volume of the second process chamber through the lid plate, and then through a thermal insulator, and then into the annular manifold, via the injection assembly, the injection assembly includes an injector surrounded by a heater jacket extending between the vaporizer and the lid plate; and
providing a cross-flow type exposure of the vaporized self-assembled monolayer precursor to the process volume between the substrate support and the heater via the injection assembly in the second process chamber, wherein the vaporized self-assembled monolayer precursor is selected from the group consisting of thiol materials, silylamine materials, chlorosilane materials, and oxysilane materials;
transferring the substrate from the second process chamber to a third process chamber via the transfer chamber;

performing an atomic layer deposition process on the substrate to form an atomic layer on the second portion of the substrate and the sections of the first portion of the substrate not covered by the self-assembled monolayer, in the third process chamber;

transferring the substrate from the third process chamber to a fourth process chamber via the transfer chamber; and

performing an anneal process on the substrate in the fourth process chamber to remove material from the substrate deposited during the self-assembled monolayer treatment process.

17. The method of claim **16**, wherein the transfer chamber is maintained under vacuum during each of the substrate transfer processes.

18. The method of claim **16**, wherein the anneal process is performed at a temperature greater than a vaporization temperature of the self-assembled monolayer precursors.

19. The method of claim **16**, wherein the surface modification process is a pre-clean process which modifies surface terminal groups on the substrate.

20. The method of claim **16**, wherein the metal comprises Cu and the dielectric material comprises SiO_2.

21. The method of claim **16**, further comprising an etch process performed after the atomic layer deposition process, the etch process removing the atomic layer deposited on the sections of the first portion of the substrate that are not covered by the self-assembled monolayer.

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