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(54) **METHOD FOR VAPOR CONDENSATION AND RECOVERY**

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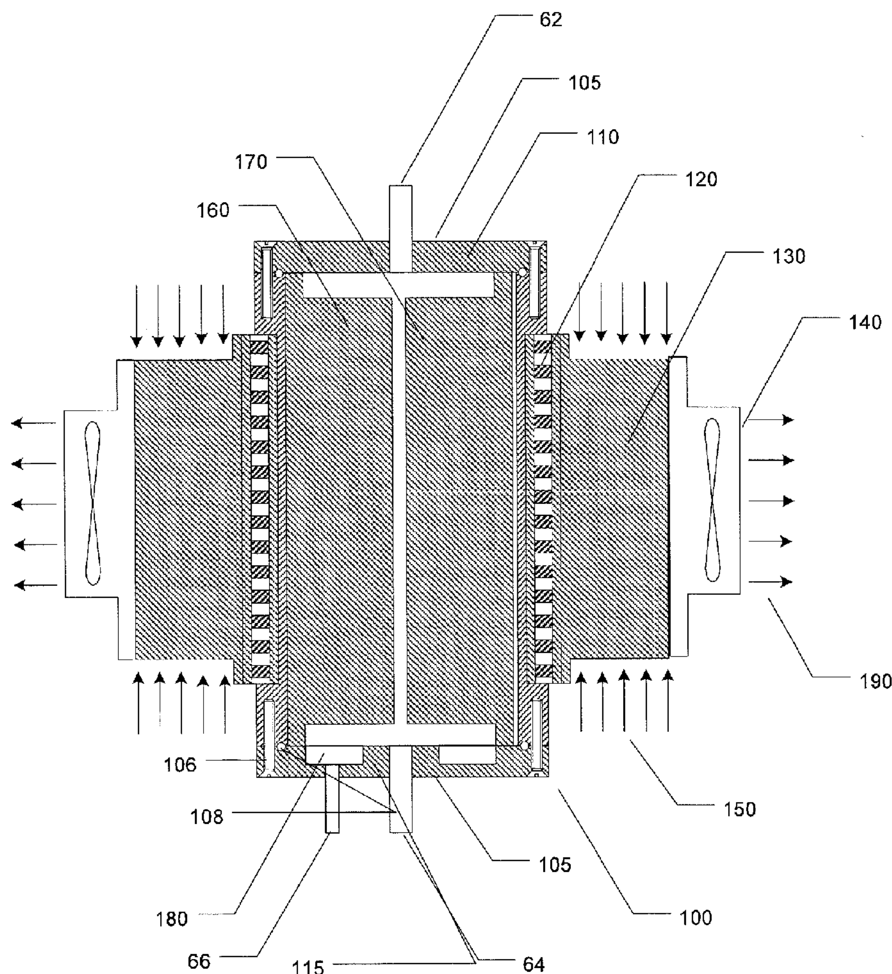
(57) **ABSTRACT**

Methods for recovery of precursor vapor from a gas and precursor vapor mixture used in a deposition process. The gas and precursor vapor mixture is passed through a multitude of heat transfer surfaces in a heat conducting housing causing the precursor vapor to condense. The precursor vapor in liquid form is then collected after condensation.



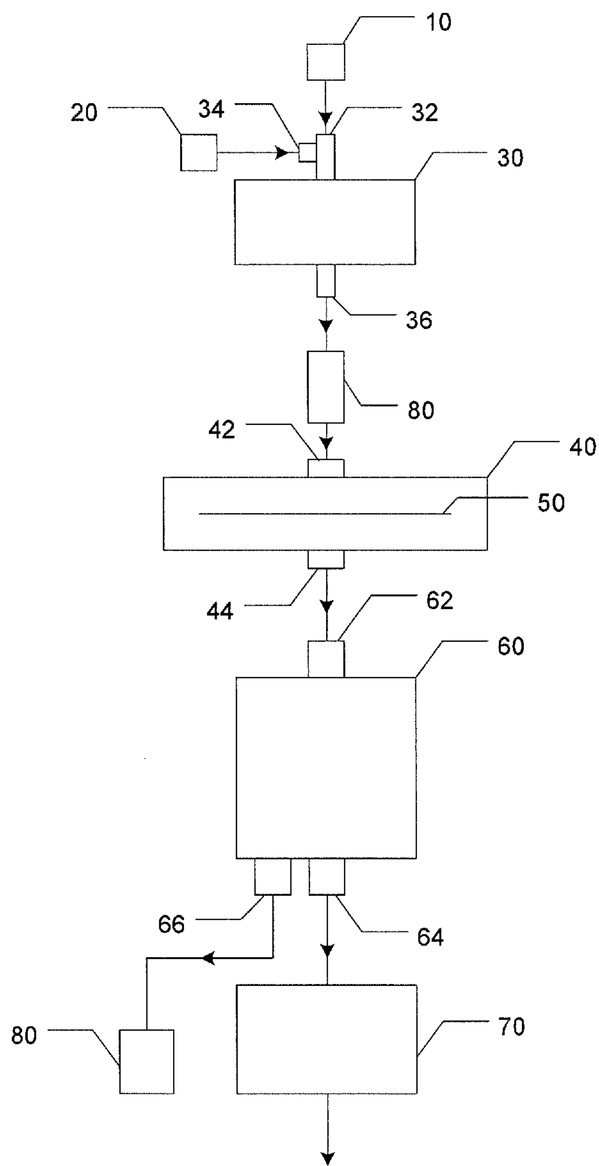


FIG. 1

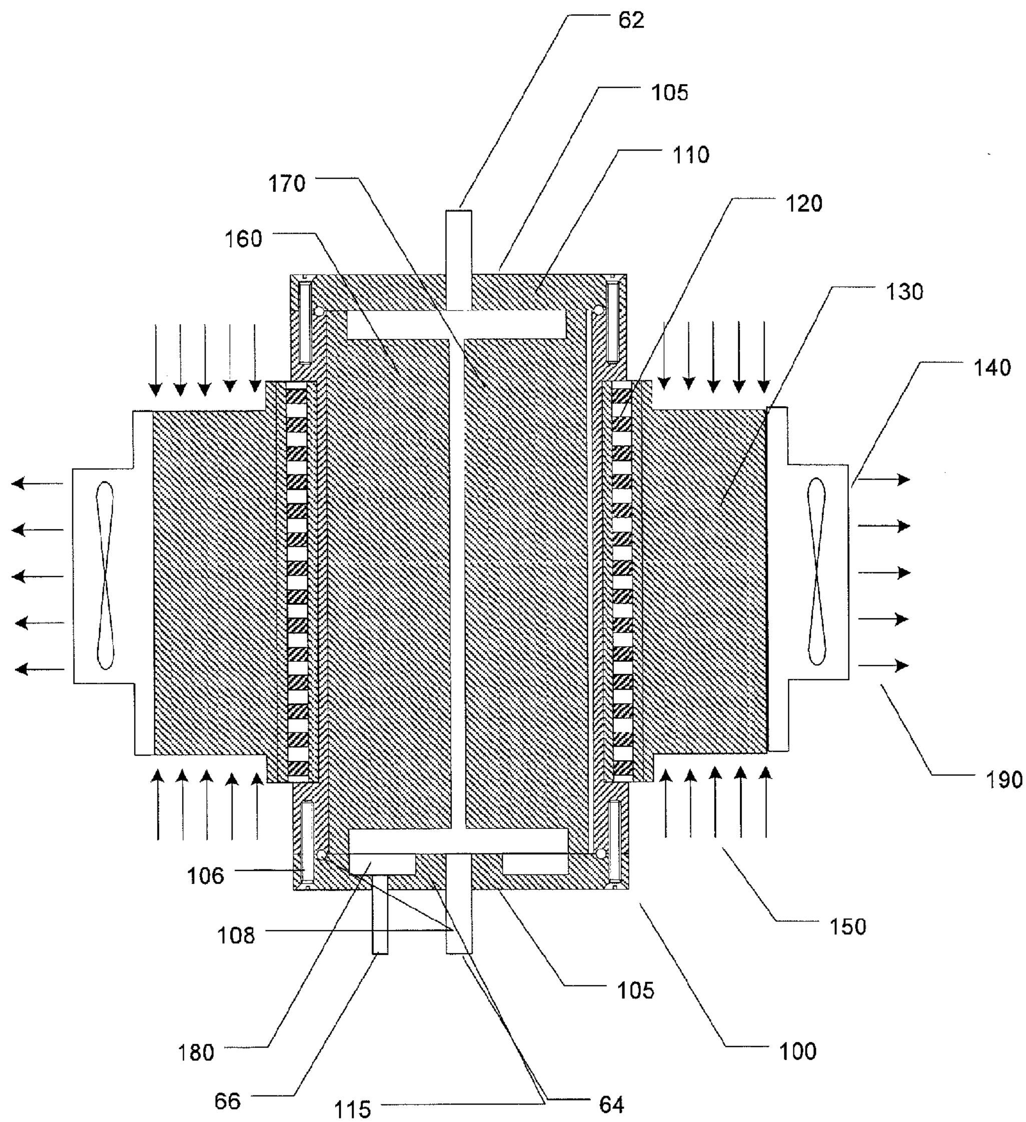


FIG. 2

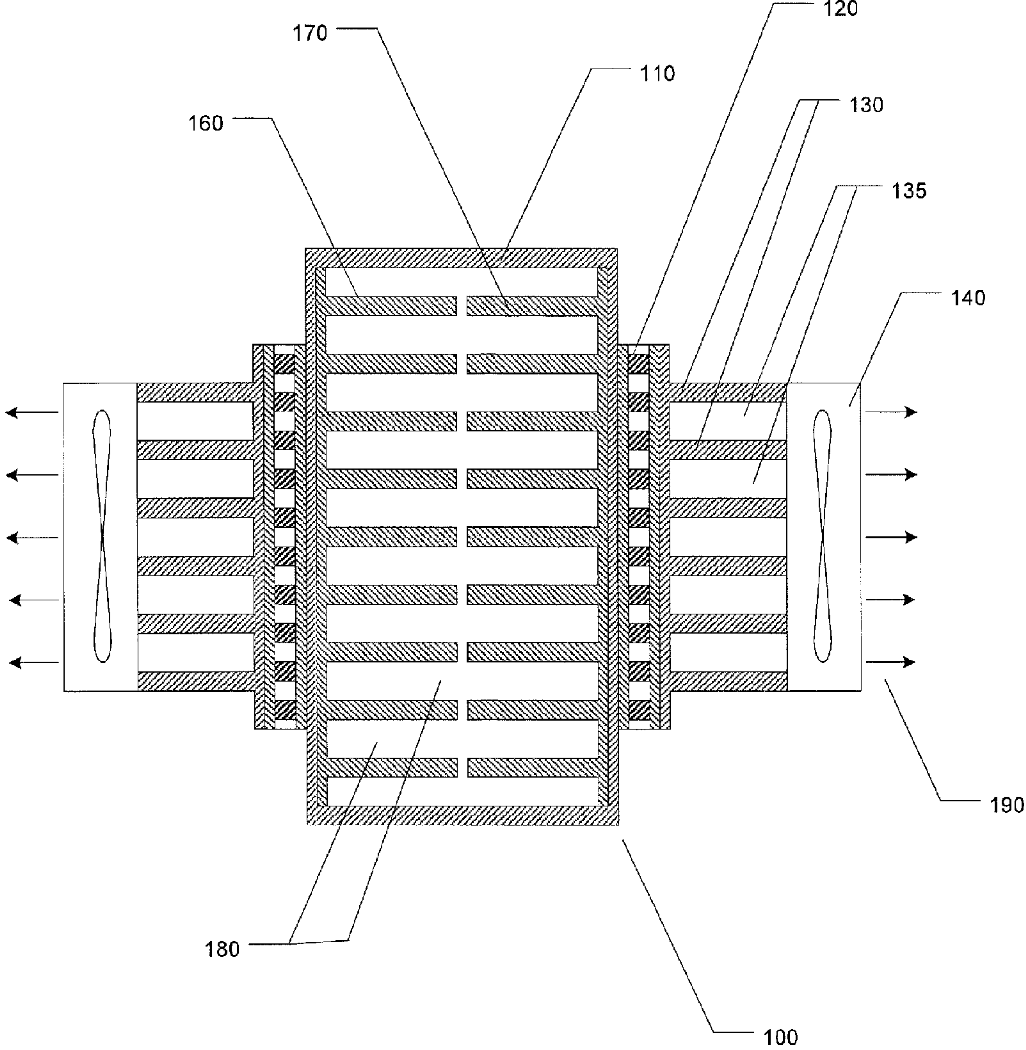


FIG. 3

METHOD FOR VAPOR CONDENSATION AND RECOVERY

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application is a divisional application of U.S. patent application Ser. No. 13/680,331, filed Nov. 19, 2012, which is based on and claims the benefit of U.S. provisional patent application Ser. No. 61/641,519, filed May 2, 2012, the contents of which are hereby incorporated by reference in their entirety.

BACKGROUND OF THE DISCLOSURE

[0002] Thin film deposition for semiconductor device fabrication is generally carried out through a gas phase process, such as chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD) or atomic layer deposition (ALD). In such a process a liquid chemical precursor is generally vaporized with the help of a carrier gas to form a vapor/gas mixture. The mixture then flows into a deposition chamber for thin film deposition on a substrate. The deposition chamber is usually maintained at a vacuum in order to meet the desired process conditions.

[0003] Following deposition, the gas/vapor mixture then flows through a vacuum pump for exhaust to the ambient atmosphere. During its passage through the pump, the vapor, which is chemically reactive, can react with the pump oil to change the physical and/or chemical characteristics of the oil. Over time, the pump oil becomes contaminated with the reactive precursor vapor and is no longer capable of maintaining the deposition chamber at the desired vacuum pressure. When this occurs, the system must be shut down for pump maintenance, leading to the loss of productivity for the deposition system.

[0004] To reduce the frequency of pump maintenance, various exhaust treatment devices have been developed and used in the semiconductor industry. They range from devices that use high temperature plasma to decompose the precursor vapor to systems that inject vapor to react with the precursor vapor to render them less harmful. While these measures can prolong or extend the operating life of the pump, they do not provide a permanent solution for the problem.

SUMMARY OF THE DISCLOSURE

[0005] In this disclosure, an apparatus is described for recovery of precursor vapor from a gas and precursor vapor mixture that is used for deposition in a semiconductor fabrication process. The apparatus comprises a housing with an inlet for the gas and precursor vapor mixture to flow into the housing. The housing also includes a first outlet for the gas of the gas precursor vapor mixture to flow out of. A second outlet of the housing permits the precursor liquid formed from the precursor vapor condensation to be discharged from the housing. The housing is maintained at a temperature sufficient for the precursor vapor to condense and form the precursor liquid.

[0006] The apparatus may include a thermal electric cooler for controlling the temperature of the housing to a selected value for condensing the precursor vapor to form the precursor liquid. The housing may be made of a heat conducting metal such as aluminum. A multitude of heat conducting surfaces for heat transfer are included in the housing which dissipates heat outside of the housing.

[0007] This disclosure also includes a method for recovery of precursor vapor from a gas and precursor mixture after use in deposition in a semiconductor fabrication process. After use in deposition, the gas/precursor mixture is directed through a multitude of heat transfer surfaces in a heat conducting housing causing precursor vapor in the gas and precursor mixture to condense. The precursor liquid formed through condensation from the precursor vapor is collected in a reservoir.

[0008] The method may include the additional steps of removing heat produced by precursor vapor condensation through the use of a thermal electric cooler so that the heat is removed through a multitude of heat transfer surfaces to outside of the housing.

[0009] Additionally, the gas and precursor mixture may be passed through a filter to remove suspended particles in the mixture prior to the gas and precursor mixture's use in deposition.

[0010] This disclosure also includes a method of fabricating integrated circuit devices including the steps of generating a gas and precursor vapor mixture; passing the gas and precursor vapor mixture through a deposition chamber to form a thin film on a substrate; and condensing unused precursor vapor of the gas and precursor vapor mixture in a condenser to collect condensed precursor vapor in liquid form.

[0011] This method also may include the additional step of removing heat produced by the precursor vapor condensation through the use of a thermal electric cooler that dissipates the heat through a multitude of heat transfer surfaces to outside of the housing.

[0012] Additionally, the gas and precursor mixture is passed through a filter to remove suspended particles in the mixture prior to the gas and precursor mixture entry into the deposition chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1** is a schematic diagram of a semiconductor thin film deposition system in which the vapor recovery condenser of the present disclosure is used to condense vapor for recovery.

[0014] FIG. **2** is a vertical sectional view of the vapor condensing apparatus of the present disclosure in its preferred embodiment.

[0015] FIG. **3** is a horizontal sectional view of the vapor condensing apparatus of the present disclosure in its preferred embodiment.

DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

[0016] The present disclosure describes a method and an apparatus for condensing the precursor vapor to form a precursor liquid downstream of the deposition chamber. The condensed liquid is substantially unchanged in its physical and/or chemical characteristics from the original precursor liquid used for film deposition. The collected liquid can be purified for recycling and reused or be disposed of in a safe manner to minimize the potential harmful effect on the environment.

[0017] FIG. **1** is a schematic diagram of a semiconductor thin film deposition system including a vapor recovery condenser of the present disclosure placed downstream of the deposition chamber to reduce pump oil contamination and

improve the reliability of the film deposition system. Like reference characters will be used for like elements throughout the figures. The system includes a vapor generating apparatus **30**, which can be a bubbler or a direct liquid injection vaporizer. The more widely used direct liquid injection vaporizer is shown for convenience.

[0018] Vaporizer **30** of FIG. **1** is provided with a gas inlet, **32**, a liquid inlet, **34**, and an outlet **36**. Gas inlet **32** is connected to a pressurized gas source, **10**, containing the desired carrier gas. Liquid inlet **34** is connected to a pressurized liquid source **20** containing the precursor liquid to be vaporized. Vaporizer **30** is generally heated to a specific operating temperature. As the gas and liquid flow through the vaporizer at the desired rates of gas and liquid flow, the gas is heated and the liquid is vaporized to form vapor at substantially the same temperature. The resulting gas/vapor mixture then flows out of vaporizer **30** through outlet **36** into a filter, **80**, to remove suspended particles that may be present in the gas/vapor mixture. The clean gas/vapor mixture then flows into deposition chamber **40** through chamber inlet **42** to form thin film on substrate **50**. The gas/vapor mixture then flows out of deposition chamber **40** through outlet **44**.

[0019] The system is typically provided with gas and liquid flow controllers in order to control the gas and liquid flow rates to the desired set point values. The vaporizer and deposition chamber are usually heated by electric heaters. They are also provided with temperature controllers in order to operate the vaporizer and the deposition chamber to their respective temperature settings. In addition, the deposition is typically carried out in vacuum. The required vacuum pressure is typically achieved by means of a vacuum pressure sensor and a vacuum pressure controller in order to operate the system at a specific vacuum pressure. For simplicity, all of these controllers including the sensors that form part of the control system for the semiconductor thin film deposition tool are not shown explicitly.

[0020] A variety of carrier gases has been used for thin film deposition. Inert gases such as nitrogen, helium and argon are quite common. Gases such as hydrogen and oxygen are also used in some applications. Precursor liquids such as TEOS (tetra ethyl ortho silicate), $TiCl_4$ (titanium tetra chloride), various metal organic compounds, and compounds such as TEMAH (tetraethyl amino hafnium) and TEMAZ (tetraethyl amino zirconium) for hi-k (high dielectric constant) film deposition by ALD (atomic layer deposition) processes are also widely used.

[0021] In the conventional vapor generation and deposition system a vacuum pump, **70**, is located downstream of deposition chamber **40** in order to maintain the deposition chamber **40** to a desired vacuum pressure. Vacuum pump, **70**, then exhausts the gas/vapor mixture to the ambient atmosphere. **100211** The thin film deposition system of FIG. **1** also includes a vapor condensing apparatus **60**, which is provided with an inlet **62** for the vapor and carrier gas mixture from deposition chamber to enter, an outlet **66** for the condensed liquid to exit, an external reservoir **80** for capture and store the condensed liquid, and an outlet, **64**, for the carrier gas to exit. The carrier gas is substantially free of the precursor vapor, which has been condensed and collected by the vapor condensing apparatus **60**, then enters pump **60** for exhaust to the ambient.

[0022] Unlike prior art exhaust treatment systems that are designed to destroy the precursor vapor to prevent or reduce pump contamination, the vapor condensing apparatus of the present disclosure condenses the precursor vapor without substantially changing its chemical nature or its physical characteristics. The condensed precursor liquid is generally quite pure. The collected liquid can be stored in the external reservoir **80**. Alternatively, the condensed liquid can be stored internally in the vapor condensing apparatus **60** from which the stored liquid can be drained out of the system from time to time for safe disposal or reuse.

[0023] FIG. **2** shows a vertical sectional view of vapor condensing apparatus **60** of FIG. **1**. The apparatus is shown generally located at **100** with an inlet, **62**, for the gas/vapor mixture to enter and an outlet **66** for the condensed liquid to flow out. The gas, which is substantially free of the precursor vapor, then exits the vapor condensing apparatus **100** through outlet **64** and flows into vacuum pump **70** for exhaust to the ambient atmosphere.

[0024] The vapor condensing apparatus **100** generally operates under vacuum. It is provided with a vacuum tight envelop **105** with removable cover plates, **110** and **115**, that are held in place by screws, **106**, and gaskets, **108**. Alternatively, cover plates **110** and **115** can be permanently welded in place to form a vacuum tight envelop. Apparatus **100** is generally constructed of a heat conducting metal, such as aluminum. A thermoelectric cooler **120** is placed in good thermal contact with the heat conducting metal envelop **105** in order to control its temperature to a suitably low value, typically below about 25 degrees C. Within the vacuum tight envelop, there are multitudes of heat transfer surfaces **160** and **170** that are in good thermal contact with the heat conducting envelop. Since heat transfer surfaces **160** and **170** are in good thermal contact with the heat conducting metal envelop **105**, the temperature of these heat transfer surfaces **160** and **170** is also substantially the same as that of envelop **105** and is thus also below about 25° C.

[0025] As the gas/vapor mixture flows along heat transfer surfaces **160** and **170** within the vacuum tight envelop **105**, precursor vapor will condense on these heat transfer surfaces to cause it to form liquid on the surfaces. This precursor condensed liquid will then flow by gravity along these surfaces into the annular liquid collecting trough **180** below. The condensed liquid will then flow out of trough **180** through exit **66** into external reservoir **80** shown in FIG. **1**

[0026] When vapor condenses on the heat transfer surfaces **160** and **170**, the vapor condensation release heat. This heat will be transferred by conduction to the vacuum tight envelop **105** for it to be carried away by the thermoelectric cooler **150** and rejected to the ambient atmosphere by the external heat transfer surface **130**. A cooling fan **140** will draw air from ambient causing it to flow in the indicated direction of the arrows **150** and blowing this air back to the ambient in the direction of arrows **190**.

[0027] Thermoelectric cooler **120** is typically operated by DC power and controlled by a temperature sensor to a selected temperature by feedback electronic control. Such controls are familiar to those skilled in the art of temperature control the thermoelectric cooler and will not be further described.

[0028] FIG. **3** is a horizontal sectional view of the vapor condensing apparatus of the present disclosure in its preferred embodiment. The internal heat transfer surfaces are spaced apart from each other by gaps of empty spaces **180**. These empty spaces form flow channels through which the vapor/gas mixture can flow through, thus permitting the vapor to condense on the vertical surfaces **160** and **170**. Similarly,

external heat transfer surfaces **130** also form vertical flow channels **135** to allow cooling air from the ambient atmosphere to flow through and be blown by cooling fan **140** in the general direction of arrows **190**.

[0029] Although the present invention has been described with reference to referred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for recovery of precursor vapor from a gas and precursor mixture after use in deposition in a semiconductor fabrication process, the method comprising:
- directing said gas and precursor mixture after deposition to pass through a multitude of heat transfer surfaces in a heat conducting housing causing precursor vapor in said gas and precursor mixture to condense; and
- collecting precursor liquid formed from the precursor vapor condensation in a reservoir.

2. The method of claim **1** including the additional steps of removing heat produced by precursor vapor condensation by a thermal electric cooler; and dissipating the heat so removed through a multitude of heat transfer surfaces outside said housing.

3. The method of claim **1** including the additional step of passing said gas and precursor mixture through a filter to remove suspended particles in the mixture prior to the gas and precursor mixture's use in deposition.

4. A method of fabricating integrated circuit devices including the steps of:
- generating a gas and precursor vapor mixture;
- passing said gas and precursor vapor mixture through a deposition chamber to form a thin film on a substrate; and
- condensing precursor vapor of said gas and precursor vapor mixture in a condenser to collect condensed precursor vapor in liquid form.

5. The method of claim **4** including the additional steps of removing heat produced by precursor vapor condensation by a thermal electric cooler; and dissipating the heat so removed through a multitude of heat transfer surfaces outside said housing.

6. The method of claim **4** including the additional step of passing said gas and precursor mixture through a filter to remove suspended particles in the mixture prior to the gas and precursor mixture entry into said deposition chamber.

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