



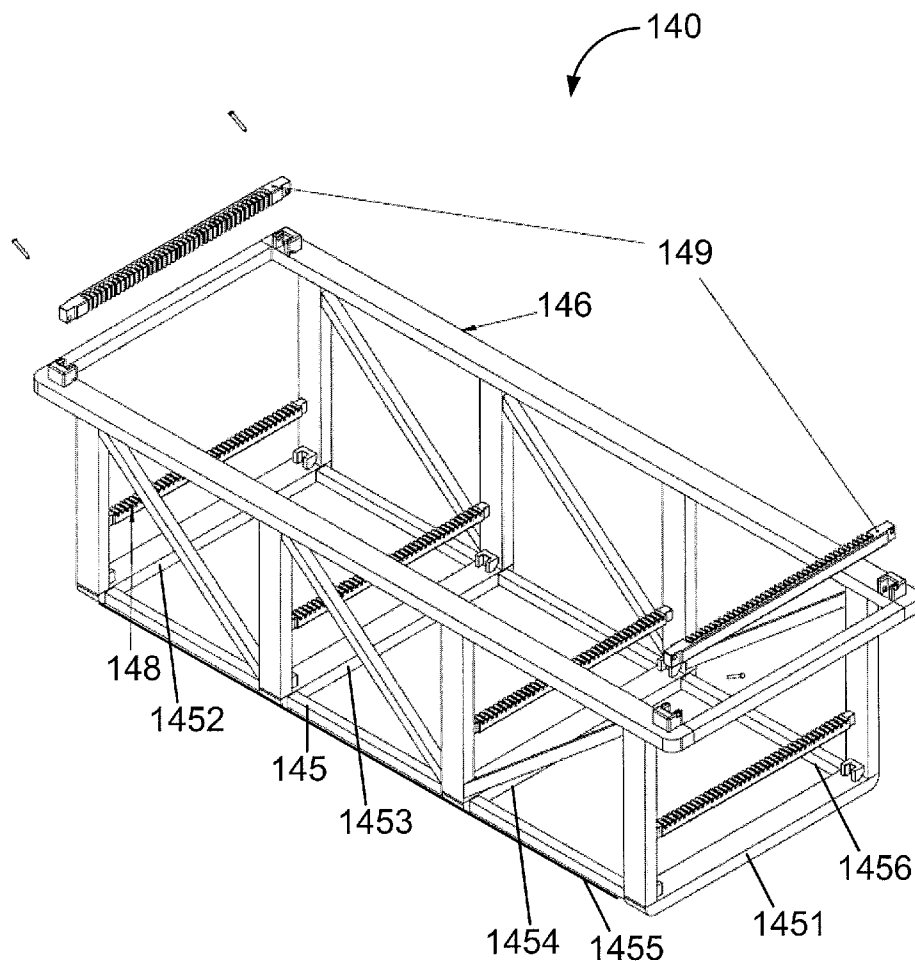
US 20140147800A1

(19) **United States**(12) **Patent Application Publication**
Alexander et al.(10) **Pub. No.: US 2014/0147800 A1**(43) **Pub. Date: May 29, 2014**(54) **QUARTZ BOAT METHOD AND APPARATUS
FOR THIN FILM THERMAL TREATMENT****Publication Classification**(71) Applicant: **Stion Corporation**, (US)(72) Inventors: **Paul Alexander**, San Jose, CA (US);
Jurg Schmitzberger, San Jose, CA
(US); **Ashish Tandon**, Sunnyvale, CA
(US); **Robert D. Wieting**, Simi Valley,
CA (US)(73) Assignee: **Stion Corporation**, San Jose, CA (US)(21) Appl. No.: **13/889,602**(22) Filed: **May 8, 2013****Related U.S. Application Data**(62) Division of application No. 13/171,089, filed on Jun.
28, 2011, now Pat. No. 8,461,061.(60) Provisional application No. 61/367,211, filed on Jul.
23, 2010.(51) **Int. Cl.****H01L 21/673** (2006.01)(52) **U.S. Cl.**CPC **H01L 21/67316** (2013.01)USPC **432/253**

(57)

ABSTRACT

A method of supporting a plurality of planar substrates in a tube shaped furnace for conducting a thermal treatment process is disclosed. The method uses a boat fixture having a base frame including two length portions and a first width portion, a second width portion, and one or more middle members connected between the two length portions. Additionally, the method includes mounting a removable first grooved rod respectively on the first width portion, the second width portion, and each of the one or more middle members, each first grooved rod having a first plurality of grooves characterized by a first spatial configuration. The method further includes inserting one or two substrates of a plurality of planar substrates into each groove in the boat fixture separated by a distance.



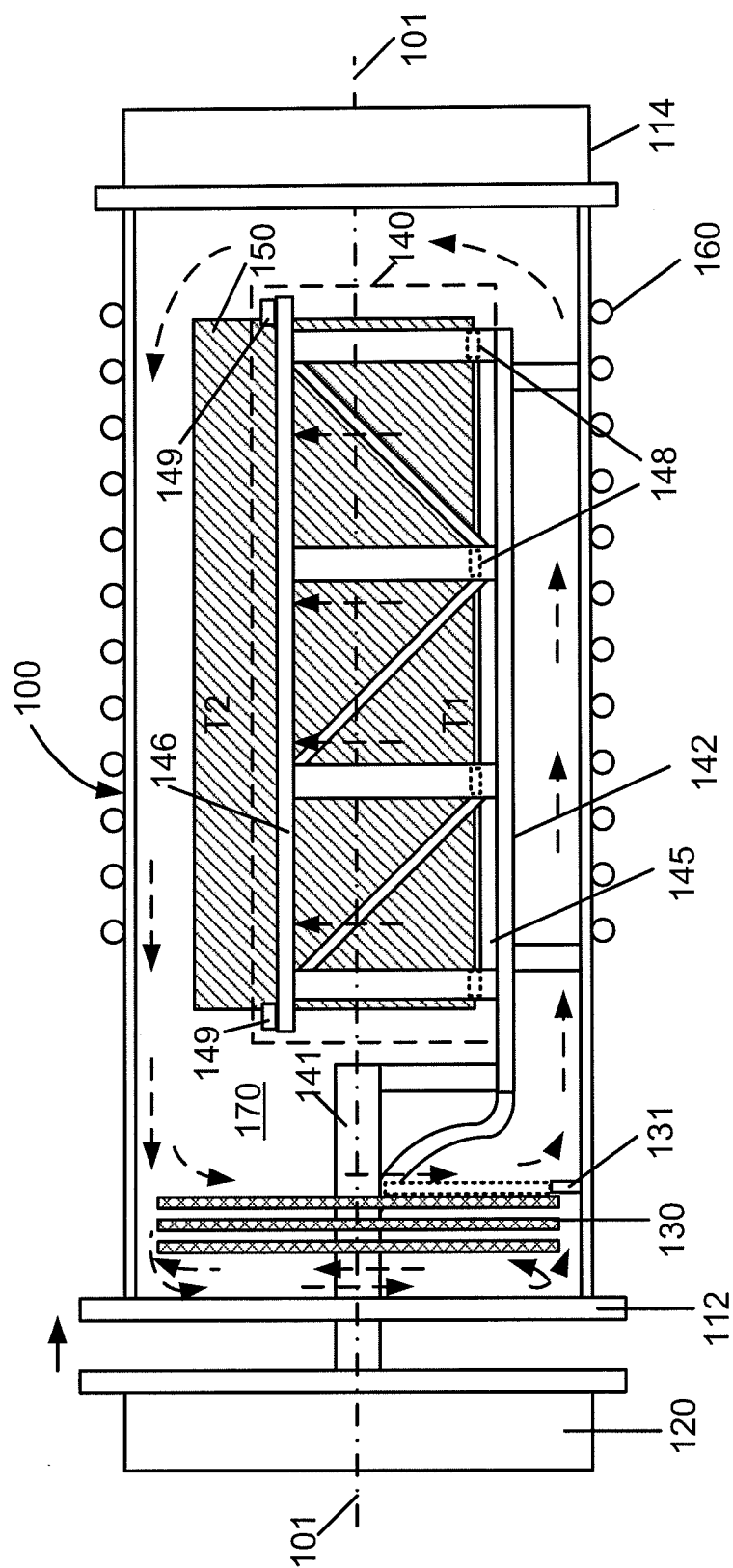


FIG. 1

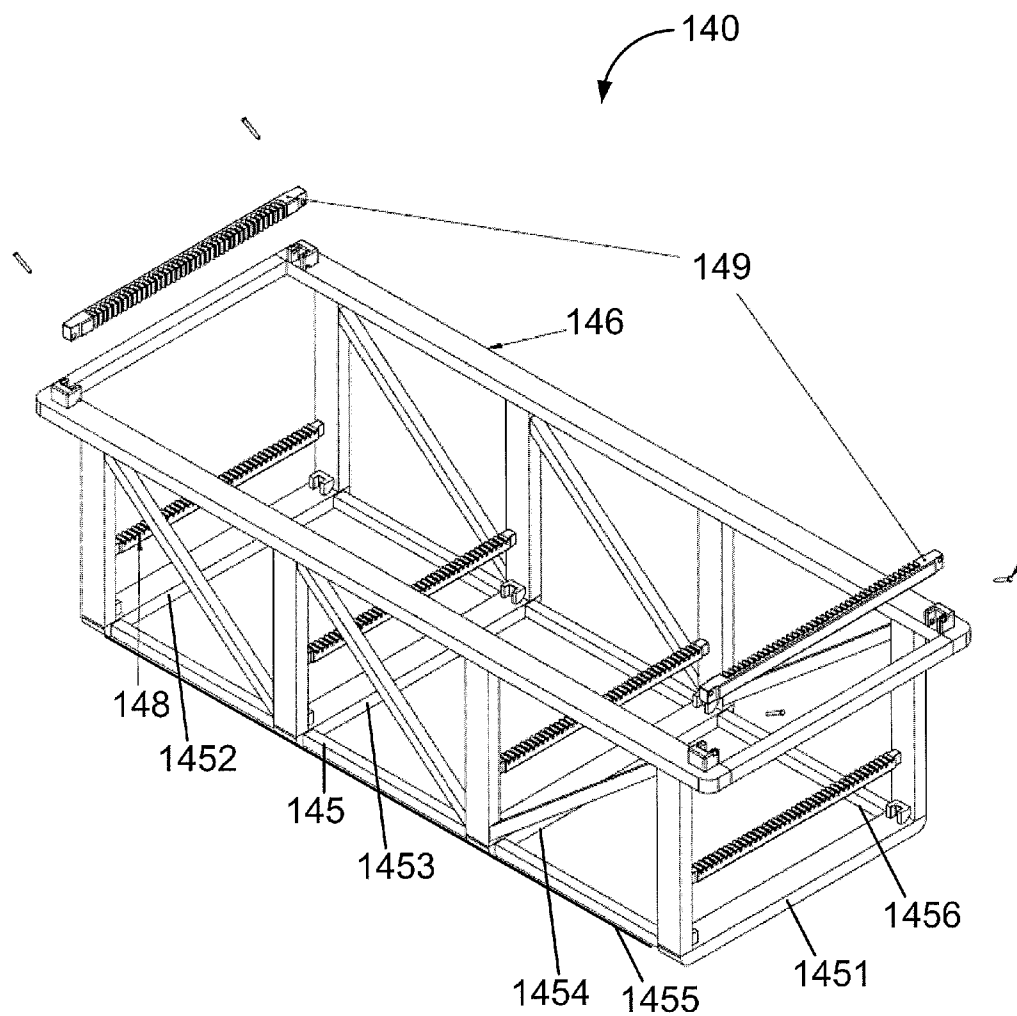


FIG. 2

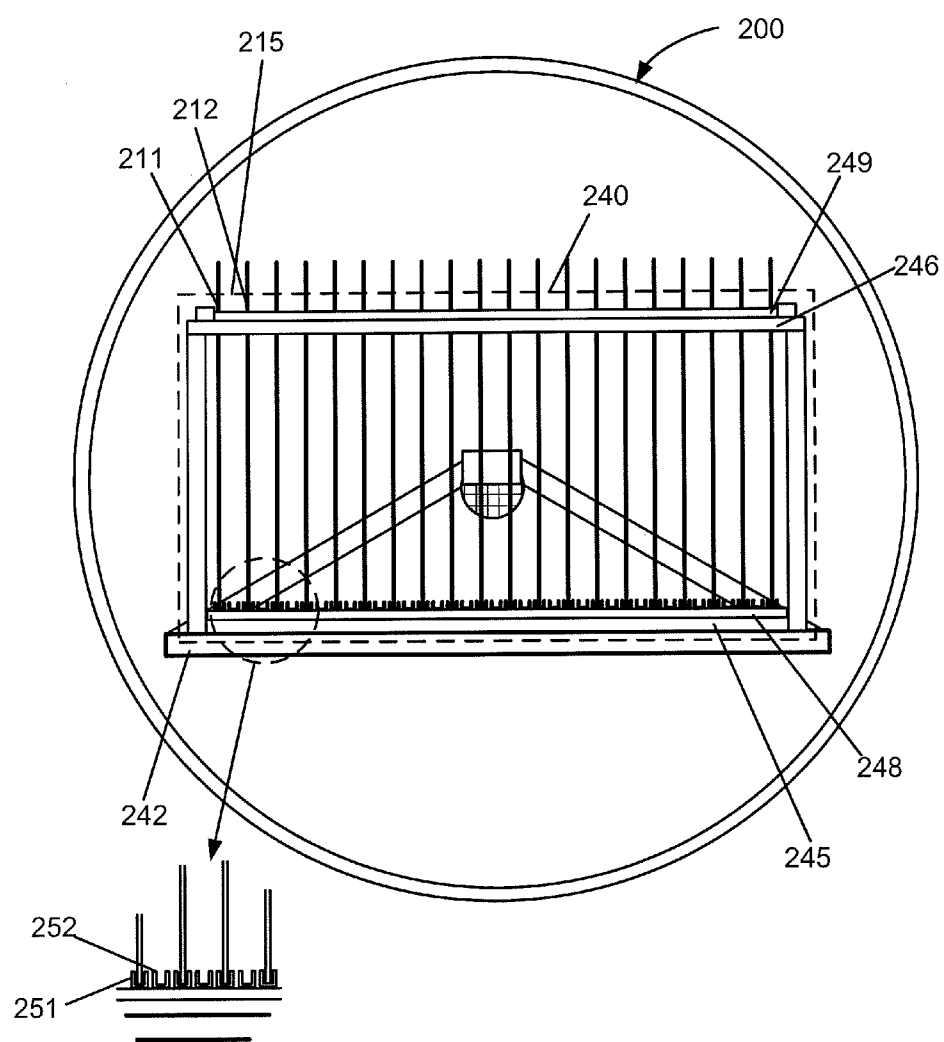


FIG. 3

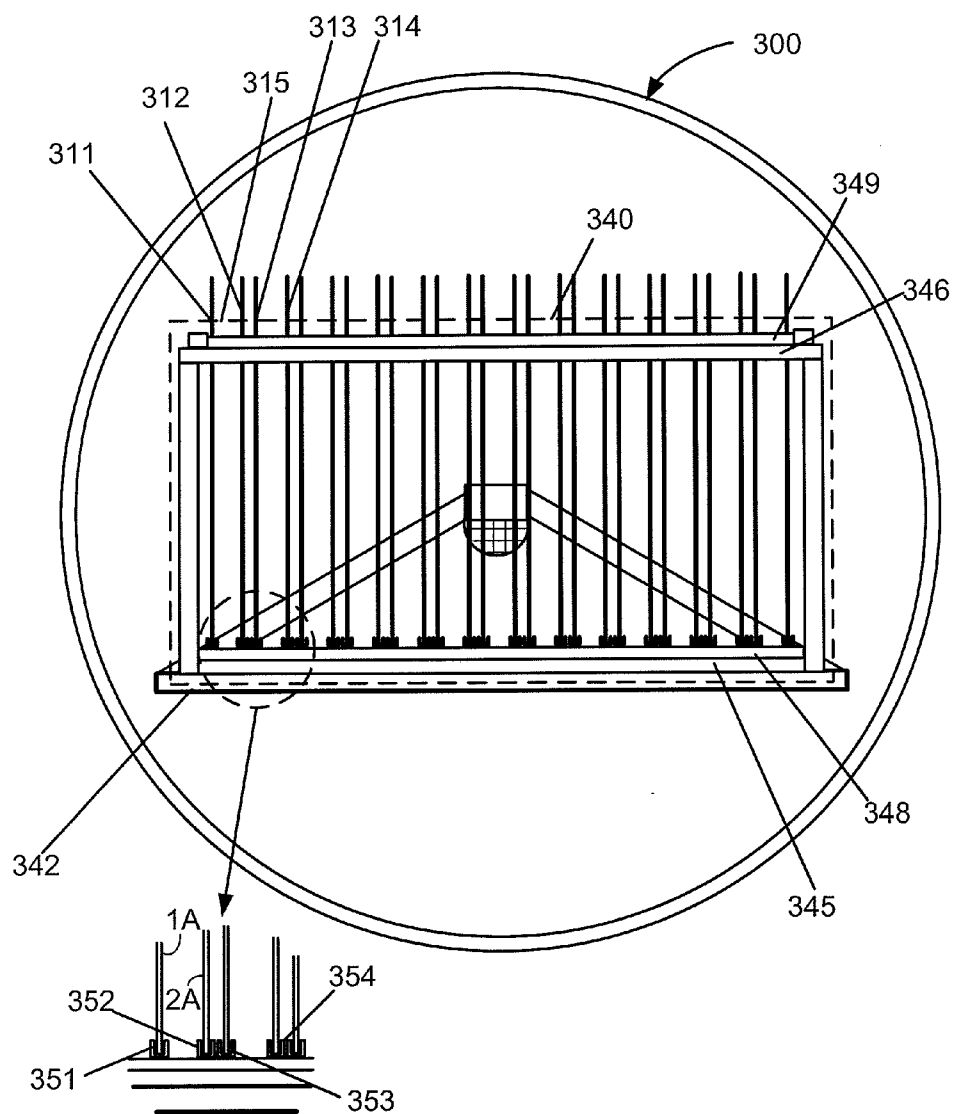


FIG. 4

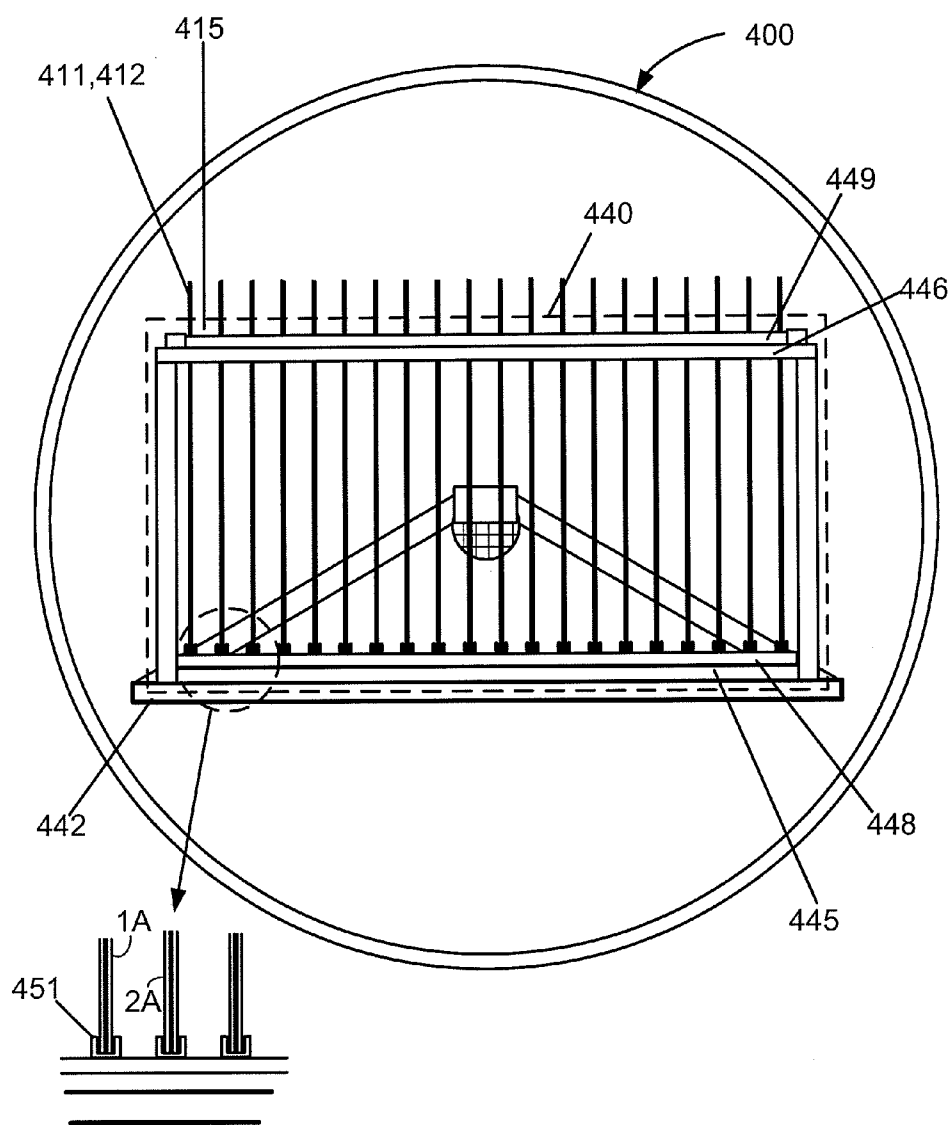


FIG. 5

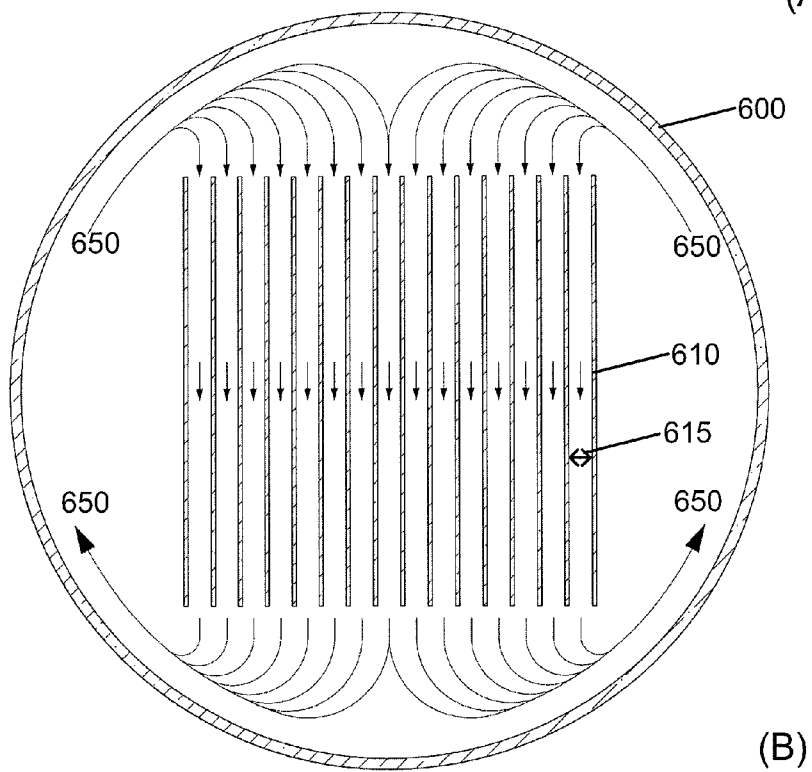
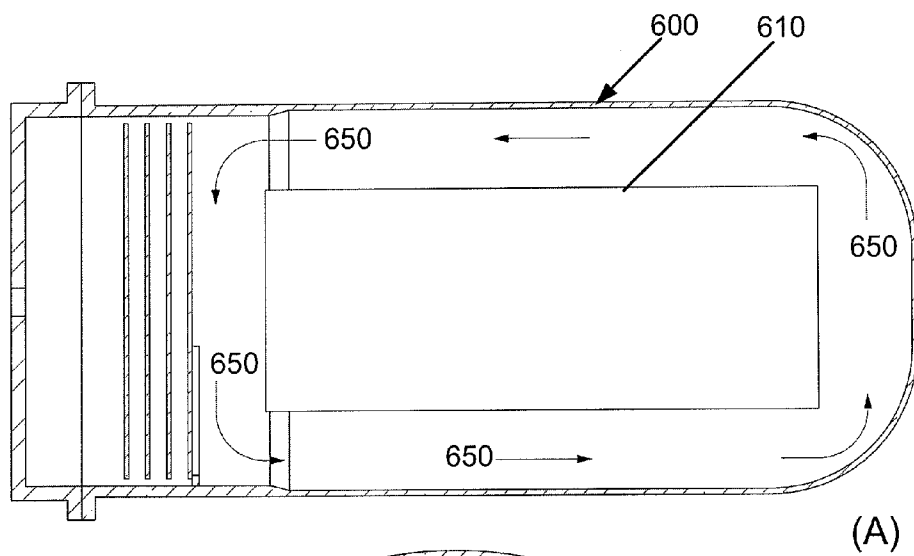


FIG. 6

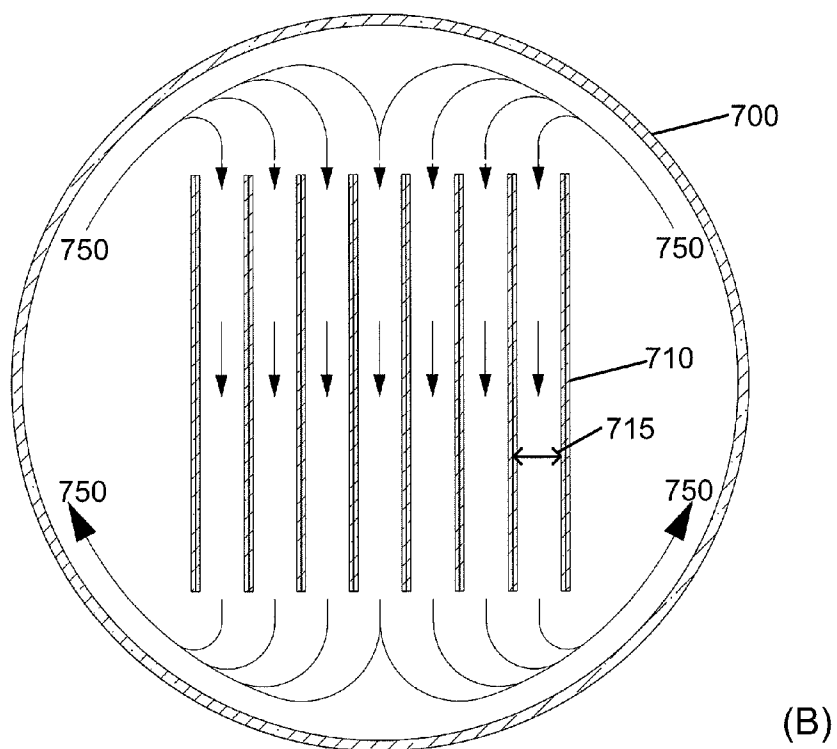
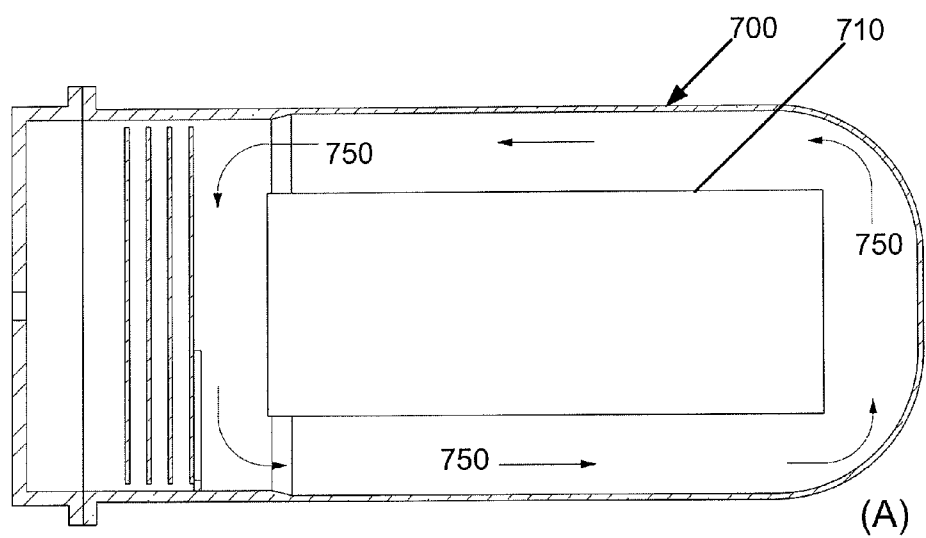


FIG. 7

QUARTZ BOAT METHOD AND APPARATUS FOR THIN FILM THERMAL TREATMENT

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a divisional of U.S. patent application Ser. No. 13/171,089, filed Jun. 28, 2011, which claims priority to U.S. Provisional Application No. 61/367,211, filed Jul. 23, 2010, commonly assigned, and hereby incorporated by reference in its entirety for all purposes.

BACKGROUND OF THE INVENTION

[0002] The present invention relates generally to photovoltaic materials and manufacturing method. More particularly, the present invention provides a method and apparatus for thin film thermal treatment. Embodiments of the invention include a method and apparatus for holding a plurality of extra large substrates for achieving substantially uniform substrate temperature during a thermal process to form a photovoltaic absorber material, but it would be recognized that the invention may be applied for other thin-film treatment applications.

[0003] From the beginning of time, mankind has been challenged to find ways of harnessing energy. Energy comes in forms such as petrochemical, hydroelectric, nuclear, wind, biomass, solar, and more primitive forms such as wood and coal. More recently, environmentally clean and renewable source energy has been desired. Clean and renewable sources of energy also include wind, waves, biomass, and the like. Still other types of clean energy include solar energy.

[0004] Solar energy technology generally converts electromagnetic radiation from the sun to other forms of energy. These other forms of energy include thermal energy and electrical power. For electrical power applications, solar cells are often used. Although solar energy is environmentally clean and has been successful to a point, many limitations remain before it becomes widely used throughout the world. As an example, one type of solar cell uses crystalline materials, which are derived from semiconductor material ingots. These crystalline materials can be used to fabricate optoelectronic devices that include photovoltaic and photodiode devices that convert electromagnetic radiation to electrical power. However, crystalline materials are often costly and difficult to make on a large scale. Additionally, devices made from such crystalline materials often have low energy conversion efficiencies. Other types of solar cells use "thin film" technology to form a thin film of photosensitive material to be used to convert electromagnetic radiation into electrical power. Similar limitations exist with the use of thin film technology in making solar cells. That is, efficiencies are often poor. Additionally, film reliability is often poor and cannot be used for extensive periods of time in conventional environmental applications. Often, thin films are difficult to mechanically integrate with each other. These and other limitations of these conventional technologies can be found throughout the present specification and more particularly below.

[0005] As an effort to improve thin film solar cell technology, processes of manufacturing an advanced CIS and/or CIGS based photovoltaic film stack on sized substrates with planar, tubular, cylindrical, circular or other shapes have been introduced. There are various manufacturing challenges in forming the photovoltaic film stack, such as maintaining

structure integrity of substrate materials, controlling chemical compositions of the ingredients in one or more precursor layers, carrying out proper reactive thermal treatment of the one or more precursor layers within a desired gaseous environment, ensuring uniformity and granularity of the thin film material during reactive thermal treatment, etc. Especially, when manufacturing the thin film based solar cell on large sized substrate, temperature uniformity across whole substrate surface is desired. While conventional techniques in the past have addressed some of these issues, they are often inadequate in various situations. Therefore, it is desirable to have improved system and method for processing thin film photovoltaic devices on planar or non-planar shaped, fixed or flexible substrates.

BRIEF SUMMARY OF THE INVENTION

[0006] This invention provides a method and apparatus for holding large substrates with precursor material for thermal treatment. The method and apparatus provide an improved loading configuration for a plurality of substrates during thermal processes for manufacture of thin film based photovoltaic devices.

[0007] This invention provides a method of holding a plurality of planar substrates for thermal treatment in a tube shaped furnace having a first end and a second end. The tube shaped furnace is surrounded by heaters for conducting a thermal treatment process. The first end has a door and the second end is insulated. The method further includes providing a boat fixture having a base frame coupled to a top frame. The base frame includes two length portions and a first width portion, a second width portion, and one or more middle members connected between the two length portions. A grooved rod is mounted respectively on the first width portion, the second width portion, and each of the one or more middle members. The substrates are placed in the boat fixture so that the grooves support spaced-apart planar substrates by a desired distance. The boat fixture is loaded via a rack fixture into the tube shaped furnace for the thermal treatment process.

[0008] The method includes a substrate arrangement where each substrate is inserted alone in one groove without a front/back phase configuration, and with a minimum spacing between any neighboring substrates at least equal to a desired value, e.g. about 1 inch.

[0009] In another embodiment, the loading configuration includes a substrate arrangement where each substrate is inserted alone in one groove with a front/back surface of any substrate directly faces another front/back surface of a neighboring substrate inserted in another groove at a desired spacing.

[0010] In yet another embodiment, the loading configuration includes replacing each first grooved rod on the base frame by a second grooved rod mounted on the first width portion, the second width portion, and each of the one or more middle members. Each second grooved rod includes a second plurality of grooves in a second spatial configuration.

[0011] In an alternative embodiment, the present invention provides an apparatus for holding one or more substrates for thermal treatment. The apparatus includes a frame fixture having a substantially rectangular prism shape including a base frame, a top frame, one or more side connection bars coupled the base frame and the top frame. The base frame has two width members and one or more middle joint members connected between two length members. The apparatus fur-

ther includes a first grooved rod removably mounted on each of the two width members and each of the one or more middle joint members. Each first grooved rod includes a first plurality of grooves respectively configured to support a plurality of planar substrates in a first configuration. Additionally, the apparatus includes a first grooved bar removably mounted on each of two width members of the top frame. Each first grooved bar includes a second plurality of grooves respectively aligned with the first plurality of grooves for guiding the plurality of planar substrates. Furthermore, the apparatus includes a rack structure configured to be a mechanical support of the frame fixture in a loading position inside a furnace for subjecting the plurality of planar substrates in the first configuration to one or more reactive thermal treatment processes.

[0012] In yet another alternative embodiment, the present invention provides a method for processing substrates through thermal treatments with each of their temperature difference being controlled to within 15 degrees Celsius at least during a dwell stage between ramping up or down stages. Moreover, the furnace provides an enclosed volume for subjecting a precursor film containing at least copper and indium species overlying one surface of each substrate to a gaseous selenium or sulfur species to produce a photovoltaic absorber for solar cell.

[0013] The invention provide an apparatus for holding a plurality of planar substrates overlaid with photovoltaic precursor layers in a furnace tube. The furnace tube has heaters to supply heat energy in a controlled manner. The furnace can be filled with desired gaseous species including selenium and/or sulfur for a reactive thermal treatment of the precursor layer for manufacture of photovoltaic cells. In particular, the apparatus utilizes a quartz boat fixture having a rack fixture configured with a plurality of grooves for supporting large planar (rectangular or square in most cases) glass substrates. Some embodiments of the invention provide loading configurations of a plurality of planar substrates in the boat fixture by aligning them vertically, arranging the plurality of grooves with a proper size for each one, and disposing them with an optimum spacing between each other and in periodic groups, and others. In some embodiments, the loading configurations of the substrates in the quartz boat fixture allow an effective convection flow in between the planar substrates to transfer heat energy from hotter regions to cooler regions of the each substrate during the reactive thermal treatment process.

[0014] In a specific embodiment, the temperature across each substrate is maintained substantially uniform or at least the temperature difference is controlled to be smaller than a set value. In another specific embodiment, an alternative loading configuration includes two substrates being inserted in each groove in a back-to-back manner with respective precursor layer exposed at front surface. The precursor layer of one of the two planar substrates loaded in a first groove faces the precursor layer of one of two planar substrates loaded in a neighboring groove at a predetermined distance away from one side, while the precursor layer of another one of the two planar substrates in the first groove faces the precursor layer of one of two planar substrates loaded in a neighboring groove at the predetermined distance away from an opposite side. Therefore, the number of planar substrates loaded in the quartz boat fixture is increased compared to loading one substrate only to one groove without reducing the spacing between the subjected surfaces of neighboring substrates. In a specific embodiment, the predetermined distance

between the neighboring substrates is associated with the furnace tube configuration, the dimension of the substrates, the gap distance between the loaded substrates and inner wall of the furnace tube, as well as the one or more thermal treatment processes. For example, the furnace is made as tube shape for facilitating gaseous convection flow therein. The furnace tube is made of quartz material which is semi-transparent to thermal radiation from several zoned heaters around tube with temperature control for different regions. Coolers also can be added for easily ramping furnace temperature down as desired in certain stages of the thermal treatment process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a side view along an axis of a furnace tube including a quartz boat fixture with loaded planar substrates for manufacture of photovoltaic cells;

[0016] FIG. 2 is a perspective view of the quartz boat fixture for loading a plurality of planar substrates;

[0017] FIG. 3 is a side view from the closed end of the furnace tube loaded with a quartz boat fixture holding a plurality of planar substrates;

[0018] FIG. 4 is a side view of the furnace tube loaded with a quartz boat fixture holding a plurality of planar substrates;

[0019] FIG. 5 is a side view of the furnace tube loaded with a quartz boat fixture holding a plurality of planar substrates;

[0020] FIG. 6 is a cross-section view of convection flows according to an embodiment of the present invention.

[0021] FIG. 7 is a cross-section view of convection flows according to another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0022] FIG. 1 is a side view along an axis of a furnace tube including a quartz boat fixture with loaded planar substrates for manufacture of photovoltaic cells according to an embodiment of the present invention. As shown, the furnace tube **100** is characterized by a length of tubular shaped container or chamber enclosing a volume of space. In an embodiment, the furnace tube **100** has a first end **112** that is configured to be engaged, covered, and sealed by a cover member (or a door) **120** and a second end **114** on the opposite side. The inner wall of the furnace tube **100** is a smooth surface for facilitating internal gas convection during thermal process. In another embodiment, the furnace tube **100** is set up in an orientation with its tube axis **101** along horizontal (or floor) direction. The second end **114** can be also opened and usually is thermally insulated. A gas supply device and/or a gas monitor (not shown) can be coupled to the furnace tube **100** for providing a controllable gaseous environment required for conducting one or more reactive thermal treatments of any work samples loaded in the furnace tube **100**. A plurality of heaters **160** are wrapped around the furnace tube for providing radiation heat required for the thermal treatments. The volume of space **170** of the furnace tube **100**, depending on its diameter and length, allows the boat fixture **140** with inserted substrates to be loaded into the furnace tube **100** and is supported by a rack fixture **142**.

[0023] The boat fixture **140** can hold a plurality of planar substrates **150** for thermal treatment within the furnace tube **100**. For example, 40 or more numbers of planar rectangular shaped substrates can be held in the boat fixture **140** at one time. Each planar substrate can have a dimension of a few tens of centimeters in width and more than 100 centimeters in

length. Glass substrates with 65 cm×165 cm rectangular shape are used for manufacture of thin-film photovoltaic cells. In certain applications, smaller sized substrates in dimensions of about 20 cm×20 cm, or 20 cm×50 cm, or other form factors, can be loaded with a slight modification of the loading configuration of the boat fixture. During the thermal treatment processes, a temperature uniformity of the substrate usually is a key process parameter. As a simple indicator of the temperature uniformity, a temperature difference across the substrate, i.e., $\Delta T = T_1 - T_2$ can be monitored, where T_1 represents a temperature near bottom region of the substrate and T_2 represents a temperature near top region of the substrate. Of course, more complete temperature mapping over a whole surface may be needed.

[0024] In an alternative embodiment as illustrated in FIG. 1, the invention also provides a method for forming a flexible loading configuration of a plurality of planar substrates in a furnace. As shown, the boat fixture **140**, which is removably supported onto the rack fixture **142**, is configured to load a plurality of planar substrates **150** substantially in a vertical orientation along the gravity direction. In a specific embodiment, the boat fixture **140** is made of quartz or other material being both a good thermal conductor and an electrical insulator. Throughout this specification, it is also directly referred to be a quartz boat, although it does not intend to limit the choice of materials for the boat fixture **140**. In another specific embodiment, the boat fixture **140** can be loaded in and out through the first end **112**. A rack member **141** can be used to couple the boat fixture **140** to a loader (not shown) when the cover member **120** is opened and load the boat fixture from the loader or unload the boat fixture back to the loader.

[0025] In a specific embodiment, the boat fixture **140** has a base frame **145** and a top frame **146**, although only side view is shown in FIG. 1. The boat fixture **140** includes several grooved rods **148** removably mounted on the base frame **145** and two grooved bars **149** removably mounted on the top frame **146**. Each grooved rod **148** includes a plurality of grooves or slots spatially aligned for respectively supporting a plurality of planar substrates **150**. The two grooved bars **149** also have the corresponding plurality of grooves for providing guide to the loaded substrates **150**. In an embodiment, each groove is disposed an equal spacing away from its neighboring groove and each groove has a size fit for support at least one substrate. In another embodiment, each grooved rods **148** or each grooved bars **149** can be replaced by another set of grooved rods or grooved bars which contain grooves in an alternative configuration with either a different groove spacing or groove spacing and groove size combination. For example, in a configuration a groove may have a first spacing from its left neighboring groove while a second spacing from its right neighboring groove. Further, each groove may have a bigger groove size for holding two planar substrates in a back-to-back configuration. In an alternative embodiment, each of the plurality of planar substrates **150** in substantially vertical orientation and parallel to each other as the quartz boat fixture **140** is loaded into the furnace tube **100**, provided that the tube axis **101** is set along a horizontal direction. Of course, there are many other variations, modifications, and alternatives.

[0026] Additionally, FIG. 1 also shows one or more baffles **130** and **131** being placed between the first end **120** (with a door) and the loaded quartz boat fixture **140**. The baffles are used for controlling the convection flow and keeping the heated gases being substantially circulated around the spatial

region occupied by the loaded substrates instead being lost to relative cold door **130**. Further a crescent shaped baffle **131** is disposed to a lower portion position of the furnace tube **100** for blocking the colder gases return to the substrate spatial regions. The crescent shaped baffle **131** is made of quartz and has a curved body with a height and a curvature substantially similar to that of the inner wall. In an embodiment, the crescent shaped baffle can have an arc length about one half of an inner perimeter of the furnace tube or less. In another embodiment, the crescent shaped baffle can have an arc length about $\frac{2}{3}$ of an inner perimeter of the furnace tube or less. In another embodiment, the crescent shaped baffle can have an arc length ranging from one half to about $\frac{2}{3}$ of an inner perimeter of the furnace tube **100**. In an embodiment, the height and the arc length are parameters adjustable for achieving desired adjustment to the convection flows or currents passed by.

[0027] As used herein, the “crescent” means a “shape produced when a circular disk has a segment of another circle removed from its edge, so that what remains is a shape enclosed by two circular arcs of different diameters which intersect at two points,” although there can be variations, modifications, and alternatives, according to one or more embodiments. For example, some descriptions or definitions can be found in public information website such as <http://en.wikipedia.org/wiki/Crescent>. As an example, the term can include one or more crescent shaped members, although there can also be partial crescent shaped members.

[0028] As used herein, “top”, “bottom”, “open”, “close”, have their plain meanings for illustrating the configuration used in the exemplary figures in the specification and should not be treated as a claimed limitation. Similarly, the terms “lower” and/or “upper” are to be interpreted by ordinary meaning, and do not have any specific reference regarding to the direction of gravity according to one or more embodiments. In some embodiments, the terms lower and/or upper can be reference to gravity, although there can be some general variations, modifications, and alternatives.

[0029] Referring to FIG. 1, utilizing the loading configuration according to the embodiments of the present invention a plurality of planar substrates **150** can be loaded into the furnace tube **100**. In an embodiment, each of the plurality of planar substrates is a panel of glass. In an example, the substrate can be a 20 cm×20 cm square shaped glass panel or a 20 cm×50 cm rectangular shaped glass panel. In another example, the substrate can be a 65 cm×165 cm rectangular shaped glass panel, though any other form factors are not excluded. Specifically, the substrate is a soda lime glass which is widely used as a transparent substrate panel for thin-film solar module. In other embodiments, the substrate can be made of other transparent materials including fused silica, quartz, and others. In some embodiments, the substrates with other shapes including planar rectangular, square, and disk, and non-planar cylindrical rod, tube, semi-cylindrical tile, or even flexible foil can be used depending on applications.

[0030] In an embodiment, on each of the plurality of planar substrates one or more over layers has formed on a front surface through some thin-film processes. For example, a precursor layer including copper species, indium species, and/or indium-gallium species may be formed on the front surface of each substrate using a sputtering technique. The substrates are then loaded into the furnace tube for subjecting the precursor layer to subsequent thermal treatment. In an embodiment, the precursor layer can be reactively treated in a

gaseous environment within the furnace tube containing selenide species, or sulfide species, and nitrogen species, etc. When the furnace tube temperature is ramped up the substrates are heated and so do the working gases within the furnace tube. The heated gaseous selenium species, which may flow around following internal convection flow, react with the copper-indium-gallium species in the precursor layer overlying the substrates. The thermal treatment process may include several steps for temperature ramping up, dwelling, and ramping down. As a result of the reactive process, the precursor layer is transformed to a photovoltaic film stack containing copper indium (gallium) diselenide (CIGS) compound, which can be served as an absorber layer of a thin-film photovoltaic cell. More detail descriptions about the thermal treatment process for forming the CIGS photovoltaic film stack of thin film solar cells can be found in U.S. Patent Application No. 61/178,459 titled "Method and System for Selenization in Fabricating CIGS/CIS Solar Cells" filed on May 14, 2009 by Robert Wieting, commonly assigned to Stion Corporation of San Jose and hereby incorporated by reference.

[0031] In another embodiment, each of the plurality of planar substrates is disposed into the quartz boat fixture **140** in a loading configurations. The loading configurations can be customized using a few grooved rods or bars mounted on a frame structure of the quartz boat fixture. FIG. 2 is a perspective view of the quartz boat fixture for loading a plurality of planar substrates according to an embodiment of the present invention. As shown, the boat fixture **140** is a frame fixture having a substantially rectangular prism shape, including a base frame **145** and a top frame **146**, the base frame **145** and the top frame **146** being fixedly coupled by several side connection bars. The base frame **145** has a first width portion **1451**, a second width portion **1452**, and one or more middle members **1453**, **1454** connected between two length portions **1455** and **1456**. Each grooved rod **148** is installed on each of the first width portion **1451**, the second width portion **1452**, and one or more middle members **1453**, **1454** of the base frame **145**. As shown, each grooved rod **148** includes a plurality of grooves, presumably facing upward, disposed in a certain configuration along the length of rod. In particular, each groove is configured to support one or more pieces of glass substrates. The four grooved rods **148** are aligned so that one groove from each grooved rod is just in position to insert at least one planar substrate. In the implementation, each loaded planar substrate sits in the four grooves of the respective grooved rods substantially in a vertical orientation in parallel to the gravity direction and all loaded planar substrates are substantially in parallel to each other. In addition, two grooved bars **149** are installed respectively at each width member of the top frame **146**. Each grooved bar **149** also has a plurality of grooves with substantially the same configuration as those on the grooved rods **148** and is aligned with corresponding groove of the grooved rods **148**. The grooved bars have their facing mainly inward to provide guides to the loaded planar substrates. For example, a quartz boat fixture designed to load a plurality of planar substrates substantially in a horizontal orientation perpendicular to the gravity direction can be an alternative option, using grooved rods or grooved bars mounted on the side connection bars as substrate support and guide.

[0032] FIG. 3 is a simplified side view of the furnace tube loaded with a quartz boat fixture holding a plurality of planar substrates according to an embodiment of the present inven-

tion. As shown, a plurality of planar substrates **211**, **212**, etc. is inserted respectively in a plurality of grooves **251**, **252**, etc. in a specific configuration within a quartz boat fixture **240** according to an embodiment of the present invention. In particular, the plurality of grooves is disposed with an equal spacing for each neighboring groove. Although each groove has a size for supporting at least one substrate, only every other groove is used for one substrate to be loaded in a vertical orientation while leaving one groove in between empty. For example, groove **251** supports a substrate **211** and the groove **252** is empty, while next groove supports a next substrate **212** and so on. In certain embodiments, number of empty grooves may be greater than one. As the plurality of planar substrates **211**, **212** etc are inserted into the quartz boat fixture **240** in the loading configuration described above, a spacing **215** is provided for every neighboring substrates. The quartz boat fixture **240** is then loaded into the tube shaped furnace **200**.

[0033] In an embodiment, the present invention provides a method for loading planar substrates in a predetermined configuration. Firstly, the method provides a plurality of equally spaced grooves. Secondly, the method provides inserting the planar substrates into the grooves with an increased spacing **215** between two neighboring planar substrates beyond that of two neighboring grooves by intentionally skipping one or more grooves. When the plurality of planar substrates in this loading configuration is subjected to a reactive thermal treatment within a gaseous environment inside the tube shaped furnace **200**, the advantage of having a relative wide spacing **215** between two neighboring substrates is to have sufficient spatial room for vertical convection flow. In a specific embodiment with the substrates in vertical orientation, the hotter work gas within the furnace tube **200** is carried by the convection flow upwards while colder gas flows down along the substrate surfaces. Wider spacing between the planar substrates can facilitate the interflowing which helps to improve temperature uniformity of each loaded substrate, especially during quick temperature ramping up or down processes. For example, when the substrates are heated from relative low temperatures which are increased in a ramping-up process via the plurality of heaters (not shown) associated with the furnace tube **200**, convection in between the substrates plays more important role in heat transfer than radiation. At higher temperatures radiation will dominate convection and major heat transfer within the substrate is not highly dependent on substrate spacing. In another example, the larger substrate spacing naturally reduces the total number of substrates loadable with a fixed dimension of the furnace tube **200**. Therefore, substrate spacing may need to be optimized and predetermined. Once a desired spacing between substrates is determined the corresponding grooves pattern can be built into the grooved bar or grooved rod just for installing onto the boat fixture for loading substrates in a desired configuration.

[0034] In alternative embodiments, other parameters affecting the effectiveness of heat transfer or subsequently the substrate temperature uniformity include time (or heater/cooler ramping rate) and thermal mass or total number of the loaded substrates. These parameters are also interrelated. For example, when total number of substrates is increased for seeking higher production yield, it actually demands a wider substrate spacing **215** for effective convection flow which ends up reducing the total number of substrates loadable. For the substrates with dimensions as large as 65×165 cm, high temperature difference (ΔT) can lead to warping and breaking of the substrate. A uniform temperature is desired for unifor-

imity of thin-film process, precursor reactions, and of course, better performance of the devices. For example, a ΔT less than 15 degrees Celsius may be desired during dwell stage of the thermal treatment process while the ΔT may become as large as 100 degree Celsius during ramping up/down stage if the ramping rate is high. Therefore, one or more embodiments of the present invention include using a simulation model to determine a trend of changing the loading configuration and how it affect the temperature uniformity. In an embodiment, the model is scaled down from a real system by using a smaller substrate and furnace size in order to reduce the computation time. The substrates in the model are 20 cm $\times$ 50 cm instead of the full size of 65 cm $\times$ 165 cm. The substrate thickness and spacing are also correspondingly scaled, and totally only 16 substrates are fit in the model with their substrate spacing set at a range from 0.5 inches to several inches. The time scale is substantially reduced so that the ramp rates can be faster than the real system. The behavior trends of this model closely track those of the full size system, although absolute values of temperatures across the substrates may be off the true values from a real system. For example, the scaled system is simulated for the tube shaped furnace 200 loaded with a quartz boat 240 including the grooved rods 248 and grooved bars 249 having a specific groove configuration with a selected spacing. This simulation model can be used as a guide for the real system implementation and finally help to determine an optimized loading configuration for a specific number of substrates. In a specific implementation, a "Computational Fluid Dynamics (CFD)" software is used for analyzing the convection fluid flow and computing heat transfer response of a simulation model system based on the scaled structure parameters. In particular, a commercially available program named CFdesign™ by Blue Ridge Numerics, Inc is applied by adjusting input parameters for system, materials, boundary, and initial conditions. Of course, other general purpose computational fluid dynamics simulation software may be used.

[0035] FIG. 4 is a simplified side view of the furnace tube loaded with a quartz boat fixture holding a plurality of planar substrates according to an alternative embodiment of the present invention. This diagram is merely an example and should not unduly limit the claims herein. One skilled in the art would recognize other variations, modifications, and alternatives. As shown, a plurality of planar substrates 311, 312, etc are inserted respectively in a plurality of grooves 351, 352 etc in a specific configuration within a quartz boat fixture 340 according to an embodiment of the present invention. In an implementation, the quartz boat fixture 340 loaded in the furnace tube 300 is substantially the same as the quartz boat fixture 240 loaded in furnace tube 200 except that the grooved rods 348 for supporting the substrates and grooved bars 349 for guiding the substrates are replaced from grooved rods 248 and grooved bars 249. Embodiment illustrated in FIG. 4 also provides a method for loading a plurality of planar substrates in an alternative configuration. In particular, this loading configuration can provide improved production yield by increasing total number of the substrates while still retaining sufficient substrate spacing for facilitating internal convection without any structural changes to the dimension of the furnace tube 300 and rack fixture 345, 346 of the quartz boat 340.

[0036] In a specific embodiment, the plurality of grooves is arranged in a periodic group in this alternative loading configuration. Each group includes at least a first groove and a second groove being disposed at a predetermined spacing

away from the first groove. The spacing in between can be smaller, equal to, or greater than a size of a single groove. Each group is disposed to be physically next to its neighboring group so that the first groove of the group is next to a second groove of its neighboring group on one side and the second groove of the group is next to a first groove of its neighboring group on another side. Each groove is configured to let one substrate being inserted. For example, a substrate 311 is inserted in the first groove 351 of the first group and substrate 312 is inserted in the second groove 352 of the group with a spacing 315 away from the substrate 311. The spacing 315 is substantially determined by the spacing between the first groove 351 and second groove 352. In addition, the first groove 353 of a very next group is disposed physically next to the second groove of the first group. Arranged in periodic fashion, the second groove 354 of the very next group is also disposed at the spacing away from the first groove 353. Correspondingly, each groove of the very next group can be inserted in a substrate 313 (in groove 353), or a substrate 314 (in groove 354).

[0037] In another specific embodiment, the loading configuration described in FIG. 4 includes a specific front/back phase configuration for each planar substrate inserted in corresponding the first and the second groove of each of the periodic groups of grooves. In an implementation, each substrate is a planar glass substrate that has been worked through one or more thin-film processes. The planar glass substrate has a front surface overlaid by a thin-film composite material while its corresponding back surface can be a bare glass. In an example, the thin-film composite material is a photovoltaic precursor film containing at least cooper species, indium species, and/or gallium species, or silver species. Therefore, an embodiment of the present invention includes inserting two such planar substrates respectively into each group with their photovoltaic precursor film on each substrate directly facing each other. For example, surface 1A of substrate 311 contains a photovoltaic precursor film which faces a photovoltaic precursor film formed on surface 2A of substrate 312. The back surface of substrate 312 faces a back surface of another substrate 313 inserted in a first groove 353 of a neighboring group. Because chemical reaction between the precursor film and ambient work gas inside the furnace 300 will occur only on the front surface of each substrate, only the convection flow between those front surfaces of two planar substrates matters while any convection flow between the back sides is less important. Embodiment of the present invention associated with this loading configuration includes further determining a minimum front surface spacing between two substrates inserted in each group. This also can be accomplished using a simulation model based on a system and substrates with scaled-down dimensions to determine a temperature trend of change following the spacing change. The simulation model is executed using a class of software program named CFdesign™ based on the scaled system structure and material parameters. Via the simulation, a range of desired spacing values can be determined so that the corresponding groove patterns can be built into each of the grooved rods 348 and grooved bars 349. Then these grooved rods and bars can be mounted to customize a standard quartz boat fixture 340 for loading a plurality of substrates in this new loading configuration. One advantage of this loading configuration is the total number of substrates loadable for a fixed quartz boat size is increased comparing to inserting substrates with a simple equal spacing but without front/back

phase configuration. Of course, there can be many variations, alternatives, and modifications.

[0038] FIG. 5 is a side view of the furnace tube loaded with a quartz boat fixture holding a plurality of planar substrates according to another alternative embodiment of the present invention. As shown, a plurality of planar substrates **411**, **412**, etc are inserted in a plurality of grooves **451** in a pairwise back-to-back configuration within a quartz boat fixture **440** according to an embodiment of the present invention. In an implementation, the quartz boat fixture **440** loaded in the furnace tube **400** is substantially the same as the quartz boat fixture **240** loaded in furnace tube **200** except that the grooved rods **448** for supporting the substrates and grooved bars **449** for guiding the substrates are replaced from grooved rods **248** and grooved bars **249**. Embodiment illustrated in FIG. 5 also provides a method for loading a plurality of planar substrates in an alternative configuration. In particular, this loading configuration can provide further improved production yield by increasing total number of the substrates while still retaining sufficient substrate spacing for facilitating internal convection without any structural changes to the dimension of the furnace tube **400** and frames **445**, **446** of the quartz boat fixture **440**.

[0039] In a specific embodiment, each of the plurality of grooves **451** is configured to be able to fit in a pair of planar substrates in a back-to-back loading configuration. In a specific embodiment, the spacing is a single constant for all neighboring grooves, although it can be varied along the grooved rod or bar from its end to its middle. Again, in this configuration the substrate loading is performed with its front/back phase configured. Depending on embodiments, each substrate **411** can be a glass panel for manufacturing photovoltaic cells. In one implementation, the glass substrate has a front surface being covered by several films of materials including a precursor layer formed on top while leaving its back surface a bare glass. A plurality of these substrates is loaded in the furnace tube fixture **400** for subjecting the precursor layers to one or more reactive thermal treatment processes and forming a photovoltaic absorber. Therefore, only front surface of each planar substrate with the precursor layer on top needs to be exposed to ambient reactive gas within the furnace tube and the back side of the same substrate can be physically touched with another back side of another substrate, and both these two substrates can be inserted into a single groove (with a enlarged size). For example, substrate **411** and substrate **412** are inserted together in a back-to-back configuration into a first groove. A second groove is disposed a distance away from the first groove. The front side **1A** of substrate **412** would be facing front side **2A** of another one of two substrates that are inserted back-to-back together in the second groove. The groove-to-groove spacing is configured to be sufficiently large so that the substrate spacing **415** (i.e., **1A-2A** spacing) is equal to or greater than a predetermined value. Because of the thermal process involves chemical reaction between solid phase film material (the precursor layer) on the substrates and gaseous phase material filled in the furnace tube, larger spacing between those vertically disposed substrates can facilitate convection flow in between during the reactive thermal treatment processes. This specific configuration minimizes the back-back spacing (substantially equal to zero) so that more spatial room is provided for increasing front-front spacing **415** between two substrates disposed in neighboring grooves and for loading more substrates in such a configuration.

[0040] In another specific embodiment, the loading configuration described in FIG. 5 includes a specific front/back phase configuration for each substrate and an additional specific size configuration for each groove to fit with just two substrates. Furthermore, embodiment of the present invention associated with this loading configuration includes further determining a minimum front-front spacing between two substrates respectively inserted in two neighboring grooves. This still can be accomplished using a simulation model based on a system and substrates with scaled-down dimensions to determine a temperature uniformity trend of change following the change of the front-front spacing. The simulation model is executed using a computational fluid dynamics software, for example, a program named CFdesign™ provided by Blue Ridge Numerics, Inc, based on the scaled system parameters. Through the simulation, a range of desired spacing values can be determined so that the corresponding groove patterns can be built into each of the grooved rods **448** and grooved bars **449**. Then these grooved rods **448** and bars **449** can be mounted to customize a standard quartz boat **440** for loading a plurality of planar substrates **411** and **412** in the corresponding configuration. One advantage of minimizing the front-front spacing is to maximize total number of substrates loadable for a fixed quartz boat size. An example is to set the substrate spacing as one single value for all the inserted substrates, although the spacing can be varied from one side of the quartz boat to another side. Of course, there can be many variations, alternatives, and modifications.

[0041] FIG. 6 is an exemplary cross-section view of simulated convection flows according to an embodiment of the present invention. In a specific embodiment, the present invention provides a method of using a simulation model for determining at least a trend of change in temperature distribution associated with substrate loading configuration inside a tube shaped furnace. As shown, the top portion (A) of FIG. 6 is a cross-section view along an axis of a modeled tube shaped furnace **600**. The modeled furnace **600** is substantially similar to real-life furnace tube **100**, but is reduced in dimensions for obtaining results with a manageable computation time. In an implementation, a class of computational fluid dynamics software is used in these simulations. For example, program named CFdesign™ provided by Blue Ridge Numerics, Inc is applied with a model based on scaled down system dimensions and material parameters and initial conditions substantially close to a real system developed according to embodiments of the present invention. Additionally shown in FIG. 6A, one of plurality of rectangular shaped planar substrates **610**, also in reduced dimensions, is loaded in a central position within the model furnace **600**. During one or more reactive thermal treatment processes, heated gaseous species tend to move upward and colder gaseous species flow downward to form convection flows within the volume of the model furnace **600**. Based on the results from simulation, FIG. 6A shows at least part of the convection flow **650** along the axial cross section plane moving in a spatial region between the furnace inner wall and the edges of the substrate **610**.

[0042] FIG. 6B provides another cross-section view of the same system setup used in the simulation model. As shown, in a configuration according to an embodiment of the present invention **16** substrates **610** are loaded one by one separately with an equal spacing **615** in vertical orientation. Although it is not explicitly included in the simplified simulation model, these substrates can be supported by a sample holder. For example, a quartz boat **140** described in FIG. 1 of the speci-

fication including several grooved rods mounted on its bottom rack fixture and aligned to let at least one substrate inserted in each groove. FIG. 6B shows at least part of the convection flow **650** moving along a cross section plane perpendicular to the tube axis. Simulation results based on the CFdesign™ program indicates that the heated gaseous species flow upward along mainly the spacing between the furnace inner wall and the edges of the substrate **610** then flow downward along the spacing between the substrates **610**.

[0043] The simulation results also include effects of geometric form factors of the system on the temperature distribution for each substrate **610**. Although the absolute values may be off the real system, trends of changes associated with at least some system parameters including the furnace dimension/shape, substrate dimension, total number of loaded substrates (thermal mass), spacing between neighboring substrates, etc. can be determined. In a specific embodiment, a trend of change associated with the substrate spacing for a particular loading configuration shown in FIG. 6 can be obtained. For example in FIG. 6B a loading configuration associated with the tube shaped furnace **600** has total number of **16** substrates **610** each being disposed alone and separated from its neighbor by a spacing **615**. A trend of change based on the simulation indicates that reducing the spacing **615** for loading substrates **610** more than **16** may limit the up-down convection flow resulting in poor temperature uniformity. In addition, the trend of change based on the simulation indicates that increasing the spacing **615** may further improve the substrate temperature uniformity while reducing the total number of loaded substrates **610**, which affects production yield. To certain degrees, further increasing substrate spacing may not substantially improve temperature uniformity (while other system parameters may become major factors). Therefore, an optimal loading configuration for a specific system setup can be practically determined and recommended for real system. Of course, there are many other alternatives, variations, and modifications.

[0044] FIG. 7 is an exemplary cross-section view of convection flows according to another embodiment of the present invention. As shown, in another embodiment of the present invention, a simulated convection flow pattern **750** is plotted for a modeled system with a plurality of planar substrates **710** being disposed in a back-to-back paired configuration within a tube shaped furnace **700**. FIG. 7A shows at least a portion of convection flow **750** along an axial plane and between inner wall of the furnace **700** and edges of the substrates **710**. FIG. 7B shows at least another portion of convection flow **750** along a cross-section plane perpendicular to the axis of the furnace tube **700**. The furnace **700** is substantially the same as model furnace **600**, based on real tube shaped furnace **100**. FIG. 7B shows that by pairing the substrates the substrate spacing **715** between each pair is doubled while total number of substrates **710** can be kept the same.

[0045] This loading configuration takes advantage of the substrate samples with only single-side surface subjected to the reactive thermal treatment. According to embodiments of the present invention, the substrates **710** are glass substrates with front surface pre-coated by several thin-film materials including bottom electrode film and an exposed precursor film overlying the electrode film and the opposite back surface may be simply a bare glass. During reactive thermal treatment processes, only the precursor film needs to be exposed to work gases filled in the volume of the furnace **700**. Therefore, placing the back surface of a planar substrate

against another back surface of another planar substrate certainly will not affect the expected treatment of the precursor film on the front surface while allowing more room for adjusting the spacing between the front surfaces containing precursor films. In another embodiment, this loading configuration allows increasing the total number of loaded substrates without reducing the spacing between the precursor films on the front surfaces from a neighboring pair of substrates. As a result, the loading configuration helps to enhance system production yield because of more substrates can be loaded for treatment in one setting but still allows sufficient room for gaseous species to flow between the subjected precursor film surfaces and induce an effective thermal convection good for substrate temperature uniformity. Again this is modeled using a system with reduced dimension or total number of loaded substrates. Although the absolute values regarding the loading configuration and resulted temperature difference across each substrates may not match real system, a trend of change can be determined and provide guidance for optimizing processing parameters of actual system depending on one or more embodiments. Of course, there are many variations, alternatives, and modifications.

[0046] While the present invention has been described using specific embodiments, it should be understood that various changes, modifications, and variations to the method utilized in the present invention may be effected without departing from the spirit and scope of the present invention as defined in the appended claims. For example, the tubular shaped furnace is illustrated as an example. In addition to use an optimized loading configuration for the plurality of substrates, a carefully optimized heating/cooling supply system and heater/cooler configuration can also significantly improve temperature uniformity across the substrates as large as about 2 feet by 5 feet or greater for thin-film photovoltaic devices. Additionally, although the above embodiments described have been applied to reactive thermal treatment for forming CIS and/or CIGS photovoltaic film stack on the substrate, other thin-film based reactive thermal treatment processes certainly can also be benefited from the embodiments, without departing from the invention described by the claims herein. Depending on the embodiment, the present method can also be applied to silicon based photovoltaic devices.

What is claimed is:

1. An apparatus for holding substrates for thermal treatment comprising:

- a frame fixture having a substantially rectangular prism shape, the frame fixture including a base frame, a top frame, side connection bars coupling the base frame and the top frame, the base frame having two width members and middle joint members connected between the two length members;
- a first grooved rod removably mounted on each of the two width members and each of the middle joint members, each first grooved rod including a first plurality of grooves for supporting planar substrates;
- a first grooved bar removably mounted on each of two width members of the top frame, each first grooved bar including a second plurality of grooves aligned with the first plurality of grooves for guiding the plurality of planar substrates into the apparatus; and
- a rack structure configured to be a mechanical support of the frame fixture in a loading position inside a furnace

for subjecting the plurality of planar substrates in the first configuration to one or more reactive thermal treatment processes.

2. The apparatus of claim 1 wherein the frame fixture and the first grooved rod and the first grooved bar comprise quartz.

3. The apparatus of claim 1 wherein each of the plurality of planar substrates comprises glass having at least one surface overlaid by a photovoltaic precursor layer which includes at least copper, indium, and gallium species.

4. The apparatus of claim 1 wherein each of the plurality of planar substrates comprises a piece of soda lime glass having a form factor selected at least from a 65 cm×165 cm rectangle, a 20 cm×50 cm rectangle, a 20 cm×20 cm square.

5. The apparatus of claim 1 wherein the first configuration comprises an arrangement of the plurality of planar substrates in a substantially vertical orientation and parallel to a neighboring planar substrate at a distance equal to or greater than a predetermined value associated with at least the furnace and the one or more thermal treatment processes.

6. The apparatus of claim 5 wherein the predetermined value comprises a minimum spacing for maintaining a sufficient convection flow so that a temperature difference across each planar substrate is smaller than 15 degrees Celsius at least during a dwell stage of the thermal treatment processes.

7. The apparatus of claim 6 further comprising a second grooved rod for replacing the first grooved rod to mount on

each of the two width members and each of the one or more middle joint members, each second grooved rod including a second plurality of grooves respectively configured to support a plurality of planar substrates in a second configuration, each groove supporting at least one planar substrate.

8. The apparatus of claim 7 wherein the second configuration comprises an arrangement of the plurality of planar substrates substantially parallel to each other with a front/back surface of one planar substrate facing another front/back surface of a neighboring planar substrate at a first/second distance away, the first distance being equal to or greater than the predetermined value, the second distance being substantially smaller than the first distance.

9. The apparatus of claim 8 wherein the front surface of each planar substrate comprises a precursor layer being subjected to the one or more thermal treatment processes.

10. The apparatus of claim 8 wherein the second distance is substantially zero and each groove is configured to support two planar substrates in back-to-back configuration.

11. The apparatus of claim 1 wherein the furnace is made of quartz material for enclosing a volume configured to form a gaseous environment comprising at least selenium species or sulfur species during the one or more thermal treatment processes.

* * * * *