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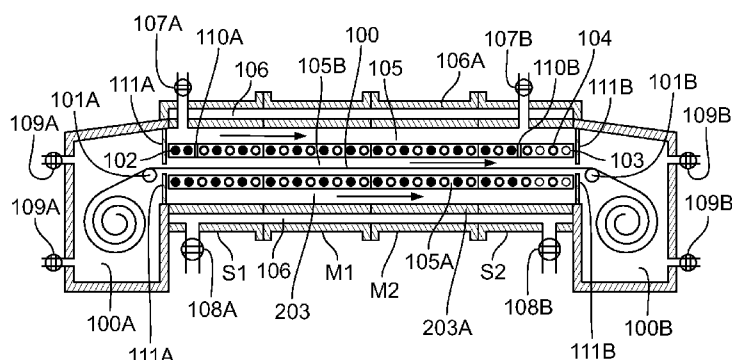
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(54) **Title:** AN ASSEMBLED REACTOR FOR FABRICATIONS OF THIN FILM SOLAR CELL ABSORBERS THROUGH ROLL-TO-ROLL PROCESSES

**FIG. 1**

(57) **Abstract:** A roll-to-roll reactor, which is assembled with a heating section, a cooling section, and a series of modular buffer sections, is provided. Its length is adjustable by adding or reducing numbers of the modular buffer sections according to required reaction time and delivery speed of a continuous flexible workpiece. The reactor contains a reaction oven assembled with a series of modular thermal control components, included inside a vacuum-tight reaction chamber. The oven temperature can be precisely controlled through combinations of heating elements, cooling elements and thermocouples. The reactor can be used for annealing and reaction of various precursor films on flexible substrates under vacuum and in inert or reactive gas ambient at temperatures ranging from a room temperature to a thousand Celsius degrees. This reactor is particularly useful in manufacturing thin film solar cells such as CIGS and CdTe solar cells on flexible substrates through a continuous roll-to-roll process.

**An Assembled Reactor for Fabrications of Thin Film Solar Cell Absorbers
through Roll-to-Roll Processes**

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CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Patent Application No. 13,084,568 filed April 12, 2011, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a reactor that can be assembled with modular sections to fabricate multiple component semiconductor materials that can be used in thin film solar cells as absorbers or other fields of applications. With a high vacuum design and a precise temperature control, this apparatus is invented for the reaction of flexible substrates through roll-to-roll or reel-to-reel processes.

BACKGROUND

[0003] Photovoltaic devices have recently been dramatically developed due to serious global warming and expectation of fossil fuel exhausting in the near future. The traditional photovoltaic devices, or solar cells, are based on silicon semiconductors such as single or multiple crystal silicon materials. However, these silicon materials are expensive, difficult for fabrication and in short supply in semiconductor industry. To overcome these problems, some substitutes such as thin film solar cells have been developed as the second generation of solar cells. At present, there are three main types of second generation thin film solar cells: amorphous silicon, CIGS and CdTe. In this thin film solar cell family, the CIGS solar cells possess the highest conversion efficiency that is as high as 20%, higher than 16% efficiency of the CdTe ones. In the periodic table of the elements, the elements of a CIGS absorber are located in Group IB-III A-VIA and the ones of CdTe absorber in Group IIB-VIA. These absorber materials all belong to multi-component *p*-type semiconductors. For such a semiconductor material, the distribution of different components, stoichiometry and crystal style may determine the quality of the materials.

[0004] Both of CIGS and CdTe solar cells contain a stack of absorber/buffer thin film layers to create an efficient photovoltaic heterojunction. A metal oxide window containing a highly resistive layer that has a band gap to transmit the sunlight to the absorber/buffer interface, and a lowly resistive layer to minimize the resistive losses and provide electric contacts, is

deposited onto the absorber/buffer surface. This kind of design significantly reduces the charge carrier recombination in the window layer and/or in the window/buffer interface because most of the charge carrier generation and separation are localized within the absorber layer. In general, CIGS solar cell is a typical case in Group IB-III A-VIA compound semiconductors comprising some of the Group IB (Cu, Ag, Au), Group III A (B, Al, Ga, In, Tl) and Group VIA (O, S, Se, Te, Po) elements of the periodic table, which are excellent absorber materials for thin film solar cells. In particular, compounds containing Cu, In, Ga, Se and S are generally referred to as CIGS(S), or Cu(In,Ga)(S,Se)_2 or $\text{CuIn}_{1-x}\text{Ga}_x(\text{S}_y\text{Se}_{1-y})_n$, where $0 \leq x \leq 1$, $0 \leq y \leq 1$ and n is approximately 2, and have already been applied in the solar cell structures that gave rise to conversion efficiencies approaching 20%. Here, Cu(In,Ga)(S,Se)_2 means the whole family of compounds with Ga/(Ga+In) molar ratio varying from 0 to 1, and Se/(Se+S) molar ratio varying from 0 to 1. It should be noted that the molar ratios of Ga/(Ga+In) and Cu/(Ga+In) are very important factors to determine the compositions and the conversion efficiencies of the CIGS solar cells. In general, a good solar cell requires a ratio of Cu/(Ga+In) between 0.75 and 0.95, and Ga/(Ga+In) between 0.3 and 0.6. In comparison with CIGS, the composition of a CdTe solar cell is much simpler. The content of Cd is usually close to 50% in the CdTe films. However, the Cd content may change after the deposition of a CdS layer and the subsequent annealing procedure. Close to the interface of the *p-n*-junction, for example, a $\text{CdS}_x\text{Te}_{1-x}$ layer is formed with x usually not exceeding 0.06. However, x has a range changing from 0 to 1, which results in a compound from CdTe ($x = 0$) to CdS ($x = 1$).

[0005] Both CIGS and CdTe films have to be annealed to form a uniform stoichiometric compound. A CIGS film is usually annealed at a temperature between 350 and 600 °C in a typical two-stage fabrication procedure. For a CdTe solar cell, a CdS film may first be annealed in a superstrate configuration and a CdS/CdTe bilayer may be annealed in a substrate configuration. The importance of annealing is not only for the formation of a stoichiometric semiconductor material, but also for the determination of the crystal and boundary structures that may seriously affect the semiconductor properties. Therefore, the annealing should be well controlled in a carefully designed apparatus. For example, a CIGS film is usually going through a Rapid Thermal Processing (RTP) to approach a high temperature quickly at the

beginning, followed by a reaction at the raised temperature in a super-pure inert, H_2Se , H_2S or Se atmosphere. After annealing, an *n*-type semiconductor buffer layer such as CdS, ZnS, or In_2S_3 should be deposited onto a CIGS semiconductor absorber. After then, transparent conductive oxide (TCO) materials, i.e., ZnO, SnO_2 , and ITO (indium-tin-oxide), should be deposited to form the solar cells.

[0006] The annealing process is sensitive to any impure species. For example, any residue oxygen or water inside a reactor may oxidize a CIGS absorber and destroy this semiconductor material. Therefore, an annealing reactor has to be totally isolated from the outside atmosphere. A vacuum apparatus should be helpful to clean the interior chambers at the beginning through some vacuum-inert gas cycles and remain a good sealing for the equipment during the reactions. However, most high temperature reactors may not be designed as high vacuum apparatus. For these equipments, lots of inert gas has to be used to maintain the annealing under a pure inert atmosphere. Especially for a roll-to-roll or reel-to-reel continuous process, more attention has to be paid to design a qualified reactor. Some high vacuum apparatus has recently been patented and assigned to SoloPower as a roll-to-roll reactor to anneal CIGS absorbers. For example, a few patent applications have been presented to provide methods and a high vacuum reactor to selenize and anneal CIGS absorbers in a roll-to-roll process, as shown in patent applications with publication numbers US2009/0183675A1, US2009/0148598A1 and US2010/0139557A1. With their designs, the reactor comprises a primary gap defined by a peripheral wall and an insert is placed within the gap to process the reaction of a continuously traveling workpiece. This insert processing gap is vacuum-tight and an inert or reactive gas can be introduced during the reaction under a certain temperature controlled by some heating elements surrounding the peripheral wall.

[0007] The main drawback for this reactor is that its integrated design requires a continuous piece of the peripheral wall. When the reaction needs time, the peripheral wall has to be designed very long or the travelling speed of the workpiece has to be very slow. The long peripheral wall may significantly increase the cost and the difficulty of fabrication, transportation and maintenance. In addition, the heating elements surrounding the body also significantly increase the temperature of the working environment. To solve these problems, the present invention provides a vacuum-tight reactor comprised with a series of modular sections. Moreover, the heating elements have been incorporated inside the reactor chamber that may be isolated with a vacuum chamber.

SUMMARY OF THE INVENTION

[0008] The present invention provides a reactor that can be assembled with some modular sections to fabricate thin film solar cell absorbers in a roll-to-roll or reel-to-reel process. This apparatus features a vacuum tight sealing and a precise temperature control. A flexible substrate is continuously delivered through this reactor that can be assembled to obtain various lengths according to requirements of the reaction time and the substrate delivery speeds.

[0009] This apparatus can be used for annealing materials deposited on the flexible substrates under a vacuum or inert atmosphere and/or carrying out the material reactions in different reaction gases. In particular, it may be used to anneal and/or conduct reaction of semiconductive absorber layers in Group IB-IIIA-VIA and Group IIB-VIA thin film solar cells.

BRIEF DESCRIPTION OF THE DRAWING

[0010] FIG. 1 shows an apparatus with two modular buffer sections in the center for reaction of a precursor layer coated on a flexible foil substrate to fabricate an absorber layer in a Group IB-IIIA-VIA or IIB-VIA solar cell with a roll-to-roll process.

[0011] FIG. 2 is the cross-section view of a modular buffer section of the apparatus shown in FIG. 1.

[0012] FIG. 3 shows a simplified apparatus without a vacuum chamber at the bottom.

[0013] FIG. 4 is the cross-section view of a modular buffer section of the simplified apparatus shown in FIG. 3.

[0014] FIG. 5 is a 3D illustration of a thermal control component with arrangement of heating elements and thermocouples in a modular buffer section.

[0015] FIG. 6 shows an apparatus with two modular buffer sections in the center, and an upside-down precursor layer for its reaction on a flexible foil substrate to fabricate an absorber layer in a Group IB-IIIA-VIA or IIB-VIA solar cell with a roll-to-roll process.

[0016] FIG. 7 is a 3D illustration of a modular thermal control component to anneal or make a reaction of a precursor on an upside-down delivered flexible substrate with arrangement of heating modules containing the heating elements and some thermocouples in a modular buffer section.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The apparatus in the present invention can be used for annealing or reaction of a single or multiple layer thin film coating on a flexible foil substrate, which is useful in preparation of semiconductor absorbers in Group IB-III A-VIA or Group IIB-VIA thin film solar cells. It can also be employed in the annealing and reaction processes in other applications. In general, such annealing and reactions may be divided into three groups, under vacuum, under an inert gas environment, or in a reaction gas atmosphere. The present invention meets all of these conditions. The apparatus is designed for operation under a high vacuum environment. With several vacuum and inert gas cycles, the whole process can be conducted under a very pure inert environment. If a toxic gas is applied in a reaction, such as H₂S or H₂Se in preparation of Group IB-III A-VIA thin film solar cells, this apparatus can provide a double protection from leaking. Moreover, a combination of heating elements and thermocouples in the thermal control component can provide a precise temperature for both constant temperature reaction and a rapid thermal process (RTP). The apparatus in the present invention can be manufactured in different widths to adapt to the substrate widths.

[0018] In an embodiment as shown in FIG.1, a reactor includes a heating section **S1**, a cooling section **S2**, and at least one modular buffer sections **M1** (and as shown, **M2**) installed between the heating section and the cooling section. Each modular buffer section includes one or more modular thermal control components **105A** and modular reaction chamber wall **203A**. The reactor further includes a reaction oven **105** that has an oven space **105B** enclosed by said one or more modular thermal control components **105A**, one or more heating elements **102**, one or more cooling elements **103**, one or more thermocouples **104**, one or more gas inlets **110A** to said oven space, and one or more gas outlets **110B** to said oven space. The gas inlets and outlets **110A** and **110B** may also be connected to vacuum sources and thus function as vacuum outlets. The oven space **105B** has a central internal height between 20 and 300 millimeters, and a internal bottom width between 100 and 2000 millimeters. The reaction oven is configured in such a way that a flexible substrate can be delivered through it. The reactor is adapted to be used in a roll-to-roll process over a continuous flexible substrate to carry out reactions at an elevated temperature under a controlled atmosphere.

[0019] In another aspect of the embodiment, the length of the reactor is adjustable by adding or reducing the numbers of the modular buffer sections. In yet another aspect, the temperature inside said reaction oven is adapted to be controllable from 25 °C to 1000 °C. In another aspect,

the reactor further includes a reaction chamber **203** enclosed by the modular reaction chamber wall **203A**, a roll unwinding chamber **100A**, and a roll winding chamber **100B**. The reaction chamber **203** substantially encloses said reaction oven **105**. The reaction chamber has at least a gas inlet **107A** and a gas outlet **107B**, which may also be connected to vacuum sources to function as vacuum outlets. The reaction chamber **203**, the roll unwinding chamber **100A**, and the roll winding chamber **100B** are joined together to form a main vacuum chamber that is adapted to be capable of being vacuumed to 1 Pa, preferably 10^{-3} Pa. In order to reach such a high vacuum, some modular sections may have to be equipped with vacuum outlets connected to turbomolecular or diffusion pumps that can cooperate with main oil-free dry mechanical pumps to achieve high vacuum. If the apparatus requires only 10^{-3} torr vacuum, these turbomolecular or diffusion pumps are not necessary.

[0020] In various aspects of the embodiment, the reactor further includes out vacuum chamber wall **106A**. The out vacuum chamber wall encloses an out vacuum chamber **106** that substantially surrounds the whole reaction chamber **203**. One or more channels (not drawn) may be set up to connect the out vacuum chamber and the reaction chamber with valves to turn on/off communication between these two chambers. In another aspect, the oven space **105B** has a central internal height between 20 and 300 millimeters, and an internal bottom width between 100 and 2000 mini-meters. The temperature inside said reaction oven **105** is adapted to be controllable from 25 °C to 1000 °C.

[0021] FIG. 2 shows a cross-section view of the modular buffer section **M1** and **M2**. A flexible substrate **100** is illustrated inside the oven space **105B** enclosed by the thermal control component **105A** that contains the heating element and the thermocouple combination. The thermal control component may include one or more bottom pieces **201** and one or more top pieces **202**. There are certain coupling mechanism between the top pieces and the flat bottom pieces, for example, tooth-and-dent coupling mechanism, which prevents gas escaping from inside the oven space. The top piece and the flat bottom piece each may include one or more items selected from the group consisting of heating elements, thermocouples, and cooling elements. The chamber **203** represents the reaction chamber, and **106** is the out vacuum chamber.

[0022] In certain aspects, the modular thermal control component **105A** includes one or more materials selected from the group consisting of graphite, ceramics and quartz glass. The modular thermal control component may also include tooth-dent coupling designs on both

cross sides to tightly connect with other pieces. In other aspects, the reaction chamber wall includes one or more materials selected from the group consisting of stainless steel, titanium, and aluminum alloy. In certain other aspects, the oven space **105B** has a *central internal height* between 20 and 300 millimeters, and an internal bottom width between 100 and 2000 millimeters. The temperature inside said reaction oven is adapted to be controllable from 25 °C to 1000 °C.

[0023] The flexible substrate roll **100** is delivered from the unwinding chamber **100A**, through the rollers **101A** and **101B**, to the winding chamber **100B** along the arrow direction with a certain speed. The unwinding chamber is directly connected to the heating section **S1** where the substrate is quickly heated up to a constant annealing or reaction temperature with a RTP process. Then the substrate goes through the annealing/reaction oven that is constituted with a series of thermal control components in modular buffer sections **M1**, **M2**...**Mn** before it passes the cooling section **S2** that is directly connected to the winding chamber. The cooling elements in **S2** may include some stainless steel tubing loaded with cold water or a cold inert gas. The whole annealing/reaction oven **105** spanning from **S1** to **S2** may be fabricated from the materials of graphite, ceramic or quartz crystal. The heating elements **102** and the cooling elements **103** can be installed inside a thermal control component or arranged above and underneath it, combined with the thermocouples **104**. The heating and the cooling elements combined with the thermocouples are densely arranged along this thermal control component to guarantee that the whole precursor film on the flexible substrate **100** is annealed or reacted at a constant temperature within a deviation of ± 1 °C..

[0024] Before the RTP and the reaction start, the substrate roll **100** is loaded in the reactor. The whole system is then carried out at least three cycles of vacuum-inert gas to remove any impurity from the apparatus. During these cycles, the valves **107A**, **107B**, **108A**, **108B**, **109A** and **109B** may be opened to vacuum pumps. One of the valves **109A** and one of **109B** may be used as the vacuum outlets and the rest two as the inert gas inlets. The present apparatus is designed to obtain a high vacuum down to 10^{-3} Pa. When the system is ready, the annealing/reaction oven **105** starts to heat the temperature up to a certain degree. During this process, the valve **108A** and/or **108B** are opened to a vacuum system. Then the roll **100A** starts to move along the arrow direction and the gas valves **107A** and **107B** are opened to a gas supply to introduce the inert or reaction gas into **107A** and out of **107B** if the annealing or the reaction is not conducted under a vacuum. The gas valves **107A** and **107B** may also function as vacuum

valves when they are connected to vacuum sources. The gas can penetrate the hole inlet **110A** and escape out of the hole outlet **110B** before it reaches the cooling section. For an annealing or a reaction of a CIGS precursor layer under an inert gas environment, the gas escaped from **110B** may contain lots of Se vapors. If formation of the CIGS absorber is required in a H_2S or H_2Se atmosphere, the escaped gas is very toxic, especially the fatal H_2Se . The reaction gas is first controlled inside the reaction chambers. A pair of shutters **111A** and **111B** is installed between the unwinding chamber and the heating section **S1** and between the winding chamber and the cooling section **S2**. During the reaction, they are closed to leave narrow slits for the roll movement. The width of these slits may be set from 1 to 10 mm, preferably around 2 - 4 mm.

The inert gas with a positive pressure from valves **109A** and **109B** is introduced through these slits to avoid the toxic gas leaking into the unwinding and winding chambers. The escaped gas from the valve **107B** is finally introduced to a treatment system. The vacuum chamber **106** is maintained under a vacuum during the whole annealing or reaction process. It has two main functions. On one hand, it is a thermal insulation buffer space to resist too much heat released to the air and stabilize the temperature in the reaction chambers. Since the vacuum space blocks heat transfer through heat conduction and thermal convection but not thermal radiation, some cold water cooling tubing can be installed on external surfaces of the chamber **106** to obtain a better heat insulation. On the other hand, **106** is a protection chamber for any possible gas leaking from the main reaction chamber because the leaked gas can be vacuumed and led to a chemical treatment system.

[0025] In another aspect as shown in FIG. 3, the reactor is simplified by having the vacuum chamber **306** only above the reaction chamber **403**. Furthermore, the reaction oven **305** is placed close to the bottom of the reactor, substantial without an empty space between the reaction oven **305** and the bottom of the reaction chamber **403**. This requires the bottom of the whole device to be equipped with excellent heat insulation materials (not shown). Alternatively, insulation materials (not shown) must be placed between the reaction oven **305** and the base section **404** of the reaction chamber wall. With this modification, the valves **308A** and **308B** preferably are placed at the top of the apparatus.

[0026] This modified device can also be seen in FIG. 4 from another cross-section view. As shown, the vacuum chamber **306** surrounds a top section of the reaction chamber **403**. The vacuum chamber **306** is formed between a vacuum chamber wall **306A** and the reaction chamber wall **403A**. The vacuum chamber wall and the reaction chamber wall may have shared base sections **404**.

[0027] FIG. 5 shows a three-dimensional illustration of an exemplary thermal control component used in the embodiment. It possesses an arc-shaped ceiling. An arc-shaped ceiling has some benefit over a flat one. If this reactor is used for the reaction of a CIGS absorber layer at a temperature ranging from 400 to 600 °C, the unreacted Se will evaporate into the gas atmosphere. If too much Se evaporates, its local concentrations above the substrate may be over-saturated and condensed even at such a high temperature. The over-saturated liquid Se may condense on the flat-shaped ceiling and drop down onto the reacted CIGS absorber surface to damage some areas of the film. If the liquid Se is condensed on an arc-shaped ceiling, however, it may flow down along the arc to the side grooves **504**. Additionally, a flat-shaped ceiling will result in right-angled corners. The gas stream may be eddy-flowing or back-flowing around these corners, which may be another reason to cause the Se condensation. An arc-shaped ceiling may avoid this problem since it does not have a dead corner. The disadvantage of this arc-shaped ceiling is that it may generate non-uniform temperature distribution for the cross-section segment area because the distance from the center is different from the sides. Since the main heat transfer mechanisms are the heat conduction and the thermal convection in a gas atmosphere, however, the thermal radiation non-uniformity arising from the different distance may be negligible if this arc is not too sharp.

[0028] In FIG. 5, the heating elements **501** consist of a top piece **501A** and a bottom piece **501B**. Similarly, the thermocouple **502** is constituted from a top piece **502A** and a bottom piece **502B**. Every pair of a heating element and a thermocouple can be independently controlled to adjust the local temperature. Pair of grooves **503A** and **503B** are cut in to tightly hold the teeth from the matched thermal control component in another modular section. The distance between the substrate **500** and the center of the ceiling may be designed from 20 to 200 mm, preferably 40 – 80 mm to hold sufficient Se vapor pressure inside the thermal control component, if a substrate moving speed is one meter per minute.

[0029] FIG. 6 illustrates another embodiment of the reactor. In this design, the precursor layer on a flexible substrate has been turned to an upside-down position. Since most of the flexible substrates going through a high temperature reaction are made from metals, they can support a large tension for the substrate delivery. Therefore, it should not have a significant gravity sag in the center of the substrate if it transports over 10 meters without any support between the unwinding and the winding chambers. As a result, a long substrate roll can be delivered through the entire oven combined with a series of thermal control components in different modular sections without touching the bottoms.

[0030] In various aspects of the embodiment, as shown in FIG. 6, the reactor includes a heating section **S6**, a cooling section **S7**, at least one modular buffer section **M7** (and as shown, **M8**) installed between the heating section and the cooling section, and a reaction oven **605** that includes an oven space **605B**, one or more modular oven bodies **605A**, one or more heating modules **602A** and **602B**, one or more cooling elements **603**, one or more thermocouples **604**, and one or more gas inlets **610A** and gas outlets **610B** to said oven space **605B**. The oven space has a rectangular cross-section shape with an internal height between 10 and 200 millimeters, and an internal width between 100 and 2000 millimeters. The reaction oven **605** is configured in such a way that a flexible substrate **600** can be delivered through said oven, and the reactor is adapted to be used in a roll-to-roll process over a continuous flexible substrate to carry out reactions at the down side of said flexible substrate at an elevated temperature under a controlled atmosphere. In a further aspect, the temperature inside the reaction oven is adapted to be controllable from 25 to 1000 °C, and preferably from 100 to 800 °C.

[0031] In another aspect, the length of the reactor is adjustable by adding or reducing number of the modular buffer sections **M7** and **M8**. In yet another aspect, the reactor further includes a reaction chamber **613** enclosed by modular reaction chamber wall **614**, and the reaction oven **605** is inside said reaction chamber **613**. In a further aspect, the reaction chamber wall **614** includes one or more materials selected from the group consisting of stainless steel, titanium, and aluminum alloy. In various aspects, the reaction chamber includes at least a gas inlet **607A** and a gas outlet **607B**, which may also function as vacuum outlets. Moreover, some vacuum outlets with valves (not shown) may be applied to some modular buffer sections to connect with some turbomolecular or diffusion pumps to obtain high vacuum. The reaction chamber is surrounding the whole reaction oven, and there is free space all around the reaction oven **605** between the reaction oven and the reaction chamber wall **614**. The space adds insulation between the reaction oven and the reaction chamber wall. In other various aspects, there is substantially not any free space between the reaction oven and the bottom reaction chamber wall. Insulating material (not shown) may be placed between the reaction oven and the reaction chamber wall; alternatively, insulating material may be placed outside the reaction chamber.

[0032] In another aspect, the reactor further includes a out vacuum chamber **606** surrounding the whole reaction chamber. The out vacuum chamber is enclosed by one or more pieces of vacuum chamber walls **606A**. There may be one or more channels with valves (not shown) to communicate the out vacuum chamber and the reaction chamber. In yet another aspect, the

reactor further includes an out vacuum chamber that substantially covers only a top section of the reaction chamber (not shown).

[0033] As shown in FIG. 6, the substrate roll **600** starts in the unwinding chamber **600A** connected with the heating section **S6**, passes the roller **601A** and goes through the reaction oven **605** that includes several pieces of modular thermal control components **605A**, then passes the roller **601B**, and ends in the winding chamber **600B** connected with the cooling section **S7**. The other structure and mechanisms are similar to the apparatus shown in FIG. 1, except for some modifications for the upside-down requirements and the thermal control components. In these modifications, the vacuum/gas inlets (or outlets) **607A** and **607B** for the reaction chamber **613**, and the gas holes **610A** and **610B** in the annealing/reaction oven **605** are opened in the bottom side of the oven. Moreover, the vacuum outlets **608A** and **608B** may be in the upper part of the vacuum chamber **606**. Two pairs of shutters **611A** and **611B** possess the same function as their analogues **111A** and **111B** in the FIG.1 device. The functions of the valves **609A** and **609B** in this figure are also the same as their analogues **109A** and **109B** in FIG. 1. The whole operation procedure for this apparatus is similar to the one shown in FIG. 1, as described above.

[0034] The main difference in this apparatus shown in FIG. 6 is in its thermal control component **605A**. The heating elements and the thermocouples are not arranged inside the oven material but above and underneath it. The oven shape is changed to a rectangle shape with round internal corners. Some heating modules **602A** and **602B** that contain heating elements and thermocouples to independently control temperatures are arranged closely above and underneath the rectangle shaped oven materials, as shown in FIG. 7 for its details. The cooling section is still the same as the one shown in FIG. 1. It contains the thermocouples **603** and the cooling elements **604**. Alternately, the thermal control components can use the same designs in FIG. 1 device as well.

[0035] In another aspect of the embodiment as shown in FIG. 7, this rectangle thermal control component **605A** contains an upper piece **605C** and a bottom piece **605D**, which makes it much easier to fabricate with a low cost. Between the contact areas of **605C** and **605D**, pairs of teeth and dent cut are made along the whole sides, respectively, in **605C** and **605D**, as **701** marked. This prevents the gas inside the thermal control components from escaping out of the oven. Similarly, the same structures (not shown in FIG. 7) are fabricated on the end sides of every modular thermal control component to keep the gas inside the oven as much as possible.

FIG. 7 also shows some upper heating modules **602A** and some bottom heating modules **602B**. These modules contain the heating elements and the thermocouples. Every one of them can be independently controlled to adjust the temperature. If the oven materials are good heat conductive materials such as graphite, quartz glass, and conductive ceramics, these heating modules can control the oven temperature very well. Because these thermal control components are working in corrosive atmosphere, the material to make these heating modules must be corrosion resistant, such as stainless steel, molybdenum, titanium or ceramics. If they are made from stainless steel, it is suggested to coat Mo on the surfaces to prevent any possibility of iron release at a high temperature. The round internal corners of this thermal control component are designed to reduce the eddy gas flowing, as shown in FIG. 7. The width of the reaction oven depends on the web width and is generally 100 – 2000 millimeters, preferably 300 – 1200 millimeter. The internal height of the oven is between 10 and 200 mm, preferably 30 – 80 mm. [0036] There are some advantages for this upside-down design. If this reactor is used to prepare CIGS absorbers under an inert gas atmosphere and excessive amounts of Se is pre-coated on the top of the precursor film, for example, lots of Se will be evaporated from the top during a high temperature heating since the Se evaporation has an opposite direction from the Se thermal diffusion into the CIGS precursor. An upside-down design can significantly reduce the Se evaporation because directions of the Se evaporation and its thermal diffusion into the precursor are the same. As a result, less excessive Se consumption is expected, and a better process control and a more stable reaction are predicted since less Se enters into the inert gas atmosphere. If this reaction needs to be carried out under a H₂S or H₂Se gas, this upside-down design should be benefit for the gas diffusion into the CIGS precursor coating. Another advantage for this upside-down arrangement is that the over-saturated Se vapor is not easy to condense on a moving substrate. Any possibly condensed Se liquid can only drop down to the back side of the substrate but not damage the absorber material.

[0037] **Example 1:** Post-treatment of a CdTe film in CdCl₂:Ar:O₂ atmosphere:

[0038] A CdTe solar cell deposited on a flexible substrate can only be a substrate configuration. In this example, a stainless steel roll coated with Mo may be used as a substrate and CdTe and CdS layers can be deposited with the methods of a vacuum evaporation and a chemical bath deposition (CBD), respectively. After CdTe and CdS deposition, a CdCl₂ anneal is usually required to increase the solar cell efficiency because the anneal increases the open circuit voltage *V*_{oc} and the fill factor *FF*. Several mechanisms for these improvements have been

proposed, such as the elimination of fast-recombination centers in the CdTe film, reduction of recombination centers in the junction, and the elimination of small grains at the grain boundaries.

[0039] An apparatus shown in FIG. 1 with a 10 meter long oven, assembled with 10 pieces of one-meter long modular buffer sections, may be used to anneal CdTe absorber/CdS window layers. The roll coated with CdTe/CdS may be loaded and the whole equipment may be vacuumed down to a level of 10^{-3} Pa and remained for about 15 minutes with the valves **107A** and **107B** opened to vacuum as well. Then turn off the vacuum pumps and close one of the vacuum valves **109A** and **109B**, followed by filling Ar to about 10^5 Pa from one of the gas valves **109A** and **109B**. Repeat this cycle twice before heating the oven up to 420 °C. Then the substrate may be delivered at a speed of one meter per minute. Meanwhile, a gas mixture of CdCl₂:Ar:O₂ may be introduced from the valve **107A** with the partial pressures $p(\text{CdCl}_2)$ from 0.65 to 1.2 Pa and $p(\text{O}_2)$ from 1.5×10^3 to 2×10^4 Pa. The valve **107B** may be partially turned on to maintain a gentle gas flowing. The escaped gases should be led to a well sealed chemical treatment system. During annealing, one of the valves **108A** and **108B** is opened to keep the chamber **106** under vacuum. After the annealing completes, the system should be vacuumed again to remove the residue gases before opening the chambers.

[0040] **Example 2:** Selenization of a CIG precursor layer in H₂Se/H₂S gas atmosphere to form CIGS absorber:

[0041] In a CIGS thin film solar cell, formation of the CIGS absorber may need several steps. In a traditional method, a CIG precursor was generated first through some different methods, vacuum or non-vacuum, and then the CIG precursor was selenized under H₂Se or H₂Se/H₂S atmosphere at an enhanced temperature to form a stoichiometric CIGS absorber. Because H₂Se is an extremely toxic gas, it has been much less used today. However, it is still used sometimes because this gas-solid selenization reaction may generate a better quality CIGS absorber.

[0042] Due to its high toxicity, H₂Se is hard to prepare and store. Therefore, an H₂Se gas cylinder is very expensive. A more economical H₂Se gas source may be from an *in-situ* generation. For example, the solid Se or S can be reduced by H₂ at an elevated temperature to generate H₂Se and H₂S gases which can be introduced into the present apparatus for a selenization reaction. This reactor is not shown in the current invention. In this example, a flexible substrate roll coated with CIG precursor layer is loaded into an apparatus described in Example 1 and the vacuum-inert gas cycles are applied as described in Example 1. During the

vacuum-inert gas cycles, a longer time, i.e., 20 - 30 minutes, to remain the system under a high vacuum may be necessary. Fill the working chambers with ultra-pure Ar. The oven temperature may be set between 500 and 550 °C. After the oven temperature becomes stable, the substrate may be delivered at a speed of one meter per minute. Make sure one of the valves **108A** and **108B** is open to vacuum and the possible residues are delivered to a sealed chemical treatment system. Make sure enough H₂Se and H₂S gas sensors are installed around the working space. The shutters **111A** and **111B** may be closed to leave a narrow slit between 2 and 4 mm and some Ar from one of the valves **109A** and one of the valves **109B** is gently released into the oven through these two shutter slits. The reaction gas, H₂Se or H₂Se/H₂S mixture, may be introduced into the oven through the valve **107A** at a pressure about 10³ Pa. This gas may be diluted with about 5% Ar flowing from the slit **111A**. The valve **107B** should be opened and the escaped toxic gas should be delivered into the sealed chemical treatment system. After the reaction completes, the gas supply is stopped and the valve **107A** is turned off. After the heating is stopped, the inert gas should be purged and the vacuum-inert gas cycle should be applied again to remove the residue gas before the chambers are opened.

[0043] If the reaction has to be carried out in two different gas atmospheres, i.e., H₂Se and H₂S, the modular buffer sections can be modified with a gas outlet followed by a gas inlet for different gas ambient. Another gas outlet may be opened in this transition zone between these gas outlet and inlet to remove the mixed gases.

[0044] **Example 3:** Selenization of a CIGS precursor layer under an inert gas ambient.

[0045] As described in Example 2, the selenization under an H₂Se ambient is not common today. Commonly, the selenization is carried out in two ways. On one hand, Cu, Ga, In and Se are co-deposited and selenized, or Se is continuously supplied during a vacuum deposition of Cu, In and Ga. The selenization may have been completed during these processes. If not, the CIGS precursors may need annealing in a reactor as shown in the present invention. On the other hand, a CIGS precursor film may be constituted from multiple layers of Cu, Ga, In and Se. The different elements are not reacted during their depositions. Under this circumstance, the CIGS precursor must be reacted and selenized to form a high quality stoichiometric CIGS absorber. The present invention is well suitable for this application.

[0046] The apparatus shown in FIG. 1 and FIG. 3 are both good for the selenization reaction. Inside these equipments, the precursor layer faces up. The Se amount in these precursors should be excessive because some Se will evaporate during the reaction at an enhanced

temperature, especially if it is deposited on the top. During the selenization reaction, partial Se thermally diffuses down to mix with the other elements and partial Se evaporates up into the ambient. In order to reduce the Se evaporation, the apparatus shown in FIG. 6 is employed as the reactor in this example.

5 [0047] The substrate roll **600** shall be loaded upside down in the unwinding chamber **600A**. This roll **600** is delivered over the roller **601A**, passing the heating section **S6**, going through the oven that consists of 10 modular buffer sections from **M7** to **M16**, cooled down in the cooling section **S7**, adjusted the position over the roller **601B**, and finally ending inside the winding chamber **600B**. Among 10 modular buffer sections, half of them possess vacuum
10 outlets to connect with turbomolecular pumps. At the beginning of a vacuum process, a main dry mechanical pump works to reach a vacuum at about 10 Pa, and then the turbomolecular pumps start to drive vacuum to about 10^{-3} Pa. The valves between these modular buffer sections and the turbomolecular pumps have to be closed during a gas filling process. At least three vacuum-inert gas cycles are performed before heating up. During vacuuming, the vacuum
15 level should be down to about 10^3 Pa and remained at this level for at least 20 minutes. The moving speed of the substrate may be still selected at one meter per minute. The oven can be heated up to 500 - 550 °C. The temperature can be controlled precisely at ± 1 °C with the heating modules. The reaction may be carried out in ultra-pure Ar or N₂ ambient. The gas may be delivered through the valve **607A** and diffuse into the oven through the holes **610A**, and
20 then escape out of the hole **610B** and the valve **607B**. During the reaction, more and more Se may be evaporated into the atmosphere. Therefore, the escaped gas may be led to a Se recovery device or a treatment system. Because the precursor faces down, there is no condensed Se dropping onto the CIGS absorber.

[0048] As described above, this apparatus can be extensively used to anneal and/or make the
25 reaction of Group IB-III A-VIA or Group IIB-VIA solar cell absorbers on the flexible continuous substrates with different widths. It can precisely control the temperatures to obtain very uniform temperature distribution on the reacted precursors. It is vacuum tight to reach a high vacuum. It can be used for the reactions under different ambient, i.e., vacuum, inert gas or toxic gas.

What is claimed is:

1. A reactor, comprising:
 - a heating section;
 - a cooling section;
 - 5 at least one modular buffer section installed between said heating section and said cooling section, said modular buffer section including one or more modular thermal control components and modular reaction chamber wall; and
 - a reaction oven that has an oven space enclosed by said one or more modular thermal control components, one or more heating elements, one or more cooling elements, one or more thermocouples, one or more gas inlets to said oven space, and one or more gas outlets to said oven space;
 - 10 wherein said oven space has a central internal height between 20 and 300 millimeters, and a internal bottom width between 100 and 2000 millimeters;
 - wherein said reaction oven is configured in such a way that a flexible substrate can be delivered through said oven; and
 - 15 wherein said reactor is adapted to be used in a roll-to-roll process over a continuous flexible substrate to carry out reactions at an elevated temperature under a controlled atmosphere.
2. The reactor of claim 1, wherein the length of the reactor is adjustable by adding or reducing the numbers of the modular buffer sections, and wherein the temperature inside said reaction oven is adapted to be controllable from 25 °C to 1000 °C.
3. The reactor of claim 1, wherein the temperature inside said reaction oven is adapted to be controllable from 100 °C to 800 °C.
4. The reactor of claim 1, further comprising a reaction chamber enclosed by said modular reaction chamber wall, a roll unwinding chamber, and a roll winding chamber, wherein:
 - said reaction chamber substantially encloses said reaction oven;
 - said reaction chamber has at least a gas inlet and a gas outlet;
 - said reaction chamber, said roll unwinding chamber, and said roll winding chamber are joined together to form a main vacuum chamber that is adapted to be capable of being vacuumed down to 1×10^{-3} Pa.
 - 25
 - 30

5. The reactor of claim 4, wherein said reaction oven is placed at bottom of the reaction chamber, without a substantial empty space between said reaction oven and a lower reaction chamber wall.

6. The reactor of claim 5, further comprising a vacuum chamber that
5 surrounds a top section of the reaction chamber.

7. The reactor of claim 4, further comprising vacuum chamber wall, said vacuum chamber wall enclosing a vacuum chamber, said vacuum chamber substantially surrounding the whole reaction chamber.

8. The reactor claim 4, wherein some modular buffer sections in said
10 reaction chamber have one or more vacuum outlets connected to one or more turbomolecular or diffusion pumps.

9. The reactor of claim 1, wherein the modular thermal control component includes one or more materials selected from the group consisting of graphite, ceramics and quartz glass.

10. The reactor of claim 1, wherein:
said modular thermal control component includes one or more top pieces, one or more flat bottom pieces, and means for coupling said top pieces and said flat bottom pieces;
said top piece and said flat bottom piece each includes one or more items selected from the group consisting of heating elements, thermocouples, and cooling elements;
20 and

said modular thermal control component includes tooth-dent coupling designs on both cross sides to tightly connect with other pieces.

11. The reactor of claim 4, wherein said reaction chamber wall includes one or more materials selected from the group consisting of stainless steel, titanium, and aluminum
25 alloy.

12. A reactor, comprising:
a heating section;
a cooling section;
at least one modular buffer section installed between said heating section and
30 said cooling section; and

a reaction oven that includes an oven space, one or more modular thermal control components, one or more heating elements, one or more cooling elements, one or more thermocouples, and one or more gas inlets and gas outlets to said oven space;

5 wherein said modular thermal control component includes a top piece and a bottom piece;

wherein said oven space has a rectangular cross-section shape with a internal height between 10 and 200 millimeters, and a internal width between 100 and 2000 millimeters;

wherein said reaction oven is configured in such a way that a flexible substrate can be delivered through said oven, and

10 wherein said reactor is adapted to be used in a roll-to-roll process over a continuous flexible substrate to carry out reactions at the down side of said flexible substrate at an elevated temperature under a controlled atmosphere.

13. The reactor of claim 12, wherein the length of the reactor is adjustable by adding or reducing number of the modular buffer sections.

15 14. The reactor of claim 12, further comprising a reaction chamber enclosed by modular reaction chamber wall, wherein the reaction oven includes said one or more heating elements and cooling elements, and the reaction oven is inside said reaction chamber.

20 15. The reactor of claim 12, wherein some modular buffer sections in said reaction chamber have one or more vacuum outlets connected to one or more turbomolecular or diffusion pumps.

16. The reactor of claim 14, wherein the temperature inside said reaction oven is adapted to be controllable from 25 to 1000 °C, preferably 100 to 800 °C.

17. The reactor of claim 14, wherein the temperature inside said reaction oven is adapted to be controllable from 100 to 800 °C.

25 18. The reactor of claim 14, wherein the reaction chamber includes at least a gas inlet and a gas outlet and is surrounding the whole reaction oven.

19. The reactor of claim 14, wherein there is substantially not any free space between said reaction oven and the bottom of said reaction chamber.

20. The reactor of claim 19, further including a vacuum chamber that substantially covers a top section of said reaction chamber.

21. The reactor of claim 14, further including a vacuum chamber surrounding the whole reaction chamber, said vacuum chamber being enclosed by vacuum chamber wall.

22. The reactor of claim 14, wherein said modular thermal control component includes one or more materials selected from the group consisting of graphite, ceramics, and quartz glass.

23. The reactor of claim 14, wherein said modular thermal control component includes a top piece and a bottom piece with a teeth-dent coupling design on their contact surfaces adapted to avoid gas escaping, and wherein said modular thermal control component includes means for tightly connecting with other pieces of modular thermal control components.

24. The reactor of claim 14, further including heating modules, wherein said heating modules include one or more heating elements and thermocouples installed on the top and the bottom of the thermal control component, in such a way that temperatures at the top and bottom of the thermal control component can be controlled independently.

25. The reactor of claim 16, wherein said reaction chamber wall includes one or more materials selected from the group consisting of stainless steel, titanium, and aluminum alloy.

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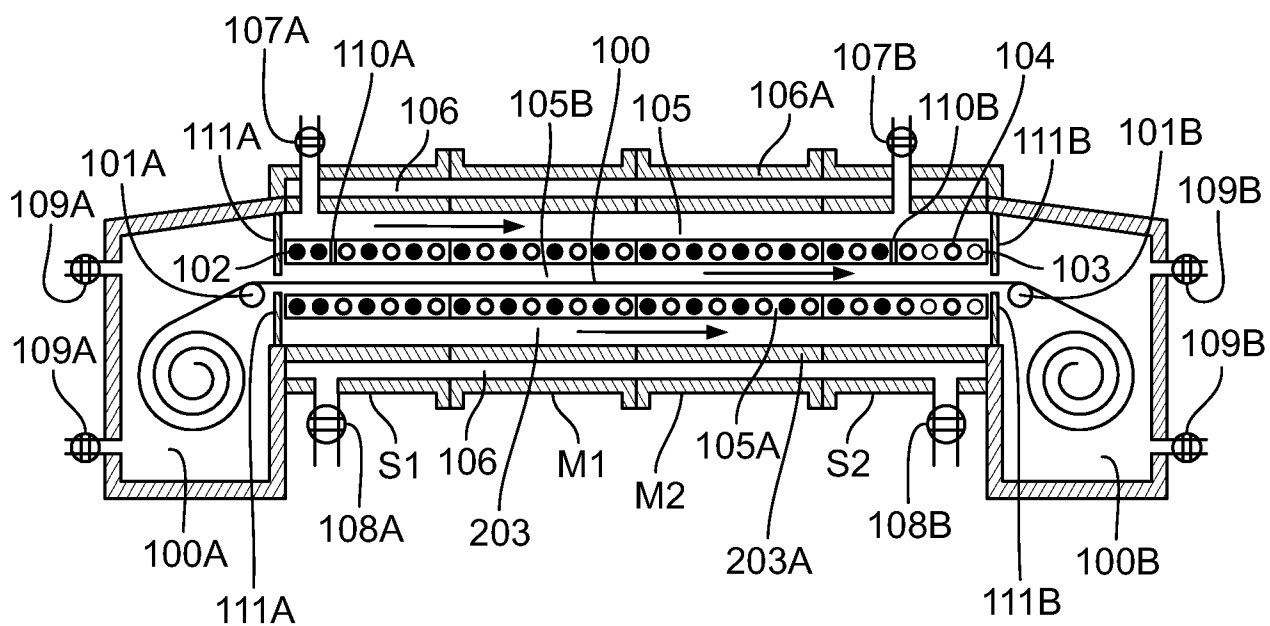


FIG. 1

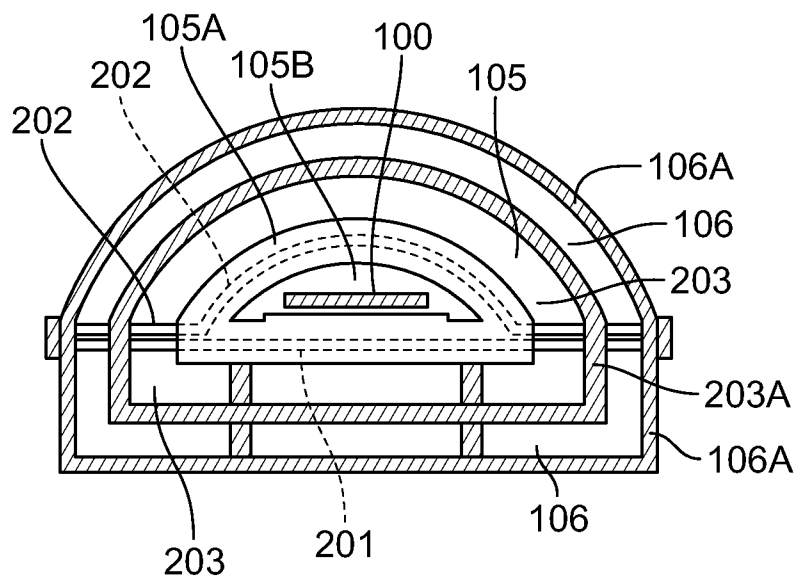


FIG. 2

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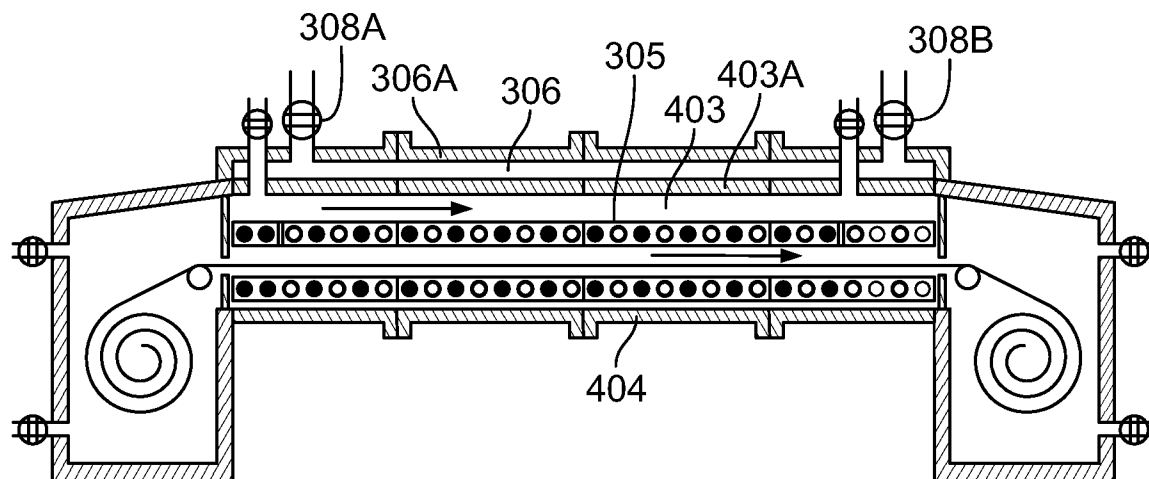


FIG. 3

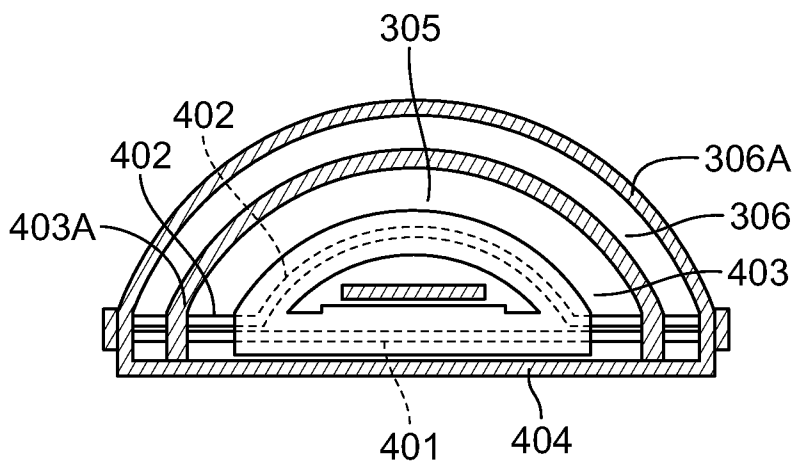


FIG. 4

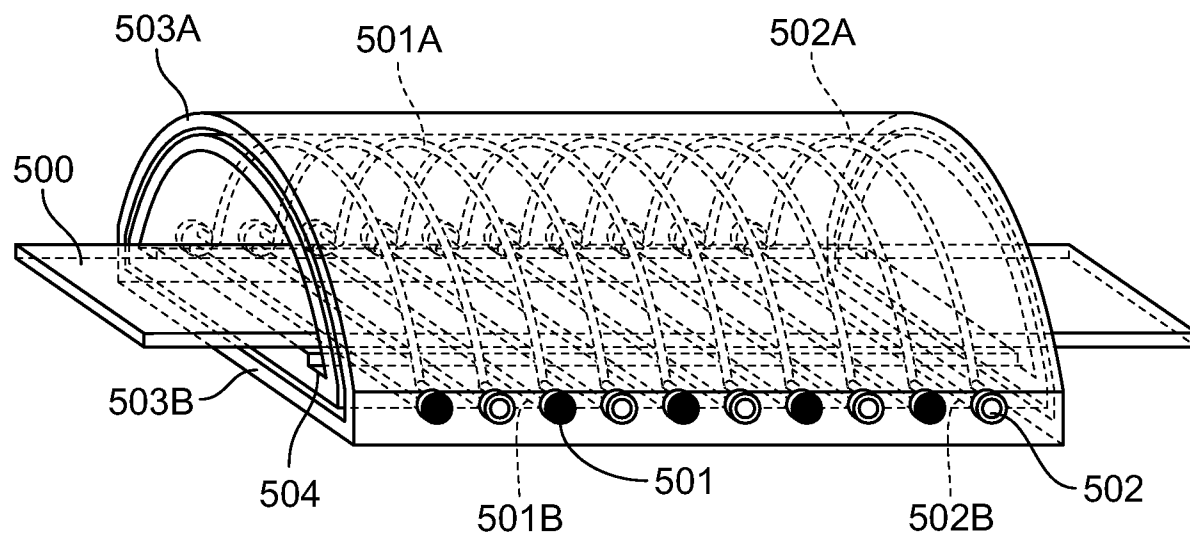


FIG. 5

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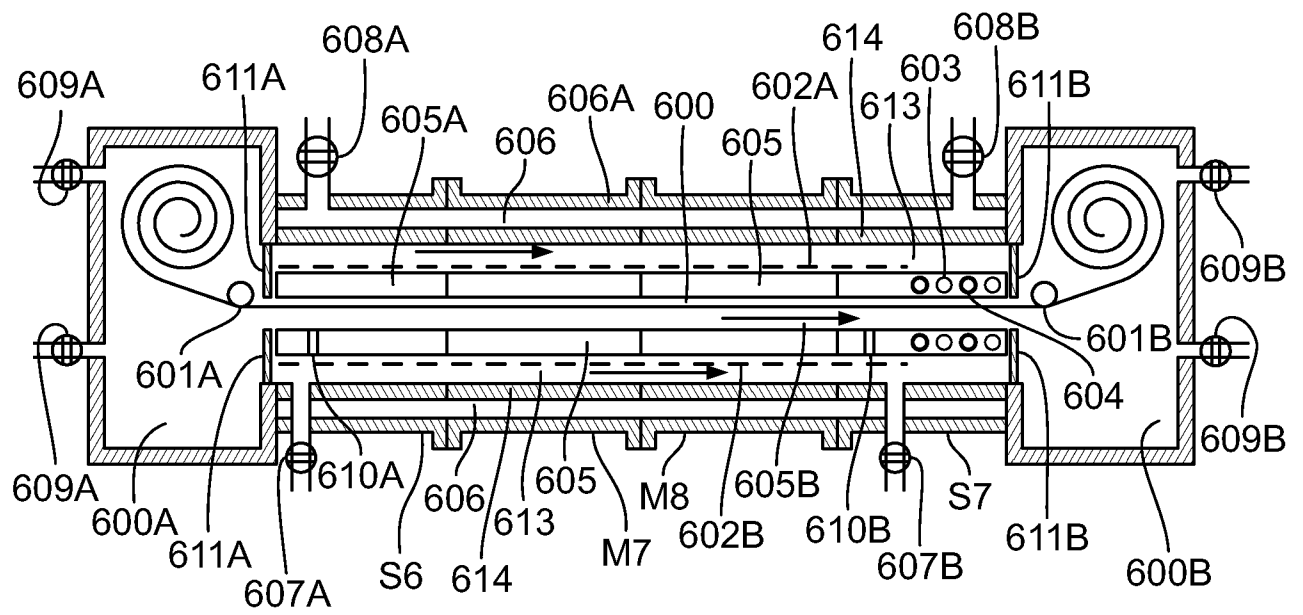


FIG. 6

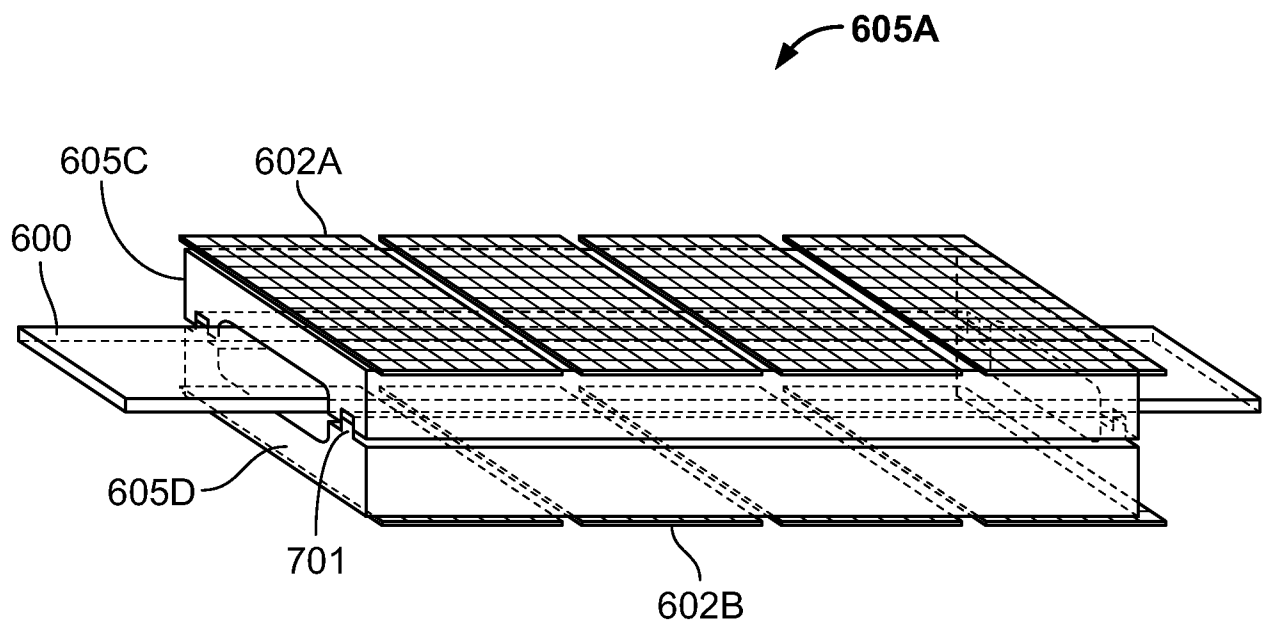


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2012/032869

A. CLASSIFICATION OF SUBJECT MATTER *H01L 31/18 (2006.01)*
H05B 6/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L 31/00, 31/18, B01J 19/00, C02F 1/08, C30B 25/02, C23C 16/44, H01L 21/203, H05B 6/00-6/78

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSearch (RUPTO internal), Esp@cenet, PAJ, DWPI, USPTO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20100288640 A1 (R3 FUSION, INC.) 18.11.2010	1-25
A	US 2010/0139557 A1 (SOLOPOWER, INC.) 10.07.2010	1-25
A	US 5855680 A (NESTE OY) 05.01.1999	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

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