Abstract: A roll-to-roll or reel-to-reel RTP tool including a reactor having a continuous insert placed in a primary gap of the reactor is provided. The primary gap of the reactor is defined by peripheral reactor walls including a top reactor wall, a bottom reactor wall and side reactor walls. The continuous insert includes a continuous process gap through which a continuous workpiece travels between an entry opening and an exit opening of the insert. An inner space exists between at least one of the insert walls and at least a portion of the peripheral reactor walls that make up the primary gap. At least one gas inlet is connected to the inner space, and at least one exhaust opening connects the process gap as well as the inner space to outside the reactor and carries any gaseous products to outside the process gap and the primary gap of the reactor.
REACTOR TO FORM SOLAR CELL ABSORBERS

BACKGROUND OF THE INVENTION

[0001] This application claims priority to US application no: 12/334,420, which is a continuation-in-part of and claims priority to U.S. Patent Application No. 12/027,169, filed February 6, 2008, entitled "Reel-To-Reel Reaction of a Precursor Film to Form Solar Cell Absorber," which is a continuation-in-part and claims priority to U.S. Patent Application No. 11/938,679, filed November 12, 2007 entitled "Reel-To-Reel Reaction Of Precursor Film To Form A Solar Cell Absorber" and U.S. Utility Application. 11/549,590 filed October 13, 2006 entitled "Method and Apparatus For Converting Precursor Layers Into Photovoltaic Absorbers," which applications are also expressly incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present invention relates to method and apparatus for preparing thin films of semiconductor films for radiation detector and photovoltaic applications.

BACKGROUND

[0003] Solar cells are photovoltaic devices that convert sunlight directly into electrical power. The most common solar cell material is silicon, which is in the form of single or polycrystalline wafers. However, the cost of electricity generated using silicon-based solar cells is higher than the cost of electricity generated by the more traditional methods. Therefore, since early 1970's there has been an effort to reduce cost of solar cells for terrestrial use. One way of reducing the cost of solar cells is to develop low-cost thin film growth techniques that can deposit solar-cell-quality absorber materials on large area substrates and to fabricate these devices using high-throughput, low-cost methods.

[0004] Group IBIIIAVIA compound semiconductors comprising some of the Group IB (Cu, Ag, Au), Group IIIA (B, Al, Ga, In, TI) and Group VIA (O, S, Se, Te, Po) materials or elements of the periodic table are excellent absorber materials for thin film solar cell structures. Especially, compounds of Cu, In, Ga, Se and S which are generally referred to as CIGS(S), or Cu(In, Ga)(S,Se)2 or CuIn1−xGax(Se1−ySx)X, where 0<x<1, 0<y≤1 and k is approximately 2, have already been employed in solar cell structures that yielded conversion efficiencies approaching
20%. Absorbers containing Group IIIA element Al and/or Group VIA element Te also showed promise. Therefore, in summary, compounds containing: i) Cu from Group IB, ii) at least one of In, Ga, and Al from Group IIIA, and iii) at least one of S, Se, and Te from Group VIA, are of great interest for solar cell applications.

[0005] The structure of a conventional Group IBIIIAVIA compound photovoltaic cell such as a Cu(In,Ga,Al)(S,Se,Te)_{2} thin film solar cell is shown in Figure 1. The device 10 is fabricated on a substrate 11, such as a sheet of glass, a sheet of metal, an insulating foil or web, or a conductive foil or web. The absorber film 12, which comprises a material in the family of Cu(In,Ga,Al)(S,Se,Te), is grown over a conductive layer 13, which is previously deposited on the substrate 11 and which acts as the electrical contact to the device. The substrate 11 and the conductive layer 13 form a base 20. Various conductive layers comprising Mo, Ta, W, Ti, and stainless steel etc. have been used in the solar cell structure of Figure 1. If the substrate itself is a properly selected conductive material, it is possible not to use a conductive layer 13, since the substrate 11 may then be used as the ohmic contact to the device. After the absorber film 12 is grown, a transparent layer 14 such as a CdS, ZnO or CdS/ZnO stack is formed on the absorber film. Radiation 15 enters the device through the transparent layer 14. Metallic grids (not shown) may also be deposited over the transparent layer 14 to reduce the effective series resistance of the device. The preferred electrical type of the absorber film 12 is p-type, and the preferred electrical type of the transparent layer 14 is n-type. However, an n-type absorber and a p-type window layer can also be utilized. The preferred device structure of Figure 1 is called a "substrate-type" structure. A "superstrate-type" structure can also be constructed by depositing a transparent conductive layer on a transparent superstrate such as glass or transparent polymeric foil, and then depositing the Cu(In,Ga,Al)(S,Se,Te)_{2} absorber film, and finally forming an ohmic contact to the device by a conductive layer. In this superstrate structure light enters the device from the transparent superstrate side. A variety of materials, deposited by a variety of methods, can be used to provide the various layers of the device shown in Figure 1.

[0006] In a thin film solar cell employing a Group IBIIIAVIA compound absorber, the cell efficiency is a strong function of the molar ratio of IB/IIIA. If there are more than one Group IIIA materials in the composition, the relative amounts or molar ratios of these IIIA elements also affect the properties. For a Cu(In,Ga)(S,Se)_{2} absorber layer, for example, the efficiency of the device is a function of the molar ratio of Cu/(In+Ga). Furthermore, some of the important parameters of the
cell, such as its open circuit voltage, short circuit current and fill factor vary with the molar ratio of the IIIA elements, i.e. the Ga/(Ga+In) molar ratio. In general, for good device performance Cu/(In+Ga) molar ratio is kept at around or below 1.0. As the Ga/(Ga+In) molar ratio increases, on the other hand, the optical bandgap of the absorber layer increases and therefore the open circuit voltage of the solar cell increases while the short circuit current typically may decrease. It is important for a thin film deposition process to have the capability of controlling both the molar ratio of IB/IIIA, and the molar ratios of the Group IIIA components in the composition. It should be noted that although the chemical formula is often written as Cu(In,Ga)(S,Se)\(_2\), a more accurate formula for the compound is Cu(In,Ga)(S,Se)\(_k\), where \(k\) is typically close to 2 but may not be exactly 2. For simplicity we will continue to use the value of \(k\) as 2. It should be further noted that the notation "Cu(X,Y)" in the chemical formula means all chemical compositions of X and Y from (X=0% and Y=100%) to (X=100% and Y=0%). For example, Cu(In,Ga) means all compositions from CuIn to CuGa. Similarly, 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.

[0007] One technique for growing Cu(In,Ga)(S,Se)\(_2\) type compound thin films for solar cell applications is a two-stage process where metallic components of the Cu(In,Ga)(S,Se)\(_2\) material are first deposited onto a substrate, and then reacted with S and/or Se in a high temperature annealing process. For example, for CuInSe\(_2\) growth, thin layers of Cu and In are first deposited on a substrate and then this stacked precursor layer is reacted with Se at elevated temperature. If the reaction atmosphere also contains sulfur, then a CuIn(S,Se)\(_2\) layer can be grown. Addition of Ga in the precursor layer, i.e. use of a Cu/In/Ga stacked film precursor, allows the growth of a Cu(In,Ga)(S,Se)\(_2\) absorber.

[0008] Two-stage process approach may also employ stacked layers comprising Group VIA materials. For example, a Cu(In,Ga)Se\(_2\) film may be obtained by depositing In-Ga-Se and Cu-Se layers in an In-Ga-Se/Cu-Se stack and reacting them in presence of Se. Similarly, stacks comprising Group VIA materials and metallic components may also be used. Stacks comprising Group VIA materials include, but are not limited to In-Ga-Se/Cu stack, Cu/In/Ga/Se stack, Cu/Se/In/Ga/Se stack, etc.

[0009] Selenization and/or sulfidation or sulfurization of precursor layers comprising metallic components may be carried out in various forms of Group VIA material(s). One approach involves using gases such as H\(_2\)Se, H\(_2\)S or their mixtures to react, either simultaneously or
consecutively, with the precursor comprising Cu, In and/or Ga. This way a Cu(In,Ga)(S,Se)₂ film may be formed after annealing and reacting at elevated temperatures. It is possible to increase the reaction rate or reactivity by striking plasma in the reactive gas during the process of compound formation. Se vapors or S vapors from elemental sources may also be used for selenization and sulfidation. Alternately, as described before, Se and/or S may be deposited over the precursor layer comprising Cu, In and/or Ga and the stacked structure can be annealed at elevated temperatures to initiate reaction between the metallic elements or components and the Group VIA material(s) to form the Cu(In,Ga)(S,Se)₂ compound.

[0010] Reaction step in a two-stage process is typically carried out in batch furnaces. In this approach, a number of pre-cut substrates, typically glass substrates, with precursor layers deposited on them are placed into a batch furnace and reaction is carried out for periods that may range from 15 minutes to several hours. Temperature of the batch furnace is typically raised to the reaction temperature, which may be in the range of 400-600 °C, after loading the substrates, The ramp rate for this temperature rise is normally lower than 5 °C/sec, typically less than 1 °C/sec. This slow heating process works for selenizing metallic precursors (such as precursor layers containing only Cu, In and/or Ga) using gaseous Se sources such as H₂Se or organometallic Se sources. For precursors containing solid Se, however, slow ramp rate causes Se de-wetting and morphological problems. For example, reacting a precursor layer with a structure of base/Cu/In/Se by placing it in a batch furnace with a low temperature rise rate (such as 1 °C/sec) yields films that are powdery and non-uniform. Such films would not yield high efficiency solar cells.

[0011] One prior art method described in U.S. Patent 5578503 utilizes a rapid thermal annealing (RTP) approach to react the precursor layers in a batch manner, one substrate at a time. Such RTP approaches are also disclosed in various publications (see, for example, Mooney et al., Solar Cells, vol:30, p:69, 1991, Gabor et al., AIP Conf. Proc. #268, PV Advanced Research & Development Project, p:236, 1992, and Kerr et al., IEEE Photovoltaics Specialist Conf., p:676, 2002). In the prior art RTP reactor design the temperature of the substrate with the precursor layer is raised to the reaction temperature at a high rate, typically at 10 °C/sec. It is believed that such high temperature rise through the melting point of Se (220 °C) avoids the problem of de-wetting and thus yields films with good morphology.

[0012] Design of the reaction chamber to carry out selenization/sulfidation processes is critical for the quality of the resulting compound film, the efficiency of the solar cells, throughput,
material utilization and cost of the process. Present invention provides methods and apparatus to carry out reaction of precursor layers for CIGS(S) type absorber formation, in a roll-to-roll manner. Roll-to-roll or reel-to-reel processing increases throughput and minimizes substrate handling. Therefore, it is a preferred method for large scale manufacturing.

SUMMARY

[0013] The present invention provides a method and integrated tool to form solar cell absorber layers on continuous flexible substrates. A roll-to-roll rapid thermal processing (RTP) tool including multiple chambers is used to react a precursor layer on a continuous flexible workpiece.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 is a cross-sectional view of a solar cell employing a Group IBIIIAVIA absorber layer;

[0015] Figure 2 shows an apparatus to react precursor layers in a reel-to-reel fashion to form a Group IBIIIAVIA layer on a flexible foil base;

[0016] Figure 3A shows an exemplary flexible structure comprising a flexible base and a precursor layer deposited on it;

[0017] Figure 3B shows a base with a Group IBIIIAVIA absorber layer formed on it by reacting the precursor layer(s) of Figure 3A;

[0018] Figure 4 shows another apparatus to react precursor layers in a reel-to-reel fashion to form a Group IBIIIAVIA layer on a flexible foil base;

[0019] Figures 5A-5B show cross-sectional views of different reaction chambers with a flexible structure placed in them;

[0020] Figure 5C shows a cross-sectional view of a reaction chamber comprising an outer chamber and an inner chamber;

[0021] Figure 6 shows such an exemplary version of the reactor of Figure 2;

[0022] Figure 7A is a schematic illustration of an embodiment of a rapid thermal processing (RTP) tool of the present invention including a buffer zone connecting a cold zone to hot zone;

[0023] Figure 7B is a graph depicting thermal profile of the RTP tool shown in Figure 7A;
Figure 8A is a schematic illustration of an embodiment of a roll to roll rapid thermal processing system of the present invention including an embodiment of an RTP tool;

Figure 8B is a schematic perspective view illustration of the RTP tool shown in Figure 8A, wherein the RTP tool includes more than one buffer zone;

Figure 9 is a schematic illustration of another embodiment of an RTP tool of the present invention;

Figure 10A is a schematic illustration of another embodiment of an RTP tool of the present invention;

Figure 10B is a graph depicting thermal profile applied by a top section of the RTP tool shown in Figure 10A;

Figure 10C is a graph depicting thermal profile applied by a bottom section of the RTP tool shown in Figure 10A;

Figure 11A is a schematic side view of an embodiment of a reactor including peripheral reactor walls and an insert placed into the primary gap defined by the peripheral reactor walls;

Figure 11B is a schematic frontal view of the reactor shown in Figure 11A;

Figure 11C is a schematic frontal view of the peripheral reactor walls;

Figure 11D is a schematic frontal view of the insert;

Figure 11E is a schematic frontal view of the reactor shown in Figure 11B, wherein the continuous insert has been set on a bottom wall of the peripheral reactor walls;

Figure 12A is a schematic side view of another embodiment of the reactor shown in Figure 11A, wherein a bottom wall of an insert includes rollers on which a continuous workpiece is moved;

Figure 12B is a schematic frontal view of the reactor shown in Figure 12A;

Figure 12C is a schematic partial view of the rollers shown in Figure 12A; and

Figure 13 is a schematic side view of an embodiment of a reactor.

DETAILED DESCRIPTION

Reaction of precursors, comprising Group IB material(s), Group HIA material(s) and optionally Group VIA material(s) or components, with Group VIA material(s) may be achieved in various ways. These techniques involve heating the precursor layer to a temperature
range of 350-600 °C, preferably to a range of 400-575 °C, in the presence of at least one of Se, S, and Te provided by sources such as; i) solid Se, S or Te sources directly deposited on the precursor, and ii) \( \text{H}_2\text{Se} \) gas, \( \text{H}_2\text{S} \) gas, \( \text{H}_2\text{Te} \) gas, Se vapors, S vapors, Te vapors etc. for periods ranging from 1 minute to several hours. The Se, S, Te vapors may be generated by heating solid sources of these materials away from the precursor also. Hydride gases such as \( \text{H}_2\text{Se} \) and \( \text{H}_2\text{S} \) may be bottled gases. Such hydride gases and short-lifetime gases such as \( \text{H}_2\text{Te} \) may also be generated in-situ, for example by electrolysis in aqueous acidic solutions of cathodes comprising S, Se and/or Te, and then provided to the reactors. Electrochemical methods to generate these hydride gases are suited for in-situ generation.

[0040] Precursor layers may be exposed to more than one Group VIA materials either simultaneously or sequentially. For example, a precursor layer comprising Cu, In, Ga, and Se may be annealed in presence of S to form \( \text{Cu(In, Ga)(S, Se)}_2 \). The precursor layer in this case may be a stacked layer comprising a metallic layer containing Cu, Ga and In and a Se layer that is deposited over the metallic layer. Alternately, Se nano-particles may be dispersed throughout the metallic layer containing Cu, In and Ga. It is also possible that the precursor layer comprises Cu, In, Ga and S and during reaction this layer is annealed in presence of Se to form a \( \text{Cu(In, Ga)(S, Se)}_2 \).

[0041] Some of the preferred embodiments of forming a \( \text{Cu(In, Ga)(S, Se)}_2 \) compound layer may be summarized as follows: i) depositing a layer of Se on a metallic precursor comprising Cu, In and Ga forming a structure and reacting the structure in gaseous S source at elevated temperature, ii) depositing a mixed layer of S and Se or a layer of S and a layer of Se on a metallic precursor comprising Cu, In and Ga forming a structure, and reacting the structure at elevated temperature in either a gaseous atmosphere free from S or Se, or in a gaseous atmosphere comprising at least one of S and Se, iii) depositing a layer of S on a metallic precursor comprising Cu, In and Ga forming a structure and reacting the structure in gaseous Se source at elevated temperature, iv) depositing a layer of Se on a metallic precursor comprising Cu, In and Ga forming a structure, and reacting the structure at elevated temperature to form a \( \text{Cu(In, Ga)}\text{Se}_2 \) layer and/or a mixed phase layer comprising selenides of Cu, In, and Ga and then reacting the \( \text{Cu(In, Ga)}\text{Se}_2 \) layer and/or the mixed phase layer with a gaseous source of S, liquid source of S or a solid source of S such as a layer of S, v) depositing a layer of S on a metallic precursor comprising Cu, In and Ga forming a structure, and reacting the structure at elevated temperature to form a \( \text{Cu(In, Ga)}\text{S}_2 \) layer and/or a mixed phase layer comprising sulfides of Cu, In, and Ga, and then reacting the
Cu(In,Ga)S<sub>2</sub> layer and/or the mixed phase layer with a gaseous source of Se, liquid source of Se or a solid source of Se such as a layer of Se.

It should be noted that Group VIA materials are corrosive. Therefore, materials for all parts of the reactors or chambers that are exposed to Group VIA materials or material vapors at elevated temperatures should be properly selected. These parts should be made of or should be coated by substantially inert materials such as ceramics, e.g. alumina, tantalum oxide, titania, zirconia etc., glass, quartz, stainless steel, graphite, refractory metals such as Ta, refractory metal nitrides and/or carbides such as Ta-nitride and/or carbide, Ti-nitride and/or carbide, W-nitride and/or carbide, other nitrides and/or carbides such as Si-nitride and/or carbide, etc.

Reaction of precursor layers comprising Cu, In, Ga and optionally at least one Group VIA material may be carried out in a reactor that applies a process temperature to the precursor layer at a low rate. Alternately, rapid thermal processing (RTP) may be used where the temperature of the precursor is raised to the high reaction temperature at rates that are at least about 10 °C/sec. Group VIA material, if included in the precursor layer, may be obtained by evaporation, sputtering, or electroplating. Alternately inks comprising Group VIA nano particles may be prepared and these inks may be deposited to form a Group VIA material layer within the precursor layer. Other liquids or solutions such as organometallic solutions comprising at least one Group VIA material may also be used. Dipping into melt or ink, spraying melt or ink, doctor-blading or ink writing techniques may be employed to deposit such layers.

A reel-to-reel apparatus 100 or roll to roll RTP reactor to carry out reaction of a precursor layer to form a Group IBIIIAVIA compound film is shown in Figure 2. It should be noted that the precursor layer to be reacted in this reactor may comprise at least one Group IB material and at least one Group IHA material. For example the precursor layer may be a stack of Cu/In/Ga, Cu-Ga/In, Cu-In/Ga, Cu/In-Ga, Cu-Ga/Cu-In, Cu-Ga/Cu-In/Ga, Cu/Cu-In/Ga, or Cu-Ga/In-Ga etc., where the order of various material layers within the stack may be changed. Here Cu-Ga, Cu-In, In-Ga mean alloys or mixtures of Cu and Ga, alloys or mixtures of Cu and In, and alloys or mixtures of In and Ga, respectively. Alternatively, the precursor layer may also include at least one Group VIA material. There are many examples of such precursor layers. Some of these are Cu/In/Ga/Group VIA material stack, Cu-Group VIA material/In/Ga stack, In-Group VIA material/Cu-Group VIA material stack, or Ga-Group VIA material/Cu/In, where Cu-Group VIA material includes alloys, mixtures or compounds of Cu and a Group VIA material (such as Cu-
selenides, Cu sulfides, etc.), In-Group VIA material includes alloys, mixtures or compounds of In and a Group VIA material (such as In-selenides, In sulfides, etc.), and Ga-Group VIA material includes alloys, mixtures or compounds of Ga and a Group VIA material (such as Ga-selenides, Ga sulfides, etc.). These precursors are deposited on a base 20 comprising a substrate 11, which may additionally comprise a conductive layer 13 as shown in Figure 1. Other types of precursors that may be processed using the method and apparatus of the invention includes Group IBIIIAVIA material layers that may be formed on a base using low temperature approaches such as compound electroplating, electroless plating, sputtering from compound targets, ink deposition using Group IBIIIAVIA nano-particle based inks, spraying metallic nanoparticles comprising Cu, In, Ga and optionally Se, etc. These material layers are then annealed in the apparatus or reactors at temperatures in the 350-600 °C range to improve their crystalline quality, composition and density.

[0045] Annealing and/or reaction steps may be carried out in the reactors of the present invention at substantially the atmospheric pressure, at a pressure lower than the atmospheric pressure or at a pressure higher than the atmospheric pressure. Lower pressures in reactors may be achieved through use of vacuum pumps.

[0046] The reel-to-reel apparatus 100 of Figure 2 may comprise an elongated heating chamber 101 that is surrounded by a heater system 102 which may have one or more heating zones such as Z1, Z2, and Z3 to form a temperature profile along the length of the chamber 101. In between zones there are preferably buffer regions of low thermal conductivity so that a sharp temperature profile may be obtained. Details of such use of buffer regions are discussed in US Application Serial No. 11/549,590 entitled Method and Apparatus for Converting Precursor layers into Photovoltaic Absorbers, filed on October 13, 2006, which is incorporated herein by reference. The chamber 101 is integrally sealably attached to a first port 103 and a second port 104. Integrally sealably means that the internal volume of chamber, the first port and the second port are sealed from air atmosphere, therefore, any gases used in the internal volume does not leak out (except at designated exhaust ports) and no air leaks into the internal volume. In other words the integration of the chamber, first and second ports are vacuum-tight. A first spool 105A and a second spool 105B are placed in the first port 103 and the second port 104, respectively, and a continuous flexible workpiece 106 or flexible structure can be moved between the first spool 105A and the second spool 105B in either direction, i.e. from left to right or from right to left. The flexible structure includes a precursor layer to be transformed into an absorber layer in the elongated
chamber. The first port 103 has at least one first port gas inlet 107A and a first port vacuum line 108A. Similarly, the second port 104 has at least one second port gas inlet 107B and may have a second port vacuum line 108B. The elongated heating chamber 101 as well as the first port 103 and the second port 104 may be evacuated through either or both of the first port vacuum line 108A and the second port vacuum line 108B. The chamber 101 is also provided with at least one gas line 113 and at least one exhaust 112. There may be additional vacuum line(s) (not shown) connected to the chamber 101. Valves 109 are preferably provided on all gas inlets, gas lines, vacuum lines and exhausts so that a common chamber is formed that can be placed under a single vacuum. There are preferably slits 110 at the two ends of the chamber 101, through which the flexible structure 106 passes through. Although, evacuation of the chamber and the first and second ports is the preferred method to get rid of air from the internal volume of the tool, purging the internal volume of the tool with a gas such as N₂ through designated exhaust port(s) is also possible.

[0047] The flexible structure 106A before the reaction may be a base with a precursor film deposited on at least one face of the base. The flexible structure 106B after the reaction comprises the base and a Group IBIII AVIA compound layer formed as a result of reaction of the precursor layer. It should be noted that we do not distinguish between the reacted and unreacted sections of the flexible structure 106 in Figure 2, calling both the flexible structure 106. We also refer to the flexible structure as a web irrespective of whether the precursor layer over it is reacted or unreacted. The substrate of the base may be a flexible metal or polymeric foil. As described above, the precursor film on the base comprises at least Cu, hi, and Ga and optionally a Group VIA material such as Se. The back side 20A of the flexible structure 106 may or may not touch a wall of the chamber 101 as it is moved through the chamber 101. The process of the present invention will now be described through specific examples.

EXAMPLE 1

[0048] A Cu(In,Ga)(Se,S)₂ absorber layer may be formed using the single chamber reactor design of Figure 2. An exemplary flexible structure 106A before the reaction is shown in Figure 3A. The base 20 may be similar to the base 20 of Figure 1. A precursor layer 200 is provided on the base 20. The precursor layer 200 comprises Cu, and at least one of In and Ga. Preferably the precursor layer 200 comprises all of Cu, In and Ga. A Se layer 201 may optionally be deposited over the precursor layer 200 forming a Se-bearing precursor layer 202. Se may also be mixed in with the precursor layer 200 (not shown) forming another version of a Se-bearing precursor layer.
The flexible structure after the reaction step is shown in Figure 3B. In this case the flexible structure 106B comprises the base 20 and the Group IBIIIAVIA compound layer 203 such as a Cu(In,Ga)(Se,S)2 film that is obtained by reacting the precursor layer 200 or the Se-bearing precursor layer 202.

[0049] After loading the unreacted flexible structure 106A or web on, for example, the first spool 105A, one end of the web may be fed through the chamber 101, passing through the gaps 111 of the slits 110, and then wound on the second spool 105B. Doors (not shown) to the first port 103 and the second port 104 are closed and the system (including the first port 103, the second port 104 and the chamber 101) is evacuated to eliminate air. Alternately the system may be purged through the exhaust 112 with an inert gas such as N2 coming through any or all of the gas inlets or gas lines for a period of time. After evacuating or purging, the system is filled with the inert gas and the heater system 102 may be turned on to establish a temperature profile along the length of the chamber 101. When the desired temperature profile is established, the reactor is ready for process.

[0050] During the process of forming, for example, a Cu(Tn,Ga)Se2 absorber layer, a gas comprising Se vapor or a source of Se such as H2Se may be introduced into the chamber, preferably through chamber gas inlet 113. The exhaust 112 may now be opened by opening its valve so that Se bearing gas can be directed to a scrubber or trap (not shown). It should be noted that Se is a volatile material and at around the typical reaction temperatures of 400-600 °C its vapor tends to go on any cold surface present and deposit in the form of solid or liquid Se. This means that, unless precautions taken during the reaction process, Se vapors may pass into the first port 103 and/or the second port 104 and deposit on all the surfaces there including the unreacted portion of the web in the first port 103 and the already reacted portion of the web in the second port 104. To minimize or eliminate such Se deposition, it is preferable to introduce a gas into the first port 103 through first port gas inlet 107A and introduce a gas into the second port 104 through the second port gas inlet 107B. The introduced gas may be a Se-bearing and/or S-bearing gas that does not breakdown into Se and/or S at low temperature, but preferably the introduced gas is an inert gas such as N2 and it pressurizes the two ports establishing a flow of inert gas from the ports towards the chamber 101 through the gaps 111 of the slits 110.

[0051] The velocity of this gas flow can be made high by reducing the gaps 111 of the slits 110 and/or increasing the flow rate of the gas into the ports. This way diffusion of Se vapor into the ports is reduced or prevented, directing such vapors to the exhaust 112 where it can be trapped.
away from the processed web. The preferred values for the gap of the slits may be in the range of 0.5-5 mm, more preferably in the range of 1-3 mm. Flow rate of the gas into the ports may be adjusted depending on the width of the slits which in turn depends on the width of the flexible structure or web. Typical web widths may be in the range of 1-4 ft.

Once the Se-bearing gas and inert gas flows are set and the desired temperature profile of the chamber is reached, the flexible structure may be moved from the first port to the second port at a pre-determined speed. This way, an unreacted portion of the flexible structure 106 comes off the first roll 105A, enters the chamber 101, passes through the chamber 101, gets reacted forming a Cu(In,Ga)Se₂ absorber layer on the base of the web and gets rolled onto the second spool 105B in the second port. It should be noted that there may be an optional cooling zone (not shown) within the second port to cool the reacted web before winding it on the second spool 105B.

The above discussion is also applicable to the formation of absorber layers containing S. For example, to form a Cu(In,Ga)S₂ layer the Se-bearing gas of the above discussion may be replaced with a S-bearing gas such as H₂S. To form a Cu(In,Ga)(Se,S)₂, a mixture of Se-bearing gas and S-bearing gas may be used. Alternately, a Se-bearing precursor may be utilized and reaction may be carried out in a S-bearing gas.

One feature of the system of Figure 2 is that the flexible structure may be moved from left to right as well as from right to left. This way more than one reaction step may be carried out. For example, a first reaction may be carried out as the web is moved from left to right, then a second reaction may be carried out as the web is moved from right to left and the reacted web may be unloaded from the first spool 105A. Of course even more steps of reaction or annealing etc., may be carried out by moving the web more times between the first spool 105A and the second spool 105B. Reaction conditions, such as gas flow rates and the reaction temperature may be different for the various reaction steps. For example, the temperature profile of the chamber may be set to a maximum temperature of 400 °C for the first reaction step when the web is moved from left to right. This way the precursor of the web may be partially or fully reacted or annealed at 400 °C.

After substantially all portions of the web is rolled on the second spool 105B, the maximum temperature of the temperature profile may be adjusted to a higher value, such as to 550 °C, and the web may be moved from right to left as the already annealed or reacted precursor layer.
may be further reacted, annealed or crystallized, this time at the higher temperature of 550 °C. It should be noted that a similar process may be achieved by making the chamber 101 longer and setting a temperature profile along the chamber 101 such that as the web travels from left to right, for example, it travels through a zone at 400 °C and then through a zone at 550 °C. However, using bi-directional motion as described above, the length of the chamber 101 may be reduced and still the two step/two temperature reaction may be achieved. To keep the temperature of the web high when it is rolled onto either one of the first spool 105A or the second spool 105B in between reaction steps, there may be optional heaters (not shown) placed in either or both of the first port 103 and the second port 104.

[0056] It should be noted that in addition to the reactor temperature and the web speed, the reaction gas composition may also be changed in the multi-step reaction approach described above. For example, during the first reaction step when the web is moved from left to right a first gas such as H₂Se may be used in the chamber 101 to form a selenized precursor layer. During the second reaction step when the web is moved from right to left, on the other hand, another gas such as H₂S may be introduced in the chamber 101. As a result, the selenized precursor layer may be reacted with S as the web is moved from the second spool 105B to the first spool 105A and thus a Cu(In,Ga)(Se,S)₂ layer may be grown by converting the already selenized precursor layer into sulfo-selenide. Selecting the gas concentrations, web speeds and reaction temperatures the amount of Se and S in the absorber layer may be controlled. For example, S/(Se+S) molar ratio in the final absorber layer may be increased by increasing the web speed and/or reducing the reaction temperature during the first process step when reaction with Se is carried out. Similarly, the S/(Se+S) molar ratio may also be increased by reducing the web speed and/or increasing the reaction temperature during the second step of reaction where reaction with S is carried out. This provides a large degree of flexibility to optimize the absorber layer composition by optimizing the two reaction steps independent from each other.

[0057] Another embodiment of the present invention is shown in Figure 4. The reactor system 400 in Figure 4 comprises a three-section chamber 450 which is an example of a more general multi-chamber design. The three-section chamber 450 of Figure 4 comprises sections A, B and C. Heaters around each section as well as the first port, the first spool, the second port and the second spool are not shown in this figure to simplify the drawing. However, designs similar to those shown in Figure 2 may be used for such missing parts. The heating means may be heat lamps,
heater coils etc. and they may have independent controls to yield different temperature values and profiles in the sections of A, B and C.

[0058] Important feature of the design of Figure 4 is that sections A and C are separated by a segment, preferably a low-volume segment 410 which is within section B of the three-section chamber 450. There are lines to bring gas into each of the sections A, B and C. For example, inlets 401 and 402 may bring gas into sections A and C, respectively, whereas inlet 403 may bring gas into the low-volume segment 410 in section B. Exhusts 404 and 405 may be provided to exhaust gases from sections A and C, respectively. A flexible structure 106 to be processed or reacted may pass through a first gap 111A of a first slit HOA, enter the three-section chamber 450 and then exit through the second gap 111B of a second slit HOB.

EXAMPLE 2

[0059] A Cu(In, Ga)(Se ,S) absorber layer may be formed using the three-section chamber reactor of Figure 4. After loading the unreacted flexible structure 106, pumping and purging the system as described in Example 1, the process may be initiated. Sections A, B and C of the three-section chamber 450 may have temperatures of T1, T2 and T3 which may or not be equal to each other. Furthermore, each of the sections A, B and C may have a temperature profile rather than just a constant temperature along their respective lengths. During processing, a first process gas such as N2 may be introduced into the low-volume segment 410 in section B through inlet 403, while a second process gas and a third process gas may be introduced in sections A and C, respectively, through inlets 401 and 402, respectively.

[0060] The second process gas and the third process gas may be the same gas or two different gases. For example, the second process gas may comprise Se and the third process gas may comprise S. This way when a portion on the flexible structure 106 enters the section A of the three-section chamber 450 through the first gap 111A of the first slit 110A, the precursor layer on the portion starts reacting with Se forming a selenized precursor layer on the portion. When portion enters the low-volume segment 410, it gets annealed in the N2 gas (if section B is heated) within this segment until it enters section C. In section C sulfidation or sulfurization takes place due to presence of gaseous S species, and a Cu(In, Ga)(Se ,S) absorber layer is thus formed on the portion before the portion exits the three-section chamber 450 through the second gap 111B of the second slit 110B. The S/(Se+S) molar ratio in the absorber layer may be controlled by the relative
temperatures and lengths of the sections A and C. For example, at a given web speed the S/(Se+S) ratio may be increased by decreasing the length and/or reducing the temperature of section A.

[0061] Alternately, or in addition, the length and/or the temperature of section C may be increased. Reverse may be done to reduce the S/(Se+S) molar ratio. It should be noted that, as in the previous example, it is possible to run the flexible structure or web backwards from right to left to continue reactions. It is also possible to change the gases introduced in each section A, B and C of the three-section chamber 450 to obtain absorber layers with different composition. The design of Figure 4 has a unique feature of allowing two different gases or vapors to be present in two different sections of the reactor so that reel-to-reel continuous processing may be done on a web substrate by applying different reaction temperatures and different reaction gases in a sequential manner to each portion of the web. Introducing an inert gas to a reduced volume segment in between the two sections (sections A and C in Figure 4) acts as a diffusion barrier and minimizes or eliminates intermixing between the different gases utilized in those two sections. The first gas introduced through inlet 403 in Figure 4 flows through the low-volume segment 410 to the right and to the left opposing any gas flows from sections A and C towards each other. It should be noted that more sections may be added to the reactor design of Figure 4 with more low-volume segments between them and each section may run with different temperature and gas to provide process flexibility for the formation of high quality Group IBIIIAVIA compound absorber layers. Also more gas inlets and/or exhaust may be added to the system of Figure 4 and locations of these gas inlets and exhaust may be changed.

[0062] A variety of different cross sectional shapes may be used for the chambers of the present invention. Two such chambers 500A and 500B having circular and rectangular cross sections, respectively, are shown in Figures 5A and 5B. Substantially cylindrical reaction chambers with circular cross section are good for pulling vacuum in the chamber even if the chamber is made from a material such as glass or quartz. The circular chambers however, get very large as the substrate or web width increases to 1 ft, 2 ft or beyond. Temperature profiles with sharp temperature changes cannot be sustained using such large cylindrical chambers and thus roll-to-roll RTP process cannot be carried out on wide flexible substrates such as substrates that may be 1-4 ft wide or even wider.

[0063] As shown in Figure 5B, the chamber 500B includes a rectangular gap defined by the top wall 510A, bottom wall 510B, and the side walls 510C. In this case the chamber is preferably
constructed of metal because for pulling vacuum in such a chamber without breaking it requires very thick walls (half an inch and larger) if the chamber is constructed of quartz or glass. In this configuration, the top wall 510A and the bottom wall 510B are substantially parallel to each other, and the flexible structure 106 is placed between them. Chambers with rectangular cross section or configuration is better for reducing reactive gas consumption since the height of such chambers may be reduced to below 10 mm, the width being approximately close to the width of the flexible structure (which may be 1-4 ft). Such small height also allows reaction in Group VIA vapor without the need to introduce too much Group VIA material into the chamber. It should be noted that the height of the chamber 500B, i.e., gap size, is the distance between the top and the bottom walls and small gap size is necessary to keep a high overpressure of Group VIA material over the surface of the precursor layer during reaction. Also these chambers can hold sharply changing temperature profiles even for flexible substrate widths beyond 4ft. For example, a temperature profile along the length of a chamber with a rectangular cross-section may comprise a temperature change of 400-500°C within a distance of a few centimeters. Such chambers, therefore, may be used in roll-to-roll RTP mode wherein a section of a precursor film on a substrate traveling at a speed of a few centimeters per second through the above mentioned temperature change experiences a temperature rise rate of 400-500 °C/sec. Even higher rates of a few thousand degrees Centigrade per second may be achieved by increasing the speed of the substrate.

As shown in cross sectional view in Figure 5C, another preferred chamber design includes a dual chamber 500C where an inner chamber 501B with rectangular cross section is placed within a cylindrical outer chamber 501A with circular cross section. In this case the flexible structure 106 or web passes through the inner chamber 501 B which may be orthorhombic in shape and all the gas flows are preferably directed to and through the inner chamber 501B which has a much smaller volume than the outer chamber 501A. This way waste of reaction gases is minimized but at the same time the whole chamber may be easily evacuated because of the cylindrical shape of the outer chamber 501 B, even though the chamber may be made out of a material such as quartz. Heaters (not shown) in this case may be placed outside the inner chamber 501B, but inside the outer chamber 501A. This way sharp temperature profiles can be sustained along the length of the rectangular cross section chamber while having the capability to evacuate the reactor body.

Figure 6 shows such an exemplary version of the reactor of Figure 2. Only the chamber portion is shown for simplifying the drawing. As can be seen from this figure, the dual-
chamber 600 comprises a cylindrical chamber 601 and an orthorhombic chamber 602 which is placed in the cylindrical chamber 601. Gas inlet 113 and exhaust 112 are connected to the orthorhombic chamber 602. It should be noted that the cylindrical chamber 601 may not be hermetically sealed from the orthorhombic chamber so that when the overall chamber is pumped down, pressure equilibrates between the cylindrical chamber 601 and the orthorhombic chamber. Otherwise, if these chambers are sealed from each other, they may have to be pumped down together at the same time so that there is not a large pressure differential between them.

[0066] Solar cells may be fabricated on the compound layers formed in the reactors of the present invention using materials and methods well known in the field. For example a thin (<0.1 microns) CdS layer may be deposited on the surface of the compound layer using the chemical dip method. A transparent window of ZnO may be deposited over the CdS layer using MOCVD or sputtering techniques. A metallic finger pattern is optionally deposited over the ZnO to complete the solar cell.

[0067] In the following, various embodiments of roll-to-roll or reel-to-reel RTP tools will be provided. The RTP tool of the present invention may have at least one cold zone, at least one hot zone and a buffer zone connecting these two zones. The zones in this embodiment are formed along a process gap of the RTP tool. A workpiece is processed in the process gap while it is moved in a process direction. It is understood that the terms "hot" or "warm" or "high temperature" zone and "cold" or "cool" or "low temperature" zone are intended as being conditionally relative, such that the hot/warm/high temperature zone is warmer than the cold/cool/low temperature zone, though the degree of differential does not require a maximum low temperature for the cold zone or a minimum high temperature for the hot zone.

[0068] In one embodiment, the zones are preferably placed along the process gap and form a section surrounding a portion of the process gap so that when a portion of the workpiece is advanced through a specific zone, that portion of the workpiece is treated with the thermal conditions that are assigned to that zone. In accordance with the principles of the present invention, buffer zones may be formed as part of a processing gap of the RTP tool and connect two zones which are kept in different temperatures. In this respect, a buffer zone may connect a lower temperature zone to a higher temperature zone, or a higher temperature zone to a lower temperature zone. For example, the low temperature zone may be kept at a first temperature so that a portion of a continuous workpiece is subjected to the first temperature as the portion of the continuous
workpiece travels through the low temperature zone. The high temperature zone, on the other hand, may be kept at a second temperature so that the portion of the continuous workpiece is subjected to the second temperature when it travels through the high temperature zone. If the buffer zone connects the lower temperature zone to the higher temperature zone and if the portion of the continuous workpiece is made to travel from the lower temperature zone to the higher temperature zone, the temperature of the portion of the continuous workpiece is increased from the first temperature to the second temperature as it travels through the buffer zone. This, in effect, provides conditions of rapid thermal processing to the portion of the continuous workpiece. The continuous workpiece is moved at a predetermined speed through the buffer zone from the low temperature to high temperature zones of the thermal processing tool zone such that the rate of heating experienced by a portion of the continuous workpiece as it travels through the buffer zone can be easily made 10 °C/second or much higher (such as 100-500 °C/sec) by selecting the values for the low temperature, the high temperature, the speed of the continuous workpiece and the length of the buffer zone. In a particular embodiment, the buffer zone is less than 10% of the length of the high temperature zone, and in a preferred embodiment the length of the buffer zone is in the range of 1-5% of the length of the high temperature zone. In preferred embodiments, the specific length of the first buffer zone is less than 10 cm, and preferably less than 5 cm. This flexibility and the ability to reach very high temperature rates at low cost, keeping the processing throughputs very high are unique features of the present design.

Figure 7A shows a section of an exemplary rapid thermal processing system 700 having a buffer zone 702 connecting a low temperature zone 704 such as a cold zone to a high temperature zone 706 or a hot zone. The system 700 may be a part of a larger system including more zones. For example, the hot zone 706 may be followed by another buffer zone and cold zone combination. Furthermore, the hot zone may be divided by one or more buffer zones to establish a desired temperature profile within the hot zone, each heated zone having a different temperature. A process gap 708 of the system is defined by a top wall 710, a bottom wall 712 and side walls 714. The process gap 708 extends through the cold zone 704, the buffer zone 702, and the hot zone 706. In each zone, the top wall, the bottom wall, and side walls may be made of the same material or different materials, and using different construction features. The gap height and width may be varied along the process gap in each zone. The process gap is preferably in the range of 2mm-20mm height and 10-200 cm width. An aspect ratio for the gap may be between 1:50 and 1:1000.
The aspect ratio is defined herein as the ratio between height (or depth) of the gap and its smallest lateral dimension (width). The height of the process gap may be increased to larger values such as up to about 50 mm if the speed of the continuous workpiece is increased, and therefore the length of the buffer zone may also be increased still keeping the temperature rise rates at or above 10 °C/sec.

[0070] A continuous workpiece 716 is moved with a predetermined speed in the process gap 708 during the process, in the direction depicted by arrow A. In this embodiment, a cooling system (not shown) may be used to maintain low temperature in cold zone 704, and a heating system (not shown) is used to maintain high temperature in the hot zone 706. As will be described more fully below, the buffer zone 702 is a low thermal conductivity zone connecting the cold zone to hot zone so that both zones are maintained in their set temperature ranges without any change by using a short buffer zone. It should be noted that the shorter the buffer zone is, the higher the temperature rise rate can be experienced by a portion of a workpiece moving at a constant speed through the buffer zone. In that respect, the present invention achieves buffer zone lengths in the range of 2-15 cm, making it possible to keep one end of the buffer zone at room temperature (about 20 °C) and the other end at a high temperature in the range of 500-600 °C. The low thermal conductivity characteristics of the buffer zone may be provided by constructing at least one of the top wall, bottom wall and optionally side wall of the buffer zone, or at least a portion of them with low thermal conductivity materials and/or features.

As shown in Figure 7B, in an exemplary temperature profile for the system 700, the low thermal conductivity characteristics of the buffer zone of the system 700 steps up the temperature of the continuous workpiece, in a sharp manner, from a colder to a hotter temperature. This way as the workpiece is moved from a cold zone to a hot zone it experiences a temperature rise rate determined by its speed. The temperature of the cold zone may be less than 50 °C, preferably 20-25 °C, and temperature of the hot zone may be 300-600 °C, preferably 500-550 °C. If the length of the buffer zone is 10 cm, and if the continuous workpiece is moved at a speed of 1cm/second, the rate of heating of the workpiece in the buffer zone will be about (550-20)/10=53°C/sec in this example. A temperature controller, not shown, can be used to control the heating of the cold zone and the hot zone. This approximation of temperature rise is valid as long as heat conduction to the substrate in the hot and cold zone is not a limiting factor.
As shown in Figure 7A each zone comprises and surrounds a predetermined portion of the process gap 708, and the workpiece portion in them is exposed to the exemplary thermal profile shown in Figure 7B. Within this context, ‘portion’ of the continuous workpiece may be defined as a rectangular portion of the workpiece having a length, width and thickness, wherein the width and the thickness are the width and thickness of the continuous flexible workpiece. For example, if a portion of the continuous flexible workpiece is in the hot zone, substantially all of that portion of the continuous workpiece material is exposed to the temperature of the hot zone. The same is true for cold and buffer zones. The portion of the continuous workpiece in these zones will be exposed to the conditions of these zones.

Figure 8A shows a roll to roll processing system 800 including an embodiment of a RTP tool 802 to process a flexible continuous workpiece 804 (workpiece hereinafter). The workpiece 804 is extended along a process gap 806 of the RTP tool 802, and between a supply spool 808 and a receiving spool 810. Figure 8B illustrates the RTP tool in side-perspective view. Referring to Figures 8A and 8B, the process gap 806 extends between an entry opening 811A and an exit opening 811B, and defined by a top wall 824, a bottom wall 826 and side walls 828. A moving mechanism (not shown) unwraps and feeds the workpiece 804 into the process gap 806, and takes up and wraps the workpiece 804 around the receiving spool 810 when it leaves the process gap 806. It should be noted that one important feature of the present design is its leak-free construction. Air and/or oxygen is preferably not allowed to enter the process gap. This requires the process gap to be preferably constructed in a leak-free manner and vacuum can be pulled in the process gap to eliminate air before the RTP process is initiated, preferably after filling back the process gap with an inert gas or a reactive gas such as a gas comprising Se and or S.

In this embodiment, the RTP tool includes a first cold zone 812A, a first buffer zone 814A, a hot zone 816, a second buffer zone 814B, and a second cold zone 812B. Accordingly, the first buffer zone 814A facilitates heating of the workpiece 804, and the second buffer zone 814B cooling of the workpiece 804. The second buffer zone 814B connects the hot zone, which is kept in a high temperature, to the cold zone, which is kept in a lower temperature. In this embodiment, in order to cause a slower rate of cooling, the second buffer zone 814B may be longer than the first buffer zone 814A which may be kept short to facilitate rapid heating of the workpiece. A cooling system with cooling members 818 cools the cold zones 812A and 812B. An exemplary cooling system may be a cooling system using a fluid coolant such as a gas or liquid coolant. The hot zone
816 includes a series of heating members 820 placed along the hot zone 816. Heating members each may be controlled separately or in groups through use of temperature controllers and thermocouples placed near the heating members in each zone. In that respect it is possible to separate the hot zone in multiple heated zones with one or more heaters that are controlled separately. In this embodiment, the buffer zones 814A and 814B include low thermal conductivity features 821 to reduce flow of heat from the hot zone towards the cool zones.

[0074] Details of buffer zones will be described using Figure 8B which shows the buffer zone 814A of the RTP tool 802 in more detail. Thermal conductivity of at least a portion of the buffer zone 814A may be lowered by forming cavities within the walls of the buffer zone without negatively impacting the mechanical integrity of the walls. This is important since, as explained before, the process gap needs to be leak-free. The cavities may extend perpendicular to the lateral axis of the process gap by forming grooves in the walls. Alternatively, as described in another embodiment below (see Figure 9), the cavities may be through cavities (or holes) formed through the width of the top wall or bottom wall portions and height of the side walls. By cutting grooves into or onto the top and bottom walls, the cross sectional area of the wall material (which may be, for example, stainless steel) interconnecting the hot and cold zones is reduced. This way thermal conduction through this cut region is reduced. In this embodiment, both the top wall and the bottom wall of the buffer zones include an equal number of cuts placed in a symmetrical manner. To form the buffer zone, the cuts on the top and the bottom extend along the same portion of the process gap 806. Although in this embodiment, side walls 828A may not include any of the features 822, it is possible to have features on the side walls as well. The cuts in the top and bottom walls may each have a width of 1 mm or greater. Their depth may be about 50-80% of the thickness of the top wall or the bottom wall. It should be noted that use of this design with cuts yield the desirable near-linear temperature change going from a hot zone to a cold zone or vice-versa as shown in Figure 7B. In one embodiment, the hot zone and the buffer zone may be enclosed in a thermal insulator to avoid heat loss from the reactor. Alternately, the RTP tool 802 may be fully covered by an insulating enclosure to protect users from high temperature and to reduce heat loss.

[0075] Figure 9 shows another embodiment of an RTP tool 900 having cold zones 902A and 9002B, buffer zones 904A and 904B, and hot zone 906. A continuous workpiece 908 is extended through a process gap 910 of the tool 900. Design of cold and hot zones are the same as
the RTP tool 802 described in the previous embodiment. In this embodiment, low thermal conductivity features in the buffer zones may be holes 912 which are drilled within the walls of the buffer zones 904A and 904B. Presence of the holes 912 reduces the cross sectional area of the metallic wall material conducting the heat from the hot zone to the cold zones, replacing this material with air. It should be noted that in Figures 7A and 8A, the workpiece is shown in the middle of the process gap. However, depending on the position of the process gap (horizontal, vertical or at an angle) one face of the workpiece may actually touch at least one of the walls defining the process gap. In Figure 1OA we show a situation where the bottom of the workpiece touches the bottom wall.

[0076] Figure 10A shows a RTP tool 850 in side partial view. The RTP tool 850 is an alternative embodiment of the RTP tool 802 shown in Figures 8A and 8B. In this embodiment, different thermal profiles are established at the upper and lower walls of the process gap by having buffer regions associated with the top and bottom walls that are disposed between hot regions and cold regions, such that the top buffer region is not necessarily co-extensive with the bottom buffer region, and in fact the bottom buffer region may overlap either or both of the top cold region and the top hot region, and vice versa. For example, the temperature profile of the upper wall may be as shown in Figure 10B and the temperature profile of the lower wall may be as shown in Figure 10C. The benefit of this design is the fact that the workpiece may be thermally coupled to one of the walls (lower wall in Figure 10A) and therefore experiences substantially the thermal profile of that wall (Figure 10C), whereas the opposite wall of the reaction chamber may be at a different temperature (Figure 10B). By keeping the top wall hot region hotter than a bottom wall cold region disposed directly below it, for example, it is possible to thermally activate the gaseous species (such as Se vapors or H₂Se vapors etc.) which may be present in the process gap while controlling the temperature of the workpiece itself by the bottom wall hot region. Having a top hot wall region across from the workpiece surface also keeps reactive species in vapor phase by not letting them condense and possibly drip down on the workpiece surface. For example, by maintaining a top hot wall region, Se condensation may be avoided during a RTP process that uses Se species to selenize precursors comprising Cu, In and Ga. Different temperature profiles at different regions of the top and bottom walls of the process gap may also be obtained by using upper wall insert 858 and lower wall insert 860 which may have different designs and thermal conductivities. For example, if an upper wall insert 858 is well thermally coupled to a hot region but poorly thermally coupled to a
cold region, then it is possible to move the high temperatures closer to the inlet 856 along the upper wall insert 858.

[0077] In the following embodiments the roll-to-roll or reel-to-reel thermal processing or RTP tools include a reactor having an insert placed in a primary gap of the reactor. The primary gap of the reactor is defined by peripheral reactor walls including a top reactor wall, a bottom reactor wall and side reactor walls as will be further described below. The insert includes a secondary gap, also called process gap hereinafter, through which a continuous workpiece travels between an entry opening and an exit opening of the insert. The process gap is defined by insert walls including a top insert wall, a bottom insert wall and side insert walls. This process gap height and width may be varied along the process gap, and there can be separate zones as described above. The process gap, within the insert is preferably in the range of 2mm-20mm height and 10-200 cm width. An aspect ratio (height to width ratio) for the process gap may be between 1:50 and 1:1000. An inner space exists between at least one of the insert walls and at least a portion of the peripheral reactor walls. The width of the inner space or the distance between the at least one of the insert walls and the portion of the peripheral reactor walls may be in the range of 2-20 mm, preferably 3-5mm. At least one gas inlet is connected to the inner space, and at least one exhaust opening connects the process gap as well as the inner space to outside and carries any gaseous products to outside the process gap and the primary gap of the reactor. Sealable doors or web valves may seal the entrance and the exit of the process gap when needed before or after the process, especially when the continuous workpiece stops moving. As the continuous workpiece with a precursor material film such as a precursor layer comprising Cu, In, Ga and Se, is continuously fed into the process gap and treated with heat and process gases (such as an inert gas, a selenium containing gas and/or a sulfur containing gas), a flushing gas such as nitrogen is delivered to the inner space through the gas inlets. Then the flush gas, the process gas and any other gaseous species that may be created in the process gap as a result of the heat treatment of the precursor layer within the process gap are exhausted through the exhaust opening. During the process, at the beginning or at the end of the process, movement of the continuous workpiece may be halted and the entrance and the exit doors may be sealed. In one embodiment the bottom insert wall may include rollers on which the continuous workpiece may be moved without damaging its back surface.

[0078] Figure 11A shows in side view a continuous reactor 1000 including peripheral reactor walls 1002 and an insert 1004 placed into the primary gap defined by the peripheral reactor
walls 1002. The insert 1004 is made of materials that are chemically stable at high temperatures (in the 400-600 °C range) in presence of Group VIA materials, especially Se and S. These materials include, but are not limited to quartz, graphite and ceramics such as alumina, zirconia, and alumina-silica, alumina+zirconia, alumina+titania composites, etc. The peripheral reactor walls 1002 are made of heat stable materials that keep their mechanical integrity up to temperatures in the range of 700-900 °C range. It is preferred that these materials are suitable, i.e. has the strength, for forming a vacuum environment within the primary gap. Such materials include, but are not limited to, various stainless steels such as 304 and 316 series stainless steels. A continuous workpiece 1005 having a front surface 1005A and a back surface 1005B is extended through a process gap 1008 of the insert 1004. The front surface 1005A of the continuous workpiece includes a precursor material such as a precursor layer comprising Cu, In, Ga and optionally Se. Figure 11B shows the reactor 1000 in cross sectional view, and Figures 11C and 11D show the peripheral reactor walls 1002 and the insert 1004 of the reactor in cross sectional view. As shown in Figure 11C, the peripheral reactor walls 1002 includes a top reactor wall 1003A, a bottom reactor wall 1003B and side reactor walls 1003C, which altogether define a primary gap 1006. The peripheral reactor walls 1002 may include the heating elements described above. As shown in Figure 11D, the insert 1004 includes a process gap 1008 defined by an insert top wall 1010A, an insert bottom wall 1010B and insert side walls 1010C.

[0079] As shown in Figures 11A and 11B the insert 1004 is placed into the primary gap 1006 of the reactor defined by the peripheral reactor walls 1002 while leaving an inner space 1012 between the peripheral reactor walls 1002 and the insert 1004. The inner space 1012 may be maintained by placing spacers (not shown), preferably made from ceramics, graphite or stainless steel between the peripheral reactor walls 1002 and at least one of the walls of the insert 1004. The inner space 1012 enables both the peripheral reactor walls 1002 and the insert 1004 to expand or contract without giving structural damage to one another. In this embodiment, the peripheral reactor walls 1002 may include heaters (not shown) which may be located within the walls or outside the walls. The heaters heat the peripheral reactor walls 1002, which in turn heat the primary gap 1006, the insert 1004 and that portion of the continuous workpiece 1005 within the process gap 1008 of the insert 1004. As discussed before, the peripheral reactor walls 1002 may be made of a metal such as stainless steel which may react with the selenium and/or sulfur vapors present in the process gap 1008 at temperatures at or over 500 °C, if such vapors find a pathway into the
primary gap 1006 at high concentrations, and are in physical contact with the peripheral reactor walls 1002. In order to prevent such reactive process gasses from leaking into the inner space, a flushing gas such as nitrogen (N\textsubscript{2}) may be delivered into the inner space 1012. Such flushing gas may establish a blanket of flowing inert gas (such as nitrogen) within the inner space 1012 and does not allow high concentration of selenium and sulfur species to enter the inner space and corrode the inner surfaces of the peripheral reactor walls 1002. The flushing gas may be preheated before being directed into the inner space 1012 through at least one gas inlet (see for example gas inlets 1114 in Figure 13) to avoid excessive heat loss from the reactor. The continuous workpiece 1005 to be processed is extended through the process gap 1008 and moved while the back surface 1005B is in physical contact with a surface 101 1 of the bottom wall 1010B of the insert 1004.

[0080] Figure 11E shows another embodiment where the insert 1004 is set on the bottom wall 1003B of the peripheral reactor walls 1002. In this embodiment, inner space 1012 is established between the respective top and side walls of the insert 1004 and the peripheral reactor walls 1002 as in the manner shown in Figure 11E.

[0081] As shown in Figures 12A and 12B, bottom wall 1010B of the insert 1004 may include a low friction surface such as rollers 1020 on which the continuous workpiece 1005 is moved without causing excessive friction between the back surface 1005B and the bottom wall 1010B. Balls or ball bearings may also be used in place of or in addition to rollers. This embodiment is especially useful if the back surface 1005B is coated with a protective layer that protects the substrate from the effects of corrosive process gasses such as selenium and sulfur. If the back surface 1005B is moved while resting against a high friction surface of the bottom wall 1010B of the insert 1004, such protective layers (such as a molybdenum layer, a chromium layer, a metal nitride layer, etc.) may get scratched and damaged exposing portions of the substrate, which may comprise aluminum or steel, to corrosive environment. Resulting corrosion of the back surface 1005B generates reaction products in the form of particles and debris which fall into the process gap 1008, reduce up time of the reactor between cleaning steps, and reduce yield of the process by generating defects in solar cells due to the particles. The design shown in Figure 12A resolves this problem. Since the back surface 1005B is rolled on the rollers 1020, the back surface 1005B is protected against damage and scratching. As shown in Figure 12C, the rollers 1020 are movably placed into roller cavities 1022 formed in the surface 101 1 of the bottom wall 1010B. They may be attached to ceramic bearings at the two ends, near the side walls 10 10C of the insert.
1004, so that they can freely rotate in the cavities 1022. The rollers can be fabricated from inert materials that do not react with selenium and sulfur at high temperatures. Such materials include, but are not limited to graphite, quartz, alumina, zirconia, etc. To prevent sliding of the continuous workpiece 1005 on the rollers 1020, the rollers are of low inertia and are sufficiently spaced. The diameter of the rollers 1020 may range from 3 mm to about 10 mm. In one embodiment, the rollers 1020 are made of alumina and are spaced at intervals ranging from 200 mm to about 600 mm. Generally, the spacing increases for lighter continuous workpieces and with higher workpiece tensions.

[0082] Figure 13 shows a reactor embodiment 1100 including peripheral walls 1102 and an insert 1104 which is placed into the primary gap 1106 defined by the peripheral walls 1102 as described above. The primary gap 1106 is defined by a top wall 1103A, a bottom wall 1103B and side walls (not shown in this figure) of the peripheral walls 1102. A continuous workpiece 1105 having a front surface 1105A and a back surface 1105B is extended through a process gap 1108 of the insert 1104 between an entrance opening 1107A or entrance and an exit opening 1107B or exit. The continuous workpiece 1105 is, as in the other embodiments, a portion of a continuous workpiece roll which may be 500-1000 meters long. As described above, in roll to roll systems, the continuous workpiece is typically fed into the reactor from a supply spool and received, after the processing, from the reactor by a receiving spool. The process gap 1108 is defined by an insert top wall 1HOA, an insert bottom wall 1HOB, and insert side walls (not shown in this figure). The entrance 1107A and the exit 1107B may include a sealable entrance door 1109A and a sealable exit door 1109B. The sealable entrance and exit doors 1109A and 1109B may be slit valves or a web valves. The sealable entrance and exit doors 1109A, 1109B include sealing members 1111 which contact the front and optionally the back surfaces of the workpiece 1105 when the sealable doors are in a sealing position. In Figure 13 the sealable entrance and exit doors 1109A, 1109B are shown in open position or a first position in which the sealing members are away from the front surface 1105A and the back surface 1105B of the workpiece 1105. As depicted with dotted lines, when the sealable entrance and exit doors 1109A, 1109B are moved into the sealing position or a second position, the sealing members 1111 contact the front and back surfaces of the workpiece 1105.

[0083] An inner space 1112 is established between the peripheral walls 1102 and the insert 1104. Plugs H 12A are placed near the entrance 1107A and exit 1107B. Gas inlet lines 1114
provided through the peripheral walls 1102 to allow a flushing gas, depicted by arrows 'F', to flow into the inner space 1112. An exhaust opening 1116 is placed between the entrance 1107A and the exit 1107B, and runs through the peripheral walls 1102 and the insert 1104 to remove the exhaust gas, depicted by the arrow 'E', from the reactor 1100. The bottom wall 1110B of the insert 1104 may have rollers 1120 on which the continuous workpiece 1105 is moved.

During the process, the flushing gas F is flown into the gas inlets 1114 and thereby into the inner space 1112. The gas is unable to escape near the entrance 1107A and exit 1107B because of the presence of the plugs 1112A, and it is directed towards the exhaust 1116. Process gases, depicted by the arrows 'P', which may be inert gases, are fed through the entrance opening 1107A and the exit opening 1107B into the process gap 1108 of the insert 1104, as a moving mechanism (not shown) moves a portion of the continuous workpiece 1105 into the process gap 1106 for reaction. The process gases P provide a barrier against discharge of selenium and sulfur vapors present in the process gap 1108 to outside of the process gap through the entrance and exit. The established process gas flow urges such vapor species to move over the top surface of the continuous workpiece 1105 towards the exhaust where they mix with the flush gas and removed as the exhaust gas E into a trap that condenses them safely. Flowing process gas moves the reactive species (such as Se and/or S) along with the continuous workpiece, keeping these species over the reacting precursor layer. This way residence time of the reacting species over the precursor layer is increased enhancing the reaction between the precursor layer the reactive species, and thus enhancing overall utilization of the volatile reactive species. For example, in batch RTP processes employed to form CIGS layers using a precursor layer comprising Cu, In, Ga and Se; an amount of selenium that is 20-100% more than what is necessary for the formation of CIGS is included in the precursor layer because these reactors lose much of the volatile Se species during the reaction process. In the present design volatile Se species, after they evaporate out of the precursor layer, stay over the precursor layer on other parts of the continuous workpiece and eventually get utilized. Therefore, in the roll-to-roll process of the present invention, precursor layers comprising Cu, In, Ga and Se may be prepared to have no excess Se or only up to about 10% excess Se. This is considerable savings over the prior art approaches that required 20-100% excess Se in the precursor layers. It should be noted that if Se amount in the reactor is not adequate, the CIGS films formed under Se deficient conditions do not yield high efficiency solar cells because they typically contain low resistivity Cu-Se binary phases. During the process, the sealable doors 1109A and 1109B are
kept in open position to let the process gases P in through the entrance 1107A and the exit 1107B. However, as will be described more fully below during the processes intervals, the sealable doors 1109A and 1109B are moved into closed position or a second position, as shown with dotted lines, to seal the entrance 1107A and the exit 1107B by pressing the seal members 1111 onto the front surface 1105A and the back surface 1105B of the continuous workpiece 1105. It should be noted that the seal members against the back surface 1105B of the continuous workpiece 1105 may or may not be employed, i.e. only the top seal members may be used and the back surface of the workpiece may be supported by a flat surface.

[0085] As mentioned above, the continuous workpiece 1105 may be supplied from a supply spool adjacent the entrance opening 1107A and received by a receiving spool adjacent the exit opening 1107B of the reactor 1100. The supply spool and the receiving spool may be kept in a supply chamber and a receiving chamber respectively, which may be sealably connected to the reactor 1100. Examples of supply and receiving chambers containing supply and receiving spools are shown in Figures 2 and 8A. Further, high vacuum pumps may be added to remove air from the supply and receiving chambers as well as the process gap, therefore eliminating excess oxygen which is very harmful for the formation of high quality CIGS layers. Vacuum pumps that are capable of removing water vapor at high speeds are preferred, because higher speeds will speed up the evacuation of the supply and receiving chambers and therefore decrease the idle time of the reactor. Removing air and impurities from the supply and receiving chambers reduces the likelihood of their incorporation into the absorber film that is processed and thus enhances the quality of the absorber film such as a CIGS type absorber film. It should be noted that even trace amounts (a few parts per million) of oxygen causes oxidation of Cu, In and Ga and lower the photovoltaic quality of CIGS. Pumping the system down to vacuum levels better than $10^{-5}$ Torr and therefore eliminating oxygen before the initiation of the reactions between Cu, In, Ga, Se and/or S is very important for the quality of the resulting CIGS layer.

[0086] There are advantages in using the reactor 1100 equipped with the sealable doors 1109A and 1109B of the present invention together with above described vacuum sealed supply and receiving chambers to process a roll of the continuous workpiece 1105.

[0087] In one exemplary process, when processing of an entire roll of the continuous workpiece 1105 in the reactor 1100, which may be 500-1000 meters long, is almost completed in the reactor 1100, the process is halted while still a portion of the continuous workpiece 1105, which
may be 2-4 meters, is still wrapped around the supply spool. Next, the sealable doors 1109A and 1109B seal the entrance opening 1107A and the exit opening 1107B by moving into the sealing position. As described above, in the sealing position, the seal members 1111 of the sealable doors 1109A, 1109B contact the front surface 1105A and the back surface 1105B of the workpiece 1105 to seal the entrance and exit openings. Once the reactor 1100 is sealed in this manner, the supply chamber is opened to atmosphere and a roll of a new continuous workpiece is loaded into the supply chamber and connected to the portion of the continuous workpiece that extends to the receiving spool. During this time the process gap is protected from aix by the sealable doors. After the supply chamber is resealed, pumped down and the sealable doors 1107A and 1107B are moved into open position, the continuous workpiece 1105 is fully advanced into the receiving chamber while pulling a leading end of the new continuous workpiece into the receiving chamber. In the following step, sealable doors are once again brought into the sealing position but this time on the front and back surfaces of the new continuous workpiece; and then the receiving chamber is unsealed and opened to detach the processed workpiece from the leading end of the new continuous workpiece and to remove the processed roll of the workpiece 1105 from the receiving chamber. Next, the leading end of the new workpiece is attached to the receiving spool; the receiving chamber is sealed and pumped down; and the sealable doors 1109A and 1109B are moved into the open position to start processing the new workpiece in the reactor 1100. Benefits of sealing the reactor in this manner especially during the workpiece loading unloading intervals are generally three fold: (1) sealing speeds up the loading a new workpiece roll and unloading the processed one; (2) sealing keeps the process gap of the reactor clean and free of oxidizing species at such intervals; and (3) sealing reduces the amount of Se in the exhaust traps since the complete removal of Se from the reactor is not required, which further enhances the utilization of Se and reduces the amount of cleaning and maintenance of the traps.

[0088] Although the present invention is described with respect to certain preferred embodiments, modifications thereto will be apparent to those skilled in the art.
We claim:

1. A reactor used to react precursor material disposed over a continuous workpiece to form a solar cell absorber, the reactor comprising:
   - a primary gap defined by a peripheral wall;
   - an insert placed within the primary gap, wherein the insert includes a process gap through which the continuous workpiece travels between an entry and an exit of the insert, wherein the process gap is defined by a top wall, a bottom wall and side walls of the insert, wherein the process gap has an aspect ratio between 1:50 and 1:1000, and wherein an inner space exists between at least one of the walls of the insert and at least a portion of the peripheral wall.

2. The reactor of Claim 1, wherein the at least one gas inlet is connected to the inner space.

3. The reactor of Claim 1, wherein at least one exhaust opening connects the process gap and the inner space to outside of the reactor.

4. The reactor of Claim 1, wherein the bottom wall of the insert includes rollers on which the continuous workpiece travels.

5. The reactor of Claim 1, wherein the entry and the exit of the insert includes sealable doors.

6. The reactor of Claim 4, wherein the bottom wall of the insert is disposed on a bottom portion of the peripheral wall.

7. The reactor of Claim 1 wherein the insert is made of quartz, graphite or ceramics.

8. The reactor of Claim 7 wherein the peripheral wall is made of stainless steel.

9. A reactor used to react precursor material disposed over a continuous workpiece to form a solar cell absorber, the reactor comprising:
   - a primary gap defined by a peripheral wall;
an insert placed within the primary gap, wherein the insert includes a process gap through which the continuous workpiece travels between an entry and an exit of the insert, wherein the process gap is defined by a top wall, a bottom wall and side walls of the insert, wherein the process gap has an aspect ratio between 1:50 and 1:1000, and wherein the bottom wall of the insert includes thereon rollers on which the continuous workpiece travels.

10. The reactor of Claim 9, wherein at least one exhaust opening connects the process gap to outside of the reactor.

11. The reactor of Claim 9, wherein the entry and the exit of the insert includes sealable doors.

12. The reactor of Claim 9, wherein the insert is made of quartz, graphite or ceramics.

13. The reactor of Claim 12, wherein the peripheral wall is made of stainless steel.
FIG. 1
FIG. 7A

FIG. 7B
INTERNATIONAL SEARCH REPORT

A  CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B05C 13/00 (2009.01)
USPC - 118/500

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)
118/500

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)
Data Bases Publ$[s]t (PGPB, USPT, EPAB, JPAB), Google Patents, Google Scholar
Terms Used solar cell absorber, reactor, chamber, furnace, wall, workpiece, quartz, stainless steel, ceramic, spool, roll$4, band gap, photovolta$6, space$4, gap, hole, opening, interval, peripher$5

C  DOCUMENTS CONSIDERED TO BE RELEVANT

Category Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No

D  Further documents are listed in the continuation of Box C

- Special categories of cited documents
  "A" document defining the general state of the art which is not considered to be of particular relevance
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  "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "&" member of the same patent family

Date of the actual completion of the international search
18 Jan 2010 (18 01 2010)

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