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(54) **PALLET BASED SYSTEM FOR FORMING THIN-FILM SOLAR CELLS**

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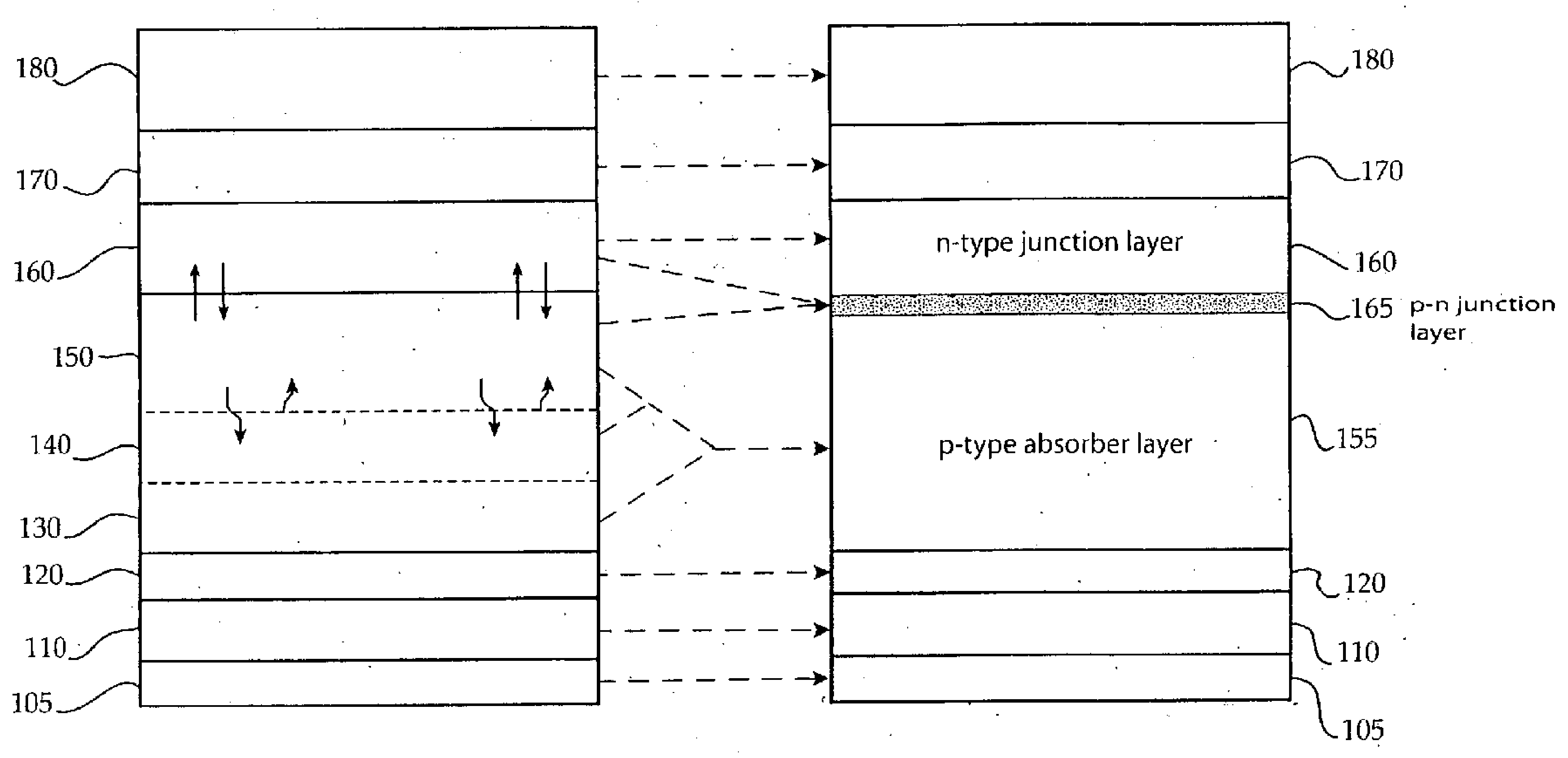
(57) **ABSTRACT**

The present invention provides a photovoltaic thin-film solar cell produced by a providing a pallet based substrate to a series of reaction chambers layers can be sequentially formed on the pallet based substrate.



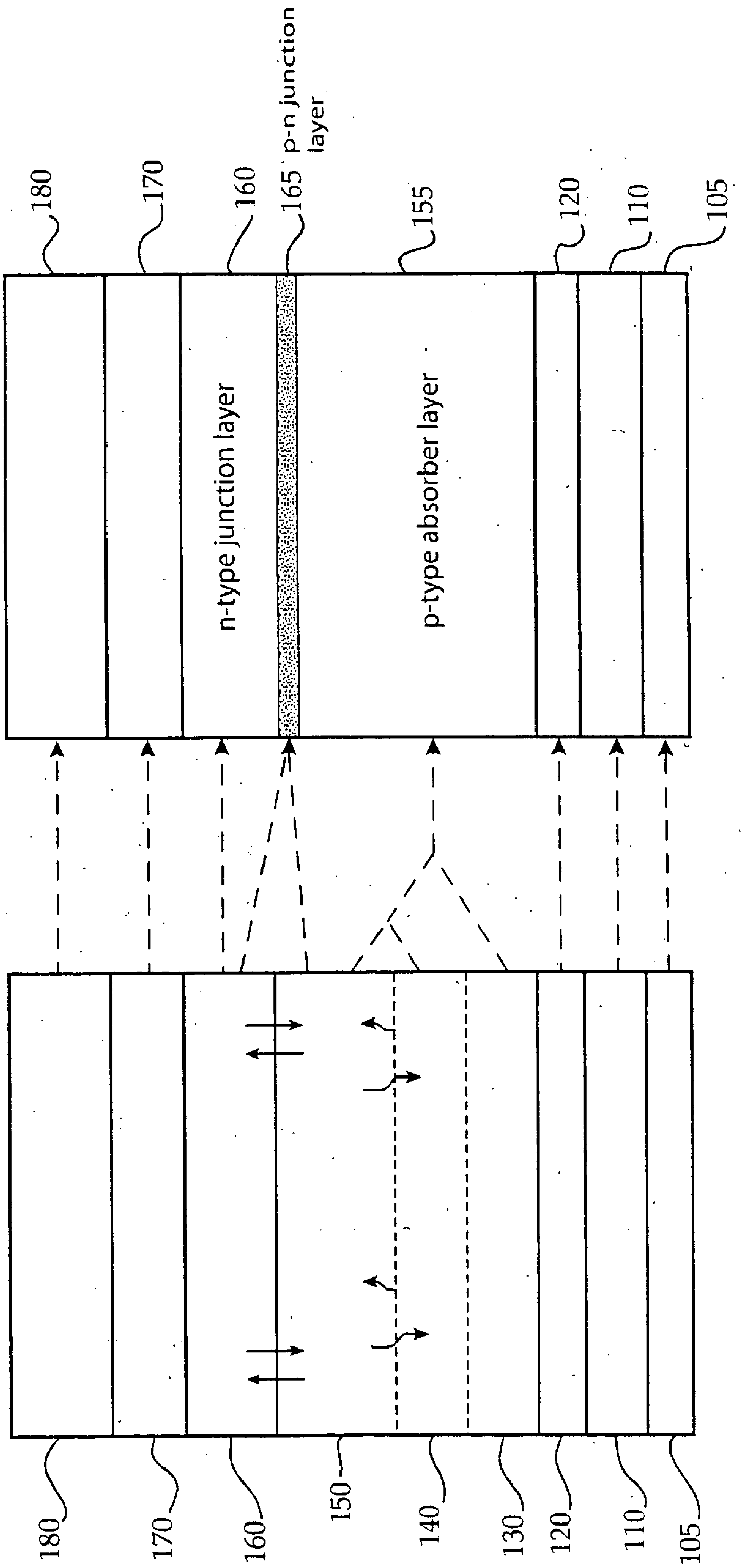
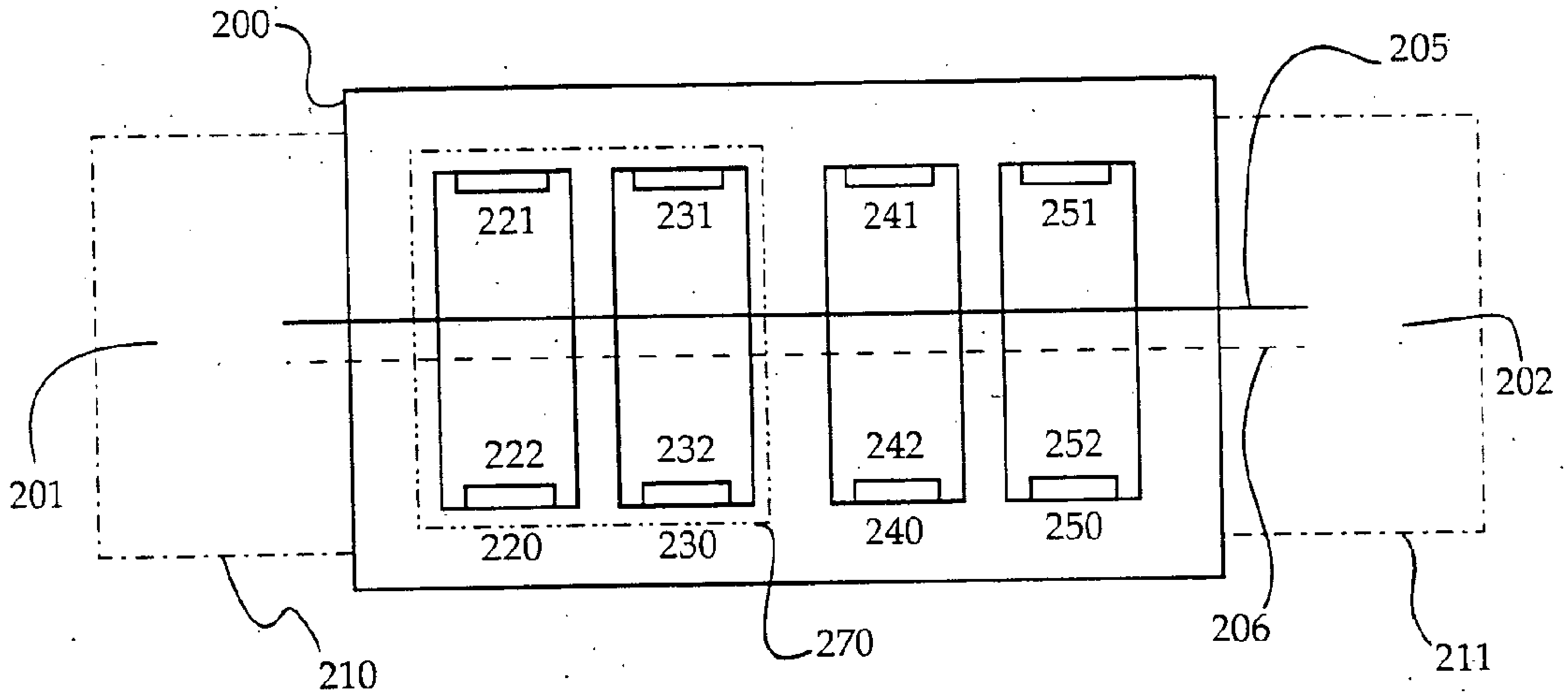

180
170
160
165
p-n junction layer
155
120
110
105
n-type junction layer
p-type absorber layer
180
170
160
150
140
130
120
110
105

Fig. 1


200
205
221
231
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250
270
206
210
211

Fig. 2

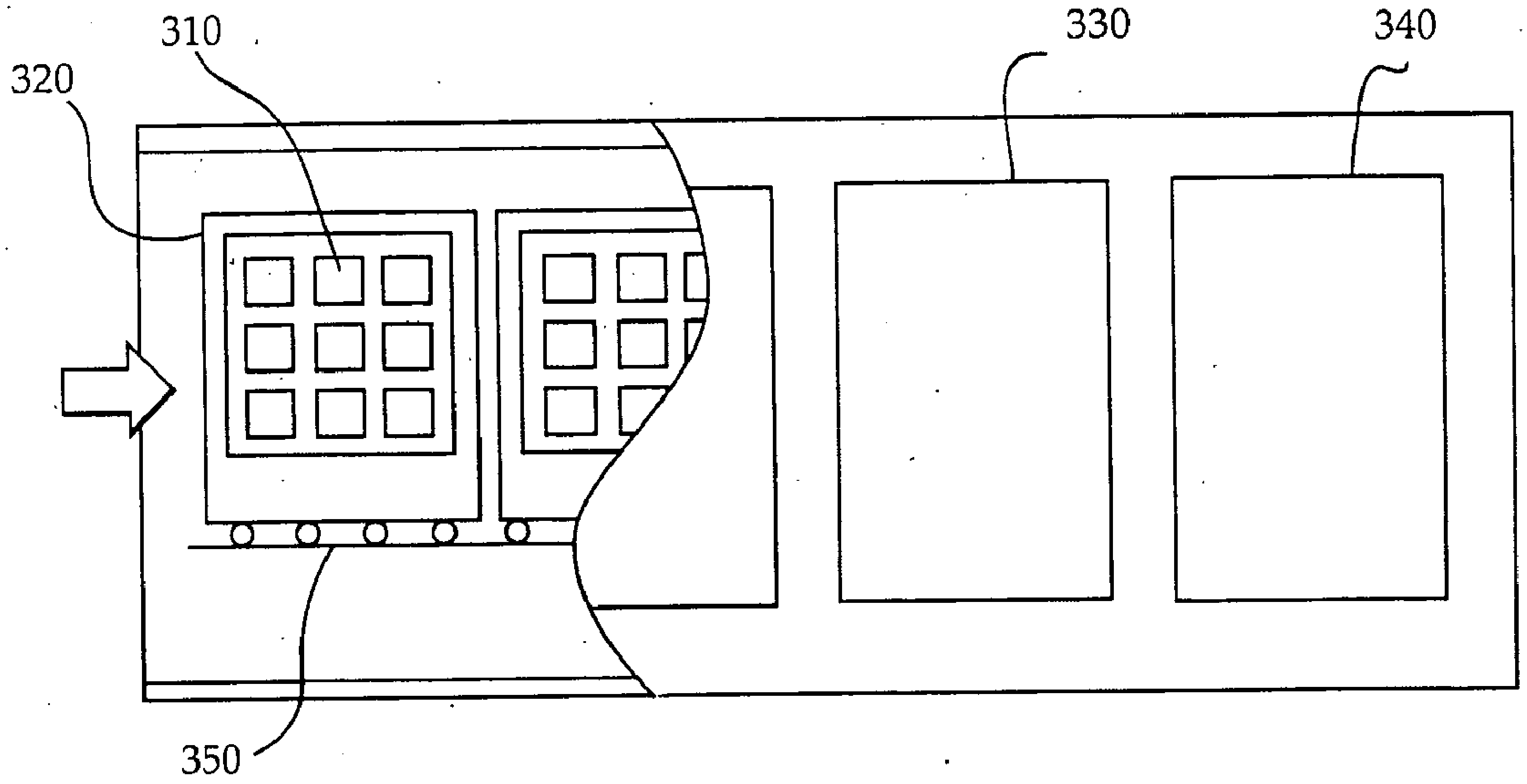


Fig. 3

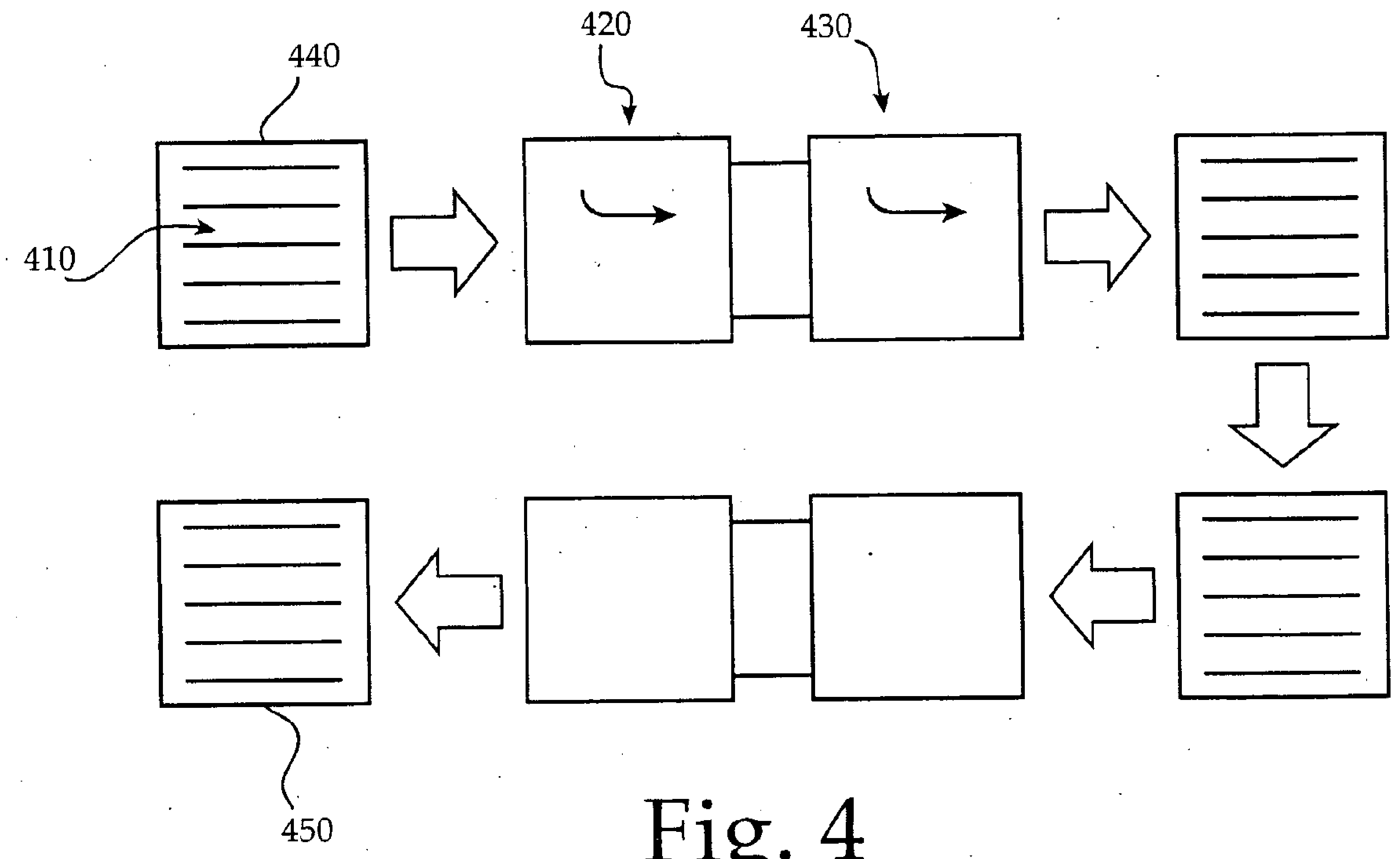
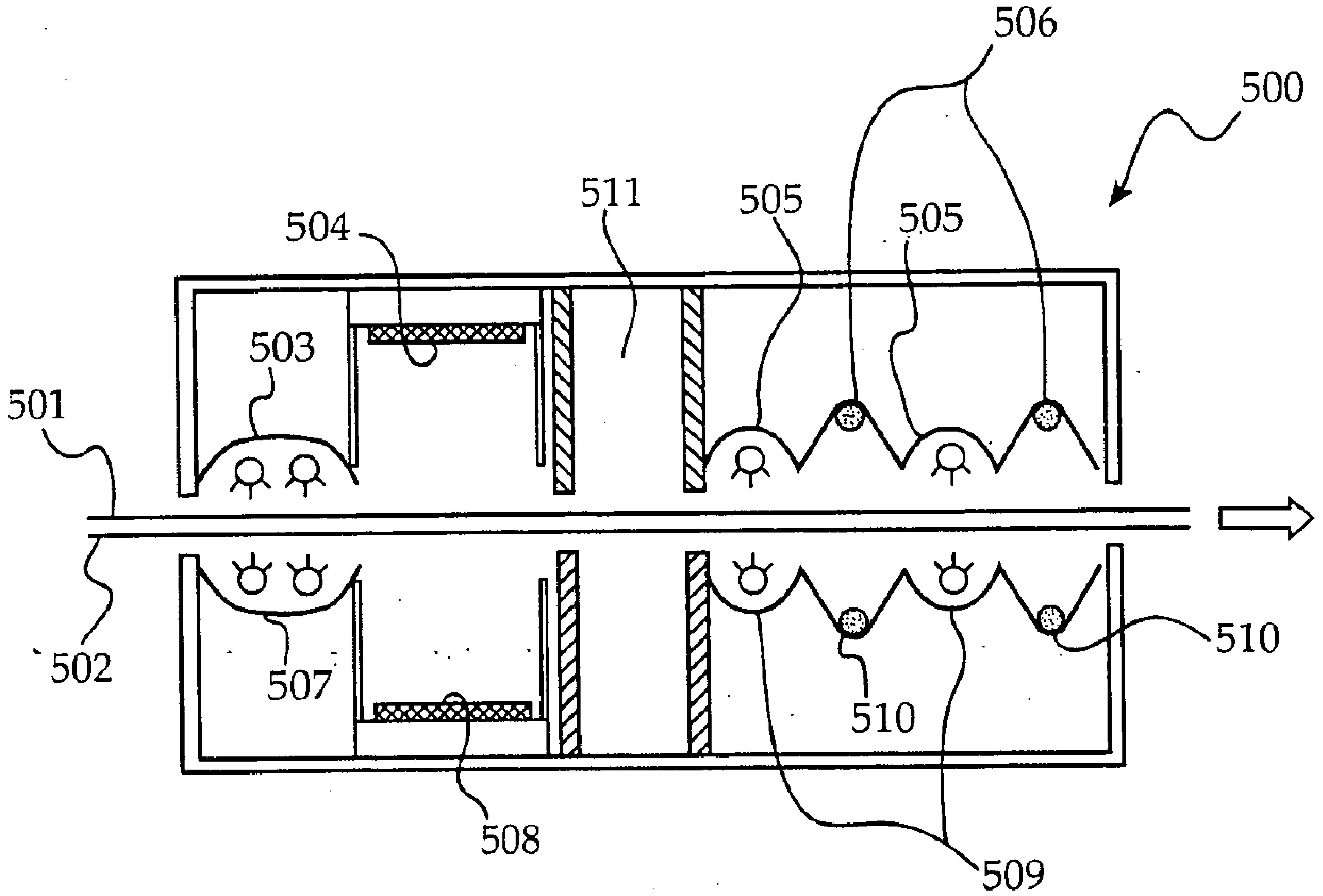


Fig. 4


506
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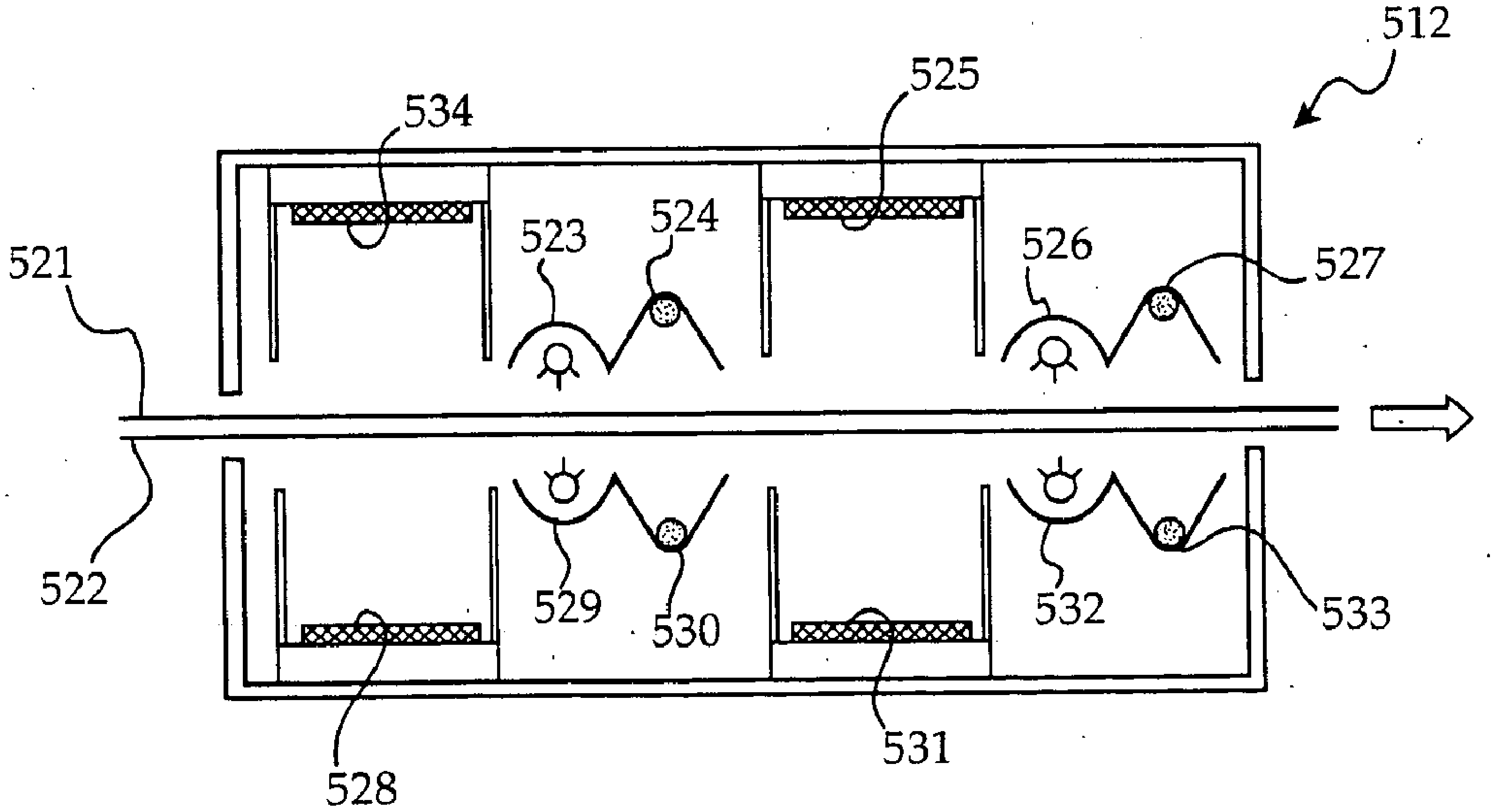
508
509

Fig. 5A


512
525
534
523
524
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521
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530
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533
528
531

Fig. 5B

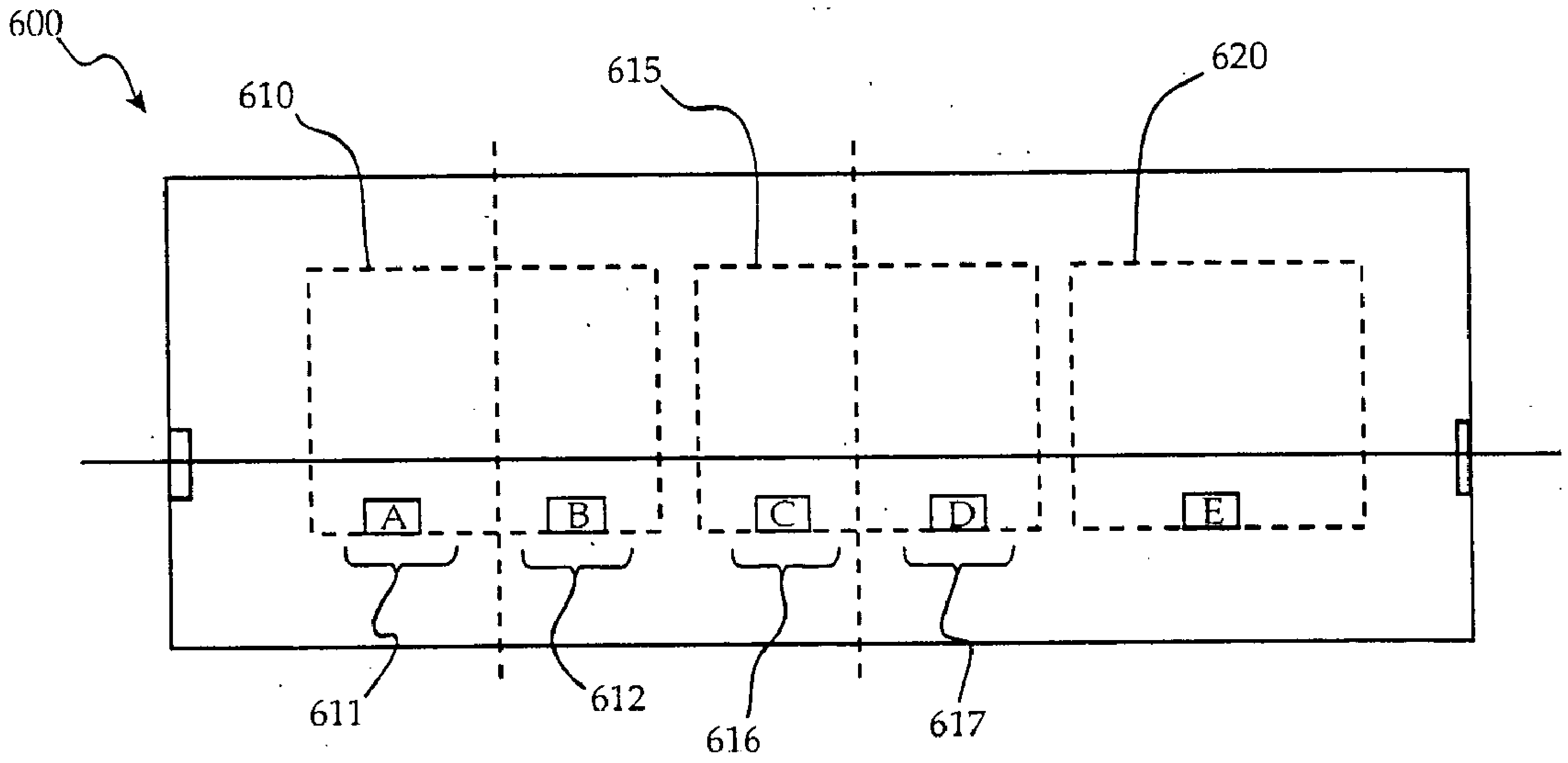

Fig. 6

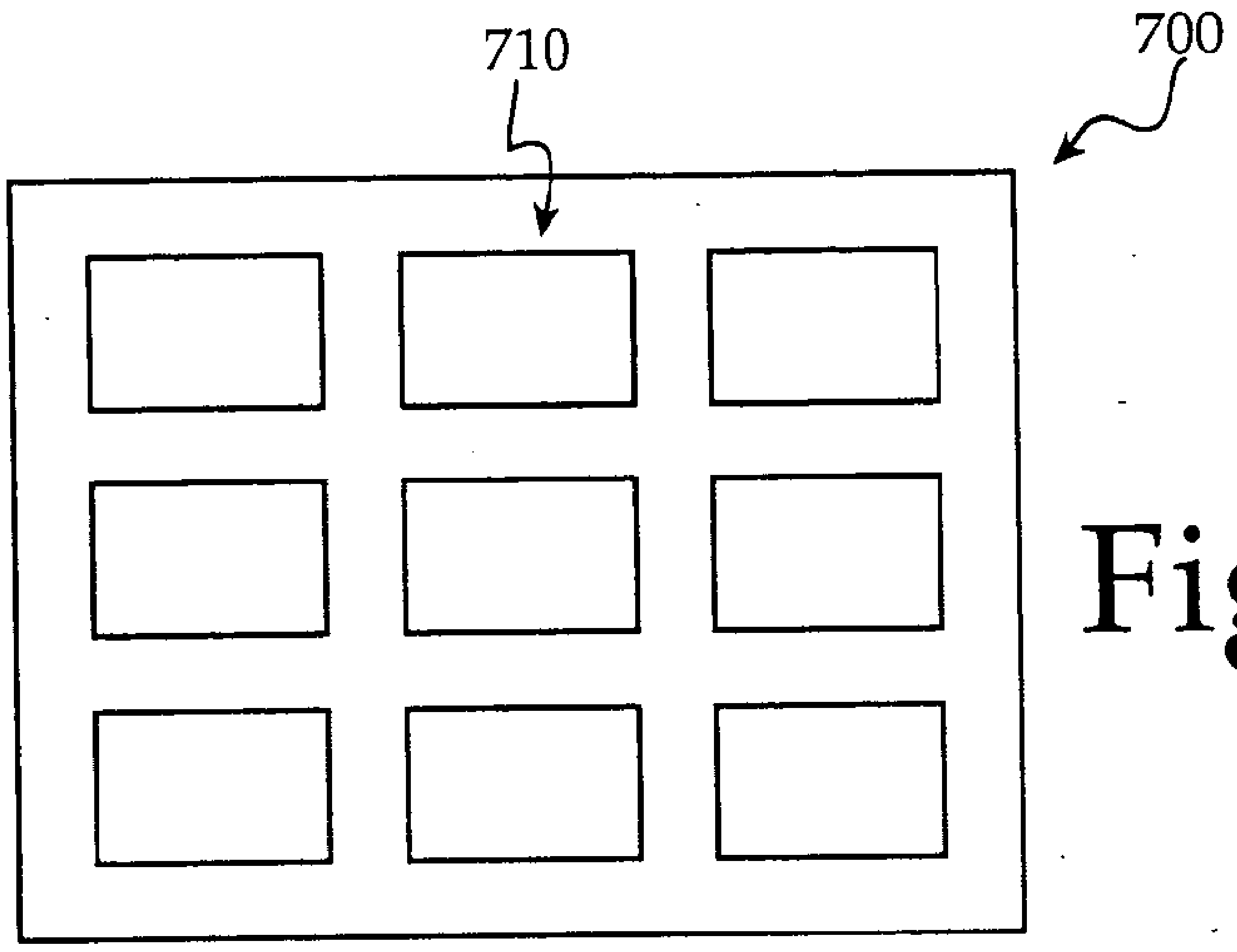

Fig. 7

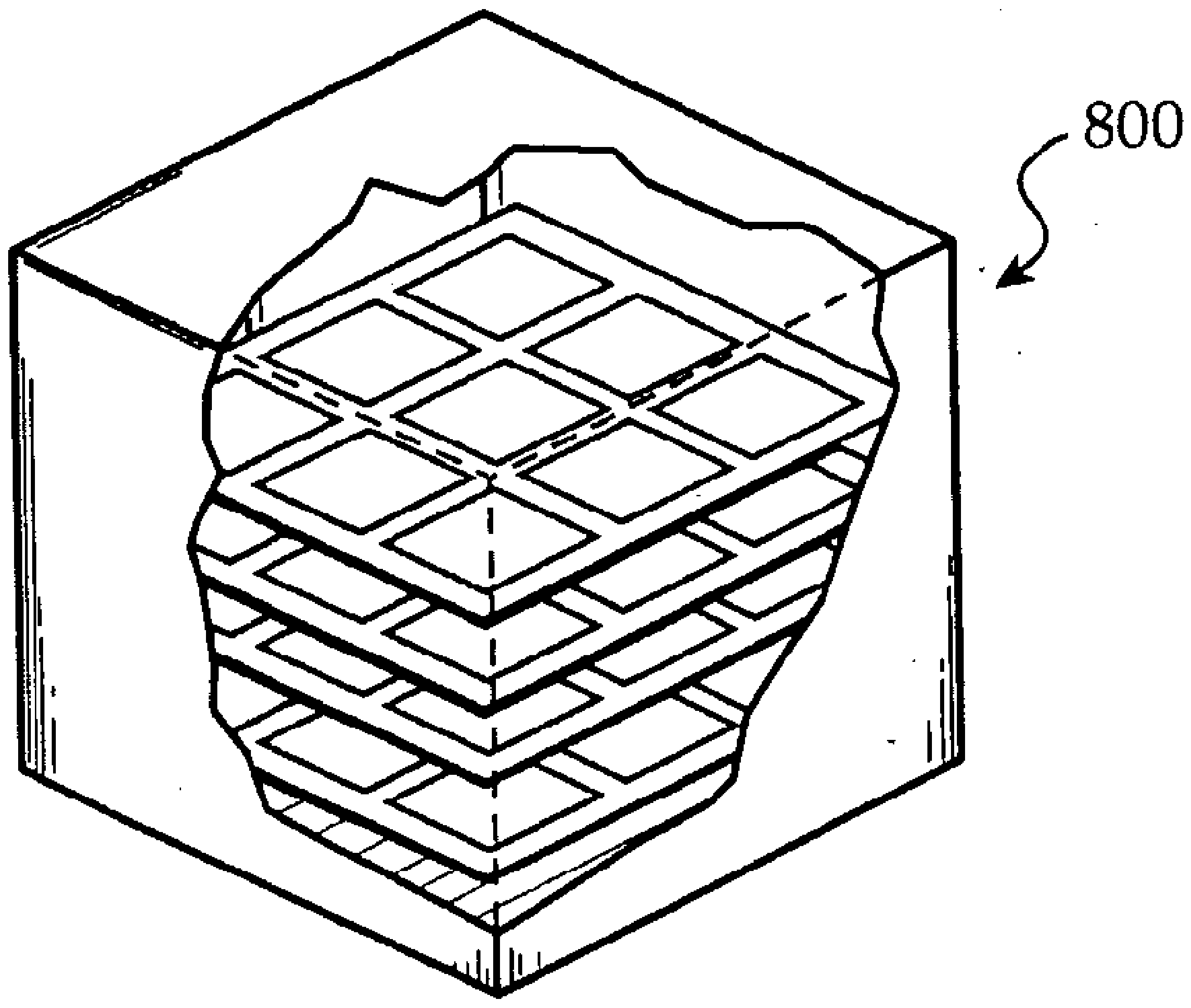

Fig. 8

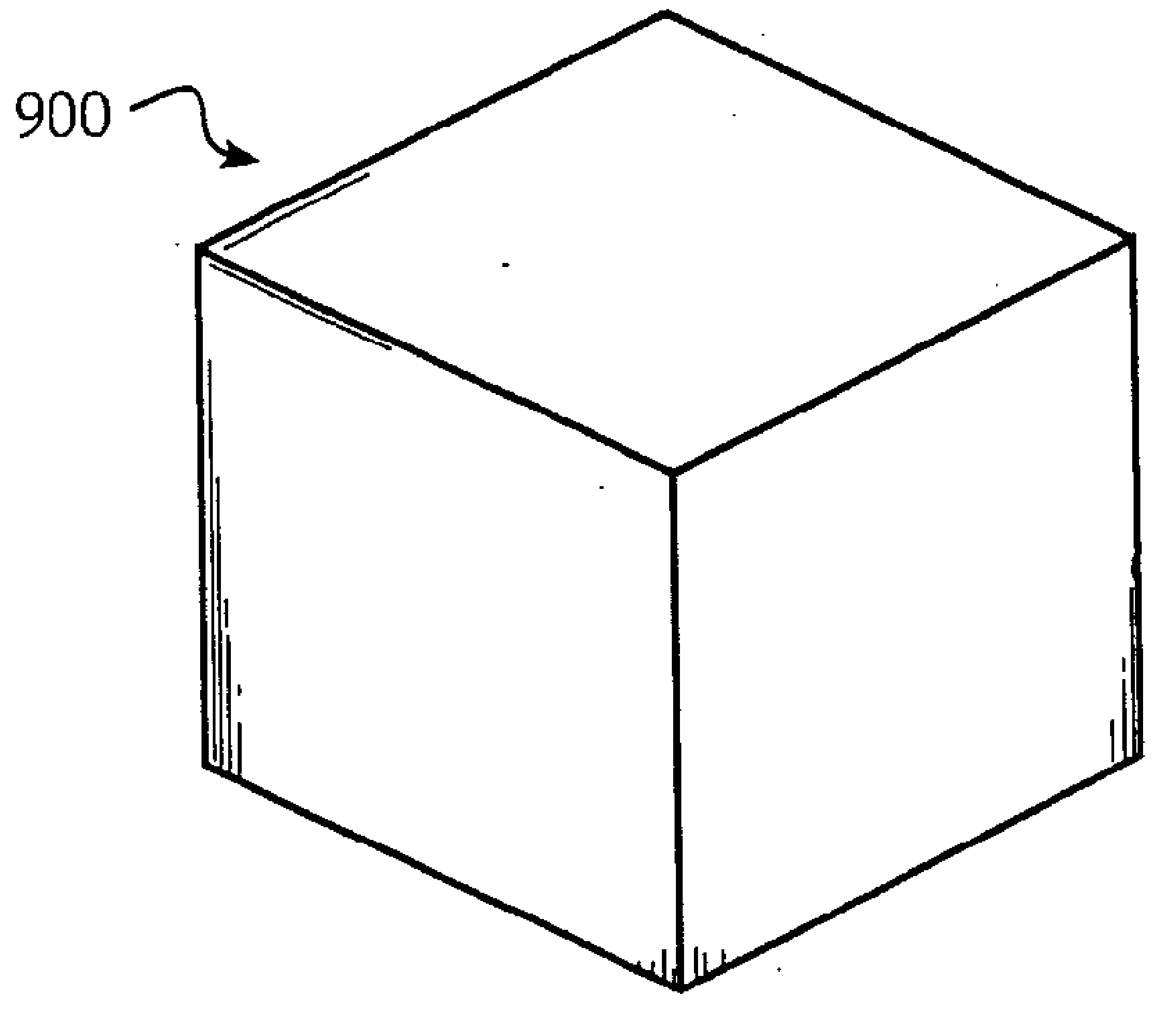

Fig. 9

PALLET BASED SYSTEM FOR FORMING THIN-FILM SOLAR CELLS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional Patent Application Ser. No. 60/626,843, filed Nov. 10, 2004.

FIELD OF THE INVENTION

[0002] The invention disclosed herein relates generally to the field of photovoltaics and more specifically to the product and method of manufacturing thin-film solar cells using a pallet based system to prevent the formation of defects during deposition.

BACKGROUND OF THE INVENTION

[0003] The benefits of renewable energy are not fully reflected in the market price. While alternative energy sources such as photovoltaic (PV) cells offer clean, reliable, and renewable energy, high product costs and lack of production reliability have kept these devices from being a viable commercial product. With the demand for energy going up, the world demand for alternatives to present energy sources is increasing.

[0004] Although relatively efficient thin-film PV cells can be manufactured in the laboratory, it has proven difficult to commercially scale manufacturing processes with the consistent repeatability and efficiency critical for commercial viability. Moreover, the cost associated with manufacturing is an important factor preventing the broader commercialization of thin-film solar cells. The lack of an efficient thin-film manufacturing process has contributed to the failure of PV cells to effectively replace alternate energy sources in the market.

[0005] Thin-film PV cells can be manufactured according to varied designs. In a thin-film PV cell, a thin semiconductor layer of PV materials is deposited on a supporting layer such as glass, metal, or plastic foil. Since thin-film materials have higher light absorptivity than crystalline materials, thin-film PV materials are deposited in extremely thin consecutive layers of atoms, molecules, or ions. The typical active area of thin-film PV cells is only a few micrometers thick. The basic photovoltaic stack design exemplifies the typical structure of a PV cell. In that design, the thin-film solar cell comprises a substrate, a barrier layer, a back contact layer, a mixed type semiconductor source layer, an absorber layer, an n-type junction buffer layer, an intrinsic transparent oxide layer, and a conductive transparent oxide layer. Compounds of copper indium gallium diselenide (CIGS) have the most promise for use in absorber layers in thin-film cells and fit within the classification of copper-indium selenium class, called CIS materials. CIGS films are typically deposited by vacuum-based techniques.

[0006] Thin-film manufacturing processes suffer from low yield due to defects in the product that occur during the course of deposition. Specifically, these defects are caused by contamination occurring during processing and materials handling, and the breakage of glass, metal, or plastic substrates. Thus, a process for manufacturing thin-film solar cells that both limits potential contamination during processing and concurrently minimizes substrate breakage is desired in the art.

[0007] Currently, cells are manufactured using a multi-step batch process wherein each product piece is transferred between reaction steps. This transfer is bulky and requires the reaction in chambers to be cycled. A typical process consists of a series of individual batch processing chambers, each specifically designed for the formation of various layers in the cell. Problematically, the substrate is transferred from vacuum to air—and back again—several times. Such vacuum breaks may result in contamination of the product. Thus, a process that minimizes vacuum breaks is desired in the art.

[0008] While an alternate system uses a series of individual batch processing chambers coupled with a roll-to-roll continuous process for each chamber, the discontinuity of the system and the need to break vacuum continues to be a major drawback. Additionally, the roll-to-roll process may impose flexing stress on substrates, resulting in fracturing and breakage. Such defects compromise layer cohesiveness and may result in a zero yield.

[0009] Also contributing to the low yield in PV cell manufacturing is the requirement of high-temperature deposition processes. High temperatures are generally incompatible with all presently known flexible polyimide or other polymer substrate materials.

[0010] For example, U.S. Patent Application 2004/0063320, published by Hollars on Apr. 1, 2004, discloses a general methodology for continuously producing photovoltaic stacks using a roll-to-roll system. As discussed above, this process requires the application of flexing stress to the substrate. This stress potentially results in fractures and breakage. Fractures or breakage reduce high quality stack structures and lower manufacturing yield. Thus, to be a commercially viable process, the disclosed system requires a flexible substrate for the production of the stack. However, no currently known flexible polymer materials can withstand the high-temperature deposition process. Therefore, a process that does not impose flexing stress on the substrates, where the substrates can withstand the high-temperature deposition process, is desired in the art. So a process for manufacturing PV work pieces effectively, and capable of large scale production are needed.

SUMMARY OF THE INVENTION

[0011] The present invention provides a photovoltaic device produced by providing a pallet-based substrate to a series of reaction chambers where sequentially a barrier layer, a back contact layer, a semiconductor layer or layers, alkali materials, an n-type junction buffer layer, an intrinsic transparent oxide layer, a transparent conducting oxide layer and a top metal grid can be formed on the pallet.

[0012] A method is further disclosed for forming a photovoltaic device in a continuous fashion by employing a train of the pallet based holders loaded with work pieces. In this embodiment, a series of pallets are passed at a defined rate through a reactor having a plurality of processing zones, wherein each zone is dedicated to one production step stage of device manufacture.

[0013] These production steps may include: a load or isolation zone for substrate preparation; environments for depositing a barrier layer, a back contact layer, semiconductor layer or layer and alkali materials; an environment for the thermal treatment of one or more of the previous layers; and an environment for the deposition of: an n-type compound semiconductor wherein this layer serves as a junction buffer layer, an intrinsic transparent oxide layer, and a conducting transparent oxide layer. In a further embodiment, the process may be adjusted to comprise greater or fewer zones in order to fabricate a thin film solar cell having more or fewer layers.

[0014] A pallet type system may be employed where a plurality of work pieces are held as a pallet and a plurality of pallets are processed though a continuous reactor step apparatus. This pallet based system allows continuous processing of smaller work pieces and alternative materials handling steps, such as pallet stacking in intermediate or final steps.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] **FIG. 1** shows an embodiment of a thin-film solar cell produced by the production technology of the present invention.

[0016] **FIG. 2** schematically represents a reactor for forming solar cells.

[0017] **FIG. 3** shows a plurality of work piece substrates on a device capable of affixing the substrates onto a carrier that also has means that allow the pieces to be advanced in a precise fashion through the production apparatus.

[0018] **FIG. 4** illustrates one embodiment of a substrate being fed from left to right through a process in accordance with the present invention.

[0019] **FIG. 5A** shows an embodiment of the processing method wherein two substrates are fed and processed simultaneously by a sequential sputter-evaporate in accordance with the present invention.

[0020] **FIG. 5B** shows a top view of an embodiment of the processing method wherein two substrates are fed and processed simultaneously by a sequential sputter-evaporate/sputter-evaporate process.

[0021] **FIG. 6** illustrates another embodiment of a process in accordance with the invention wherein zones further comprise one or more sub-zones.

[0022] **FIG. 7** shows a schematic of the pallet used in the present invention populated with a plurality of substrate work pieces.

[0023] **FIG. 8** shows a schematic of a cartridge used to stack a plurality of substrates in a controlled environment.

[0024] **FIG. 9** shows a schematic production technique employing the cartridge system to allow discontinuations in a photovoltaic manufacturing process.

DETAILED DESCRIPTION OF THE INVENTION

General Photovoltaic Stack Designs

[0025] The present invention employs a new production apparatus to produce photovoltaic devices. Of course, the particular apparatus will depend upon the specific photovoltaic device design, which can be varied. However, the base premise is that each photovoltaic device has a photovoltaic device or thin-film solar cell **100** comprises a substrate **105**, a barrier layer **110**, a back contact layer **120**, a semiconductor layer **130**, an alkali materials **140**, another semiconductor layer **150**, an n-type junction buffer layer **160**, an intrinsic transparent oxide layer **170**, and a transparent conducting oxide layer **180**. This stack of layers, according to the present invention, will be made on a plurality of substrates arrayed on a pallet **700**, shown in **FIG. 7**. The individual substrate pieces **710** will be arrayed on the pallet, fixed by a fixture means.

General Apparatus Configurations

[0026] A first embodiment of the invention is an apparatus for manufacturing a photovoltaic device comprising a means for providing a plurality of pallets holding multiple substrate pieces, in sequence, to a plurality of reaction zones. These reaction zones include at least a zone capable of providing an environment for deposition of a semiconductor layer, and a zone capable of providing an environment for depositing a precursor p-type absorber layer.

[0027] **FIG. 7** shows a schematic top view of a pallet. The pallet provides a holding basis **700** for a plurality of small PV work piece substrates **710**, or working substrates fixedly attached to the pallet in a pre-determined manner so that the individual work pieces are presented in each treatment chamber in a precise and controllable fashion. The pallet itself is engineered so that the position of the pallet can be precisely determined. The pallet also has a means for allowing attachment to a drive means to advance the pallet through the treatment chamber. Materials of the body of the pallet are chosen so that they are thermally stable and do not interact with the treatment or deposition materials used in the reaction or deposition chamber.

Fixturing Means

[0028] Furthermore, the means for securing the work pieces to the pallet are releasable. In some instances the means for affixing the work piece is magnetic, either because the substrate of the work piece is itself ferro-magnetic, or with an overlay that hold the individual pieces to the body of the pallet. A mask may be employed to hold each piece where there is a frame and a plurality of panes that allow deposition through said pane on the work piece substrates.

[0029] **FIG. 4** shows as the plurality of pallets are processed through the series of treatment chambers **420**, **430** used to deposit the multiple required layers for a photovoltaic device, the train of reaction/deposition chambers may be fed by loaded cartridges containing a plurality of pallets **440** (see also **FIG. 8**), and after the desired layers are deposited and processed the finished work pieces are collected in a cartridge **450** and stored for further processing or manufacturing steps (see also **FIG. 9**).

[0030] In an alternative method, the starting piece cartridge **440** feeds a system that might provide surface treatment of the substrate, deposition of the junction layer, deposition of the alkali-containing semiconductor source layer, deposition of a p-type absorber layer, and then formation of the junction and n-type layer, and a buffer so that the worked-on pieces can be taken from the controlled reaction train and inventories for further processing.

Method of Thin Film Manufacturing

[0031] One form of the invention provides a method for manufacturing a photovoltaic device comprising the step of providing a pallet, capable of holding a substrate, in sequence to a plurality of reactor zones wherein the plurality of zones includes at least one zone depositing a precursor p-type absorber layer.

[0032] In another form, the invention provides a method for manufacturing a photovoltaic cell comprising the steps of providing a plurality of substrate pieces affixed to a pallet carrier means, depositing a conductive film on the surface of said plurality of substrate pieces, wherein the conductive film includes a plurality of discrete layers of conductive materials, depositing at least one p-type absorber layer on the conductive film, wherein the p-type semiconductor absorber layer includes a metal based alloy material, e.g., alloys of Cu, In, Ga, and possibly Se or S, and depositing an n-type semiconductor layer on the p-type semiconductor layer forming a p-n junction.

[0033] A series of treatment chambers are provided where each chamber provides a specific treatment environment, as well as the means for depositing specified materials onto the working surface, or interface of the work pieces being processed in order to produce a specific layer deposition or layer treatment. Each of these treatment chambers allow a means to transport the work pieces (marked on the pallet being made into the photovoltaic device) to be transported from the first designed chamber, through the sequential plurality of chambers, until the work piece has been made into the designed photovoltaic stack.

[0034] This plurality of reaction or treatment chambers provided with a transport mechanism may also include one or more isolation chambers that ensure effective reactants are maintained in specifically desired chambers and do not contaminate downstream processes. This isolation system is particularly important in the formation of the semiconductor layers of the photovoltaic device, where relatively small amounts of material determine whether a layer is a p-type or n-type semiconductor. This carrier may be configured with referencing means to ensure the work pieces are positioned within the production apparatus at defined positions.

[0035] **FIG. 3** shows a plurality of work piece substrates **310** on a device capable of affixing the substrates onto a carrier **320**, that also has means that allow the pieces to be advanced in a precise fashion through the production apparatus. These pallets are generally flat and have means for holding a plurality of work pieces on a surface of the pallet so as to present each of the work piece surfaces to a deposition source or treatment source.

General Photovoltaic Stack Designs

[0036] The present invention employs a new production apparatus to produce photovoltaic devices. Of course, the particular apparatus will depend upon the specific photovoltaic device design, which can be varied.

[0037] Viewing **FIG. 1**, all layers are deposited on a substrate **105** which may comprise one of a plurality of functional materials, for example, glass, metal, ceramic, or plastic. Deposited directly on the substrate **105** is a barrier layer **110**. The barrier layer **110** comprises a thin conductor or very thin insulating material and serves to block the out diffusion of undesirable elements or compounds from the substrate to the rest of the cell. This barrier layer **110** may comprise chromium, titanium, silicon oxide, titanium nitride and related materials that have the requisite conductivity and durability. The next deposited layer is the back contact layer **120** comprising non-reactive metals such as molybdenum. The next layer is deposited upon the back contact layer **120** and is a p-type semiconductor layer **130** to improve adhesion between an absorber layer and the back contact layer. The p-type semiconductor layer **130** may be a I-$\text{III}_{a,b}$-VI isotype semiconductor, but the preferred composition is Cu:Ga:Se; Cu:Al:Se or Cu:In:Se alloyed with either of the previous compounds.

[0038] In this embodiment, the formation of a p-type absorber layer involves the interdiffusion of a number of discrete layers. Ultimately, as seen in **FIG. 1**, the p-type semiconductor layers **130** and **150** combine into a single composite layer **155** which serves as the prime absorber of solar energy. In this embodiment, however, alkali materials **140** are added for the purpose of seeding the growth of subsequent layers as well as increasing the carrier concentration and grain size of the absorber layer **155**, thereby increasing the conversion efficiency of the solar cell. The layers are then thermally treated at a temperature of about 400° C.-600° C.

[0039] After the thermal treatment, the photovoltaic production process is continued by the deposition of an n-type junction buffer layer **160**. This layer **160** will ultimately interact with the absorber layer **155** to form the necessary p-n junction **165**. A transparent intrinsic oxide layer **170** is deposited next to serve as a hetero-junction with the CIGS absorber. Finally, a conducting transparent oxide layer **180** is deposited to function as the top of the electrode of the cell. This final layer is conductive and may carry current to a grid carrier that allows the current generated to be carried away.

Alternative Pallet Based Manufacturing Schemes

[0040] **FIG. 2** schematically represents a reactor **200** for forming solar cells. A substrate **205** is fed left to right through the reactor. The reactor **200** includes one or more processing zones, referred to in **FIG. 2** as **220**, **230**, **240** and **250**, wherein each processing zone comprises an environment for depositing materials on a substrate **205**. The zones are mechanically or operatively linked together within the reactor **200**. As used herein, the term environment refers to a profile of conditions for depositing or reacting a material layer or mixture of materials on the substrate **205** while the substrate **205** is in a particular zone.

[0041] Each zone is configured according to which layer of the solar cell is being processed. For example, a zone may be configured to perform a sputtering operation, including heat sources and one or more source targets.

[0042] Preferably, an elongated substrate **205** is passed through the various processing zones at a controllable rate. It is further contemplated that the substrate **205** may have a translational speed of 0.5 m/min to about 2 m/min. Accordingly, the process internal to each of the zones is preferably tuned to form the desired cross-section given the residence time the material is proximate to a particular source material, given the desired transport speed. Thus, the characteristics of each process, such as material and process choice, temperature, pressure, or sputtering delivery rate, etc., may be chosen to insure that constituent materials are properly delivered given the stack's residence time as determined by the transport or translation speed.

[0043] According to the invention, the substrate **205** may be transported continually through the process in a palletized fashion in a "picture frame" type mount for indexing and transportation through the process, the latter of which is illustrated in **FIG. 3**. Referring to **FIG. 3** one substrate or group of substrates **310** are mounted on a pallet **320** that translates through one or more zones **330** and **340** on track **350**. In alternate embodiments the process may further comprise a second substrate or set of substrates placed in a back to back configuration with substrate **310**.

[0044] It is contemplated that the background pressure within the various zones will range from 10^{-6} torr to 10^{-3} torr. Pressures above base-vacuum (10^{-6} torr) may be achieved by the addition of a pure gas such as Argon, Nitrogen or Oxygen. Preferably, the rate R is constant resulting in the substrate **205** passing through the reactor **200** from entrance to exit without stopping. It will be appreciated by those of ordinary skill in the art that a solar cell stack may thus be formed in a continuous fashion on the substrate **205**, without the need for the substrate **205** to ever stop within the reactor **200**.

[0045] The reactor in **FIG. 2** may further comprise vacuum isolation sub-zones or slit valves configured to isolate adjacent process zones. The vacuum isolation sub-zones or slit valves are provided to facilitate the continuous transport of the substrate between different pressure environments.

[0046] The reactor shown in **FIG. 2** is a plurality of N-processing zones **220**, **230**, **240** and **250**. However, it should be recognized by one skilled in the art that the reactor may comprise zones **220**, **230**, **240**, **250** . . . N zones. The load/unload zones **210/211** comprise zones that can be isolated from the rest of the reactor and can be open to atmosphere.

[0047] In a preferred embodiment, the process may further comprise a substrate **206** that runs back-to-back with substrate **205**. In this embodiment substrates **206** and **205** are oriented in a back-to-back configuration and run through zones **220**, **230**, **240**, and **250** performing identical process operations **222/221**, **232/231**, **242/241** and **252/251**.

[0048] **FIG. 5A** shows a top illustration of a portion of a reactor **500** processing substrates **501** and **502** in a back-to-back fashion and also illustrates a sequential sputter-evaporate process isolated by zone **511**. To achieve back-to-back processing, heat sources **503** for substrate **501** are mirrored as heat sources **507** for substrate **502**. Likewise, sputtering source **504**, heat sources **505**, and evaporative sources **506** for substrate **501** are mirrored for substrate **502** as sputtering source **508**, heat sources **509**, and evaporative sources **510**.

[0049] **FIG. 5B** shows a top illustration of a portion of a reactor **512** processing substrates **521** and **522** in a back-to-back fashion with a sequential sputter-evaporate/sputter-evaporate process. As in FIG, 5A, sputter sources **534** for substrate **521** are mirrored as sputter sources **528** for substrate **522**. Likewise, heat sources **523** and **526**, evaporative sources **524** and **527**, and sputtering source **525** for substrate **521** are mirrored for substrate **522** as heat sources **529** and **532**, evaporative sources **530** and **533**, and sputtering source **531**. Hence, with the simple duplication of heat and material sources, solar cell production may be effectively doubled within the same machine.

Specific Processing Steps

[0050] Of course, the method steps for producing a particular PV article depends upon the specific design of that article. CIGS based PVs will have a different production method than Si based systems. The present invention is not so limited to one PV type and in general any PV could be made with the technology of the invention.

[0051] In cases of CIGS, the specific steps might include: loading a pallet based substrate through an isolated loading zone or like unit **210**. In various embodiments, the isolation zone **210** is contained within the reactor **200**. Alternatively, the isolation zone **210** may be attached to the outer portion of the reactor **200**. The first processing zone **210** may further comprise a substrate preparation environment to remove any residual imperfections at the atomic level of the surface. The substrate preparation may include: ion beam, deposition, heating, or sputter-etching. These methods are known in the art and will not be discussed further.

[0052] A second processing zone may be an environment for depositing a barrier layer for substrate impurity isolation, wherein the barrier layer provides an electrically conductive path between the substrate and subsequent layers. In a preferred embodiment, the barrier layer comprises an element such as chromium or titanium delivered by a sputtering process. Preferably, the environment comprises a pressure in the range of about 10^{-6} torr to about 10^{-2} torr at ambient temperature.

[0053] A third processing zone downstream from the previous zones comprises an environment for the deposition of a metallic layer to serve as a back contact layer. The back contact layer comprises a thickness that provides a conductive path for electrical current. In addition, the back contact layer serves as the first conducting layer of the solar cell stack. The layer may further serve to prevent the diffusion of chemical compounds such as impurities from the substrate to the remainder of the solar cell structure or as a thermal expansion buffer between the substrate layer and the remainder of the solar cell structure. Preferably, the back contact layer comprises molybdenum, however, the back contact layer may comprise other conductive metals such as aluminum, copper or silver.

[0054] A fourth zone provides an environment for deposition of a p-type semiconductor layer. As used herein, this layer may serve as an epitaxial template for absorber growth. Preferably, the p-type semiconductor layer is an isotype I-IIIVI$_2$ material, wherein the optical band gap of this material is higher than the average optical band gap of the p-type absorber layer. For example, a semiconductor layer may comprise Cu:Ga:Se; Cu:Al:Se or alloys of Cu:In:Se with either of the previous compounds. Preferably, the materials are delivered by a sputtering process at a background pressure of 10^{-6} to 10^{-2} torr and at temperatures ranging from ambient up to about 300° C. More preferably, temperatures range from ambient to about 200° C.

[0055] A fifth zone, downstream from the previous zones, provides an environment for the deposition of alkali materials to enhance the growth and the electrical performance of a p-type absorber. Preferably, the alkali materials are sputtered, at ambient temperature and a pressure range of about 10^{-6} torr to 10^{-2} torr. Preferably, the material comprises NaF, Na_2Se, Na_2S or KCl or like compounds wherein the thickness ranges from about 150 nm to about 500 nm.

[0056] A sixth zone, also downstream from the previous zones, may comprise an environment for the deposition of another semiconductor layer comprising p-type absorber precursor materials. In a preferred embodiment, the sixth zone may further comprise one or more sub-zones for the deposition of the precursor materials. In one embodiment, the semiconductor layer is formed by first delivering precursor materials in one or more contiguous sub-zones, then reacting the precursor materials into the final p-type absorber in a downstream thermal treatment zone. Thus, especially for CIGS Systems, there may be two material deposition steps and a third thermal treatment step in the format of the layer.

[0057] In the precursor delivery zones, the layer of precursor materials is deposited in a wide variety of ways, including evaporation, sputtering, and chemical vapor deposition or combinations thereof preferably, the precursor material may be delivered at temperatures ranging from about 200° C.-300° C. It is desired that the precursor materials react to form the p-type absorber as rapidly as possible. As previously discussed, to this end, the precursor layer or layers may be formed as a mixture or a series of thin layers.

[0058] A manufacturing device may also have seventh processing zone downstream from previous processing zones for the thermal treatment of one or more of the previous layers. The term multinaries includes binaries, ternaries, and the like. Preferably, thermal treatment reacts previously unreacted elements or multinaries. For example, in one embodiment it is preferred to have Cu, In, Se, and Ga in various combinations and ratios of multinary compounds of elements as the source for deposition on the work piece. The reactive environment includes selenium and sulfur in varying proportions and ranges in temperature from about 400° C. to about 600° C. with or without a background inert gas environment. In various embodiments, processing time may be minimized to one minute or less by optimizing mixing of the precursors. Optimal pressures within the environment depend on whether the environment is reactive or inert. According to the invention, within the thermal treatment zone, the pressures range from about 10^{-5} to about 10^{-2} torr. However, it should be noted that these ranges depend very much on the reactor design for the stage, the designer of the photovoltaic device and the operational variables of the apparatus as a whole.

[0059] The reactor may have an eighth processing zone for the formation of an n-type semiconductor layer or junction partner. The junction layer is selected from the family II-VI, or IIIx VI. For example, the junction layer may comprise ZnO, ZnSe, ZnS, In, Se or In_NS deposited by evaporation, sublimation or chemical vapor deposition methodologies. The temperatures range from about 200° C. to about 400° C.

[0060] Additionally, the process may also have a ninth zone having an environment for deposition of an intrinsic layer of a transparent oxide, for example ZnO. According to the invention, the intrinsic transparent oxide layer may be deposited by a variety of methods including for example, RF sputtering, CVD or MOCVD.

[0061] In various embodiments, the process further has a tenth zone with an environment for the deposition of a transparent conductive oxide layer to serve as the top electrode for the solar cell. In one embodiment for example, aluminum doped ZnO is sputter deposited. Preferably, the environment comprises a temperature of about 200° C. and a pressure of about 5 millitorr. Alternatively, ITO (Indium Tin Oxide) or similar may be used.

[0062] In one embodiment, as described above, the reactor may comprise discrete zones wherein each zone corresponds to one layer of photovoltaic device formation. In a preferred embodiment however, zones comprising similar constituents and or environment conditions may be combined thereby reducing the total number of zones in the reactor.

[0063] For example, in **FIG. 6**, zone **610** comprises sub-zones **611** and **612**, zone **615** comprises sub-zones **616** and **617**, and zone **620** comprises one zone, wherein each zone and sub-zone comprises a predetermined environment. In this example, a material A may be deposited in sub-zone **611** and a different material B may be deposited in sub-zone **612**, wherein the environment of sub-zone **612** downstream from material A differs from the environment in sub-zone **611**. Thus, the substrate **605** may be subjected to a different temperature or other process profiles while in different regions of the same zone **610**. According to this embodiment, the zone may be defined as having a predetermined pressure, and a zone may include one or more regions, sub-zones, or phases therein, with each sub-zone configured to deposit or react a desired material or materials within the same pressure environment.

[0064] The substrate **605** may then be passed to chamber **615**, where material C is deposited within sub-zone **616**, and material D is deposited in sub-zone **617**. Finally, the substrate **605** reaches a zone **620**, where a single material E is deposited.

[0065] As will be appreciated by those of ordinary skill in the art, the reactor **600** may be described as having a series of zones disposed between the entrance and exit of the reactor along a path defined by the translation of the substrate. Within each zone, one or more constituent environments or sub-zones may be provided to deposit or react a selected target material or materials, resulting in a continuous process for forming a solar cell stack. Once the substrate enters the reactor, the various layers of a solar stack are deposited and formed in a sequential fashion, with each downstream process in succession contributing to the formation of the solar cell stack until a finished thin film solar cell is presented at the exit of the reactor.

[0066] While the present technique has been couched in terms of CIGS based photovoltaic stack designs, it must be understood that the technique may also be employed for the production of other photovoltaic designs including production of silicon based systems such as those discussed in state of the art. For instance, it would be possible to use or include carbon or germanium atoms in hydrogenated amorphous silicon alloys in order to adjust their optical bandgap. For example, carbon has a larger bandgap than silicon and thus inclusion of carbon in a hydrogenated amorphous silicon alloy increases the alloy's bandgap. Conversely, germanium has a smaller bandgap than silicon and thus inclusion of germanium in a hydrogenated amorphous silicon alloy decreases the alloy's bandgap.

[0067] Similarly one could incorporate boron or phosphorus atoms in hydrogenated amorphous silicon alloys in order to adjust their conductive properties. Including boron in a hydrogenated amorphous silicon alloy creates a positively doped conductive region. Conversely, including phosphorus in a hydrogenated amorphous silicon alloy creates a negatively doped conductive region.

[0068] Hydrogenated amorphous silicon alloy films are prepared by deposition in a deposition chamber. Heretofore, in preparing hydrogenated amorphous silicon alloys by deposition in a deposition chamber, carbon, germanium, boron or phosphorus have been incorporated into the alloys by including in the deposition gas mixture carbon, germanium, boron or phosphorus containing gases such as methane (CH_4), germane (GeH_4), germanium tetrafluoride (GeF_4), higher order germanes such as digermane ($Ge_2 H_6$), diborane ($B_2 H_6$) or phosphine (PH_3). See for example, U.S. Pat. Nos. 4,491,626, 4,142,195, 4,363,828, 4,504,518, 4,344,984, 4,435,445, and 4,394,400. A drawback of this practice, however, is that the way in which the carbon, germanium, boron or phosphorus atoms are incorporated into the hydrogenated amorphous silicon alloy is not controlled. That is, these elements are incorporated into the resulting alloy in a highly random manner thereby increasing the likelihood of undesirable chemical bonds.

[0069] Thus, in cases where PV devices are manufactured, and specific and controlled reaction and or deposition conditions are required to produce the films of the PV, the present invention technology will be useful.

What is claimed is:

1. An apparatus for manufacturing a photovoltaic device comprising a means for providing a plurality of pallets holding multiple substrate pieces in sequence to a plurality of reaction zones including at least:

a zone capable of providing an environment for deposition of a semiconductor layer; and a zone capable of providing an environment for depositing a p-type absorber layer.

2. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a means for providing in sequence a substrate to a plurality of reactor zones for preparing said substrate.

3. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a first processing zone capable of providing an environment for transition of the substrate from an ambient environment to the processing environment.

4. The apparatus of claim 3 wherein the substrate transitions, in part or whole, from atmospheric pressure to reduced pressure consistent with the subsequent processing environment.

5. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of a barrier layer.

6. The apparatus of claim 5 wherein the barrier layer comprises a thin conductor or very thin insulating material.

7. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of a conductive back contact layer.

8. The apparatus of claim 7 wherein the deposition of a conductive back contact layer comprises a metallic layer.

9. The apparatus of claim 8 wherein the metallic layer is comprise conductive metals chosen from the group consisting of molybdenum, titanium, tantalum, or other acceptable metals or alloys.

10. The apparatus of claim 9 wherein the metallic layer is molybdenum.

11. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of alkali materials.

12. The apparatus of claim 11 wherein the alkali materials are Na-VII or Na_2-VII.

13. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of a semiconductor layer.

14. The apparatus of claim 13 wherein the semiconductor layer comprises Group I, III, VI elements.

15. The apparatus of claim 14 wherein the semiconductor layer comprises $CuGaSe_2$, $CuAlSe_2$, or $CuInSe_2$ alloyed with one or more of the I, III, VI elements.

16. The apparatus of claim 15 wherein the semiconductor layer comprises $CuGaSe_2$.

17. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of a semiconductor layer wherein the layer comprises precursor materials.

18. The apparatus of claim 17 wherein the precursor materials comprise Group I, III, VI elements.

19. The apparatus of claim 18 wherein the precursor materials comprise a I-(IIIa,IIIb)-VI_2 layer.

20. The apparatus of claim 19 wherein the precursor materials comprise one or more of the elements of a I-(IIIa, IIIb)-VI_2 layer where the $0.0<\text{IIIb}/(\text{IIIa}+\text{IIIb})<0.4$.

21. The apparatus of claim 19 wherein the precursor materials comprise one or more of the alloys of a I-(IIIa, IIIb)-VI_2 layer where the $0.0<\text{IIIb}/(\text{IIIa}+\text{IIIb})<0.4$.

22. The apparatus of claim 19 wherein the semiconductor layer comprises a CIGS absorber layer comprising In_{1-x}:Ga_x:Se_2 where x ranges between 0.2 to 0.3 wherein the thickness ranges from about 1 μm to about 3 μm.

23. The apparatus of claim 22 where the CIGS absorber layer is formed by the delivery of type I, III and VI precursor metals where Cu, In_{1-x}, Ga_x, and Se_2 layers are sequentially deposited on the substrate.

24. The apparatus of claim 22 where the CIGS absorber layer is formed by the delivery of the type I, III and VI precursor metals where Cu, In_{1-x}, Ga_x, and Se_2 layers are sequentially deposited on the substrate and then synthesized into an alloy mixture with a thermal treatment.

25. The apparatus of claim 22 where the CIGS absorber layer is formed by the delivery of type I, III and VI precursor metals where an Cu:Ga_x layer is separately synthesized, and then co-deposited with an In_{x-1} layer and Se_2 layer on a substrate.

26. The apparatus of claim 22 where the CIGS absorber layer is formed by the delivery of type I, III and VI precursor metals where a Cu:Ga_x layer is separately synthesized, and then co-deposited with an In_{1-x} layer and Se_2 layer on a substrate; and then synthesized into an alloy mixture with a thermal treatment.

27. The apparatus of claim 22 where the CIGS absorber layer is formed by the delivery of type I, III and VI precursor metals where an Cu:Ga_x:In_{x-1} layer is separately synthesized, and then co-deposited with an Se_2 layer on a substrate.

28. The apparatus of claim 22 where the CIGS absorber layer is formed by the delivery of type I, III and VI precursor metals where a Cu:Ga_x:In_{x-1} layer is separately synthesized, and then co-deposited with an Se_2 layer on a substrate; and then synthesized into an alloy mixture with a thermal treatment.

29. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for thermal treatment of one or more layers.

30. The apparatus of claim 29 wherein the treatment occurs in the pressure range of 10^{-6} torr up to atmospheric pressure and temperature range of 300° C. to 700° C.

31. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of an n-type semiconductor layer.

32. The apparatus of claim 31 wherein the n-type semiconductor layer is discrete.

33. The apparatus of claim 32 wherein the discrete layer comprises one or more of Group II-VI, III-VI elements.

34. The apparatus of claim 32 wherein the discrete layer materials comprise one or more of the following groups $(In,Ga)_y(Se,S,O)$ and (Zn,Cd) (Se,S,O).

35. The apparatus of claim 32 wherein the discrete layer materials comprise one or more of the following materials chosen from the group consisting of $(In,Ga)_2Se_3$, $(In,Ga)_2S_3$, ZnSe, ZnS, and ZnO.

36. The apparatus of claim 32 wherein the n-type semiconductor layer is formed by diffusion of a dopant species into the p-type absorber layer.

37. The apparatus of claim 36 wherein the dopant species is chosen from the group consisting of one or more Group II or III elements.

38. The apparatus of claim 37 wherein the dopant species comprises either Zn or Cd.

39. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of an insulating transparent oxide layer.

40. The apparatus of claim 39 wherein the insulating transparent oxide layer comprises one or more materials from Group II-VI or II-IV-VI.

41. The apparatus of claim 39 wherein the insulating transparent oxide layer comprises one or more materials ZnO or ITO.

42. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a processing zone capable of providing an environment for deposition of a conducting transparent layer.

43. The apparatus of claim 42 wherein the conducting transparent layer comprises one or more materials from Group II-VI or II-IV-VI.

44. The apparatus of claim 42 wherein the conducting transparent layer comprises one or more materials ZnO, Cd_2SnO_4 or ITO.

45. The apparatus for manufacturing a photovoltaic device of claim 1 further comprising a first processing zone capable of providing an environment for transition of the substrate from the processing environment back to the ambient environment.

46. The apparatus of claim 45 wherein the substrate transitions, in part or whole, from atmospheric pressure to the reduced pressure consistent with the subsequent processing environment.

47. A method for manufacturing a photovoltaic device comprising providing a pallet, capable of holding a substrate, in sequence to a plurality of reactor zones wherein said plurality of zones includes at least one zone capable of providing an environment for depositing a p-type absorber layer.

48. A method for manufacturing a photovoltaic cell comprising:

a. providing a plurality of substrate pieces affixed to a pallet carrier means;

b. depositing a conductive film on the surface of said plurality of substrate pieces;

c. wherein the conductive film includes a plurality of discrete layers of conductive materials;

d. depositing at least one p-type semiconductor layer on the conductive film, wherein the p-type semiconductor layer includes a copper indium diselenide based alloy material;

e. depositing an n-type semiconductor layer on the p-type absorber layer forming a p-n junction.

49. A pallet system for production of photovoltaic devices comprising:

a. a pallet base with a first side and a second side where disposed on said first side of said pallet base is a plurality of regularly disposed target areas; wherein each of said plurality of disposed target areas has means for fixing a work substrate in a removable fashion;

b. indexing means disposed on said pallet base allowing control of the positioning of said pallet base;

c. fixing means is magnetic means;

d. magnetic means have thermal reservoir capacity disposed evenly over said designated target areas;

e. work substrate is a magnetic material such as stainless steel;

f. fixable means is mechanical.

50. A pallet system for production of photovoltaic devices comprising:

a. a pallet base with a first side and a second side where said first side has a plurality of regularly disposed target areas disposed on said first side of said pallet base;

b. a plurality of regularly disposed target areas disposed on said second side of said pallet base; wherein each of said plurality of disposed target areas has means for fixing a work substrate in a removable fashion;

c. indexing means disposed on said pallet base allowing control of the positioning of said pallet base.

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