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(54) **BACK-CONTACTED SOLAR CELLS WITH INTEGRAL CONDUCTIVE VIAS AND METHOD OF MAKING**

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Continuation-in-part of application No. 10/606,487, filed on Jun. 26, 2003.

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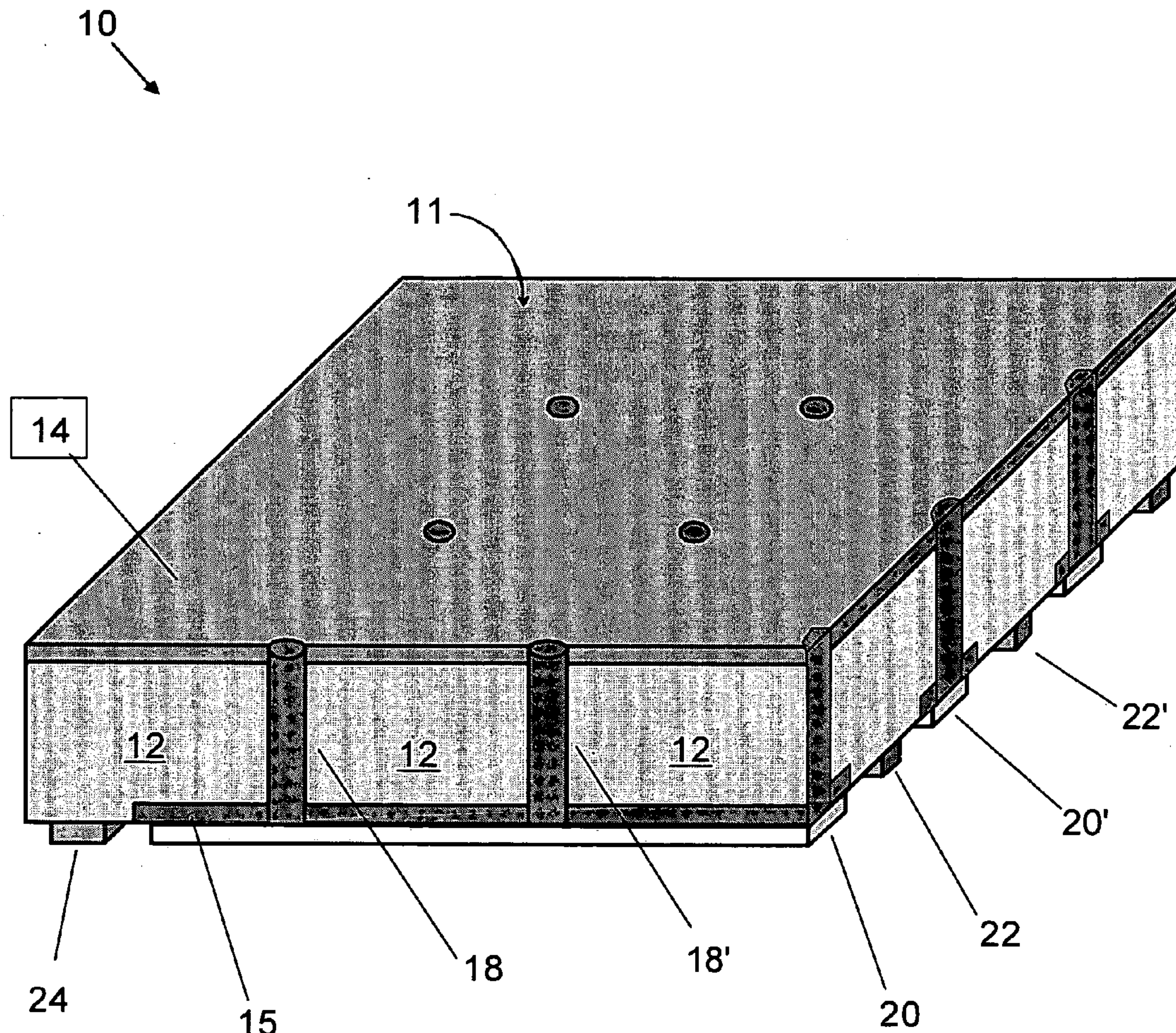
(57) **ABSTRACT**

Methods of manufacturing back-contacted p-type semiconductor substrate solar cells fabricated using a gradient-driven solute transport process, such as thermomigration or electromigration, to create n-type conductive vias connecting the n-type emitter layer on the front side to n-type ohmic contacts located on the back side, and back-contacted solar cells with integral n-type conductive vias, such as made by a gradient-driven solute transport process.

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(21) Appl. No.: **11/319,868**

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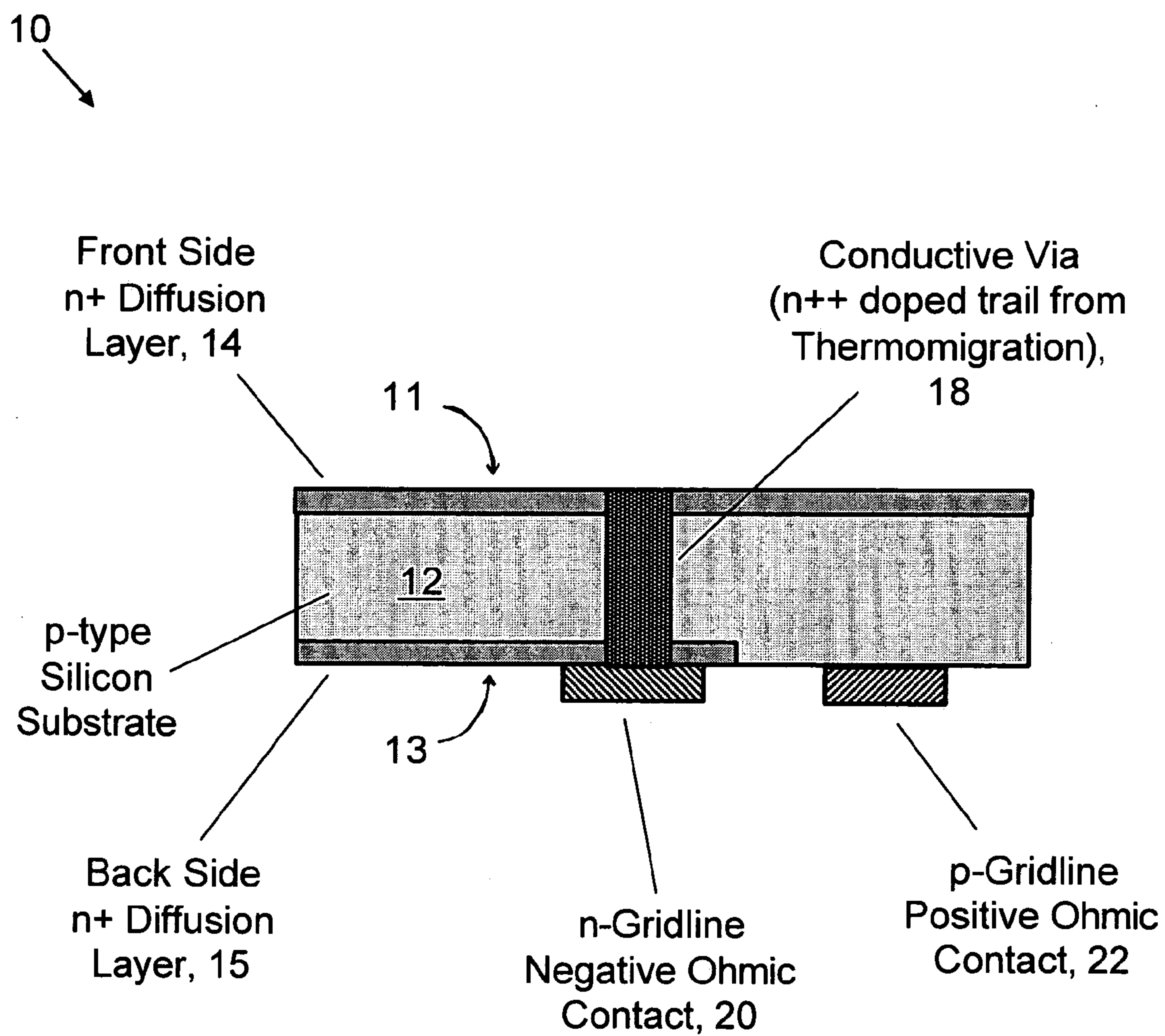


Fig. 1A



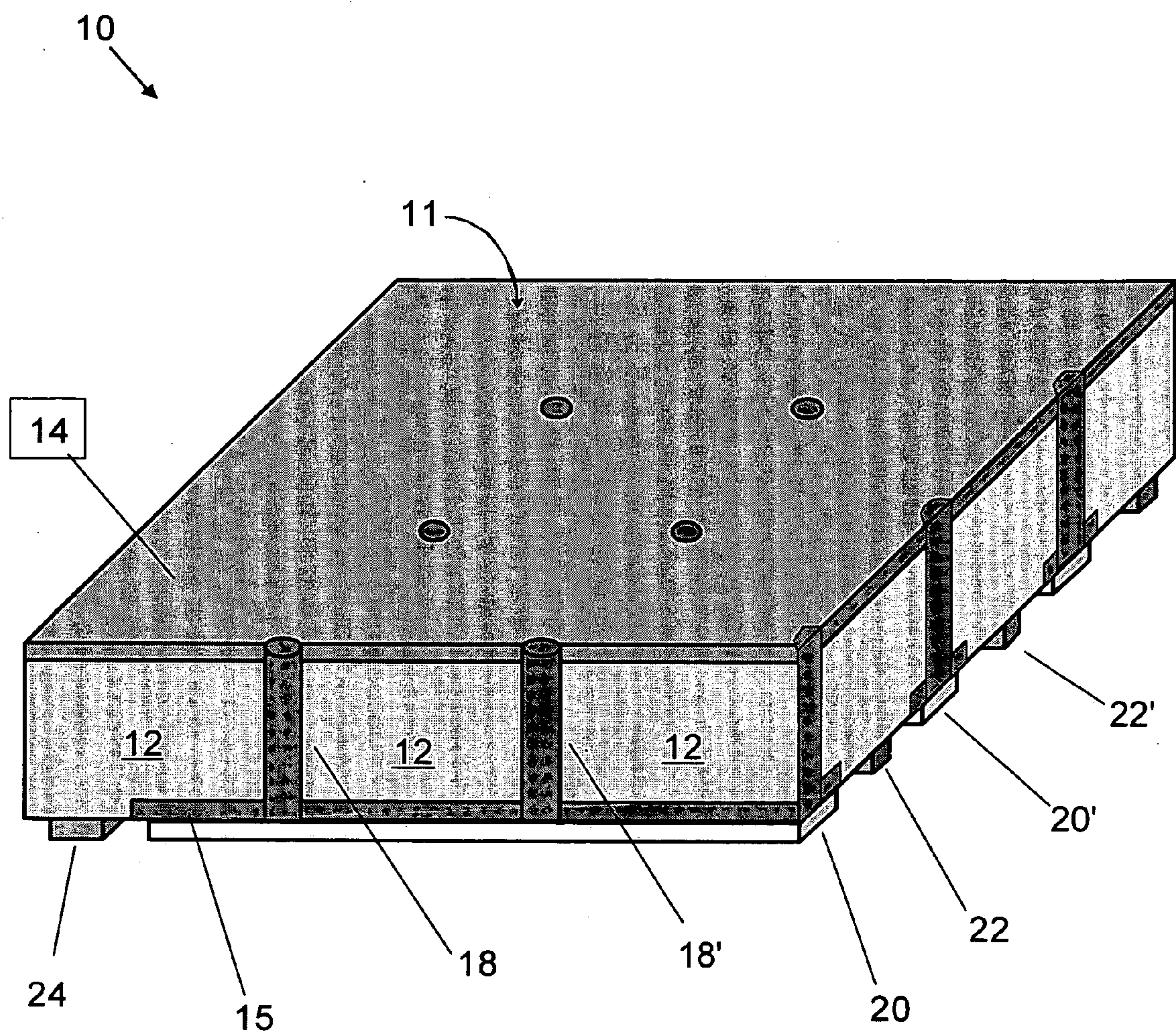


Fig. 1B



10

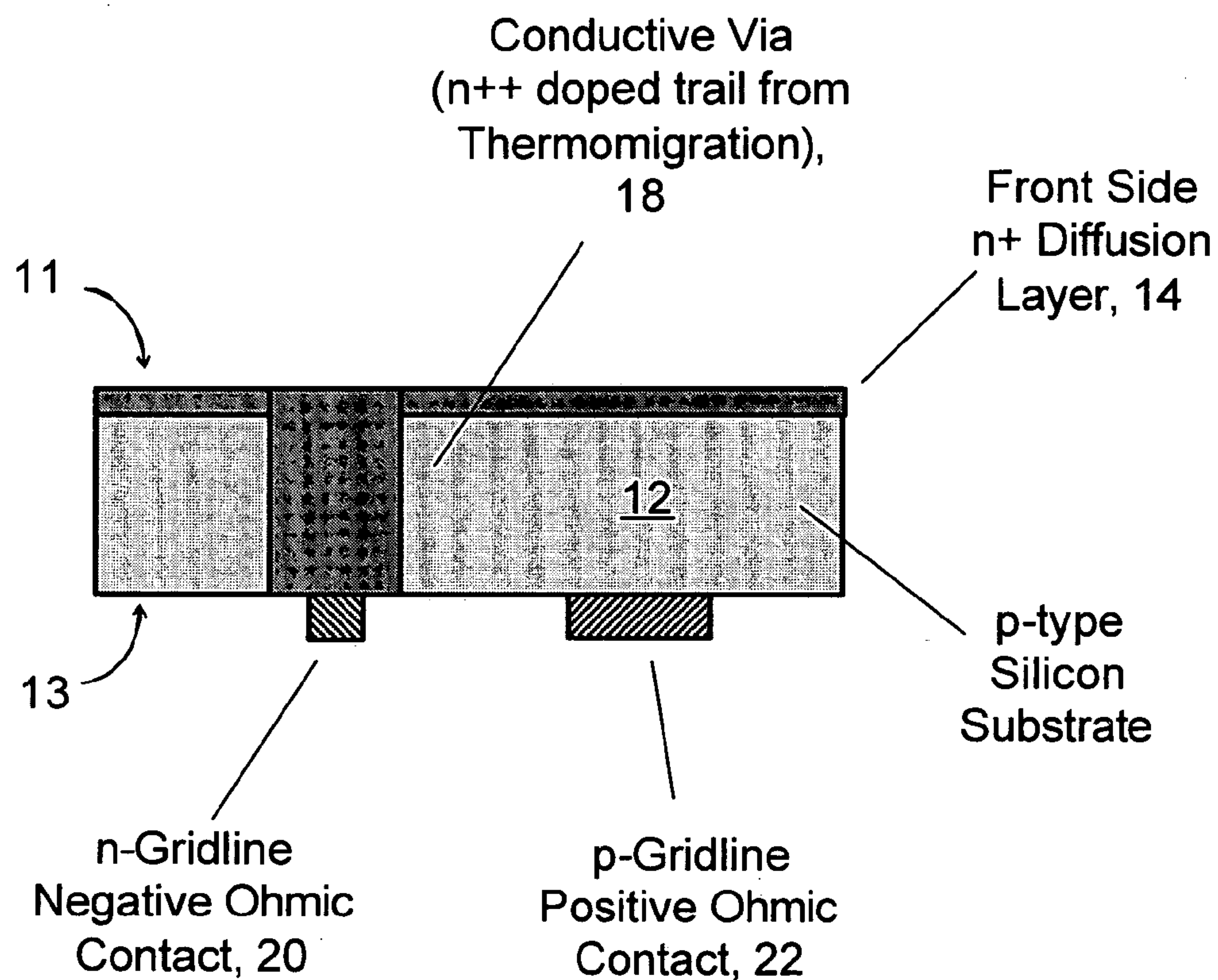


Fig. 1C

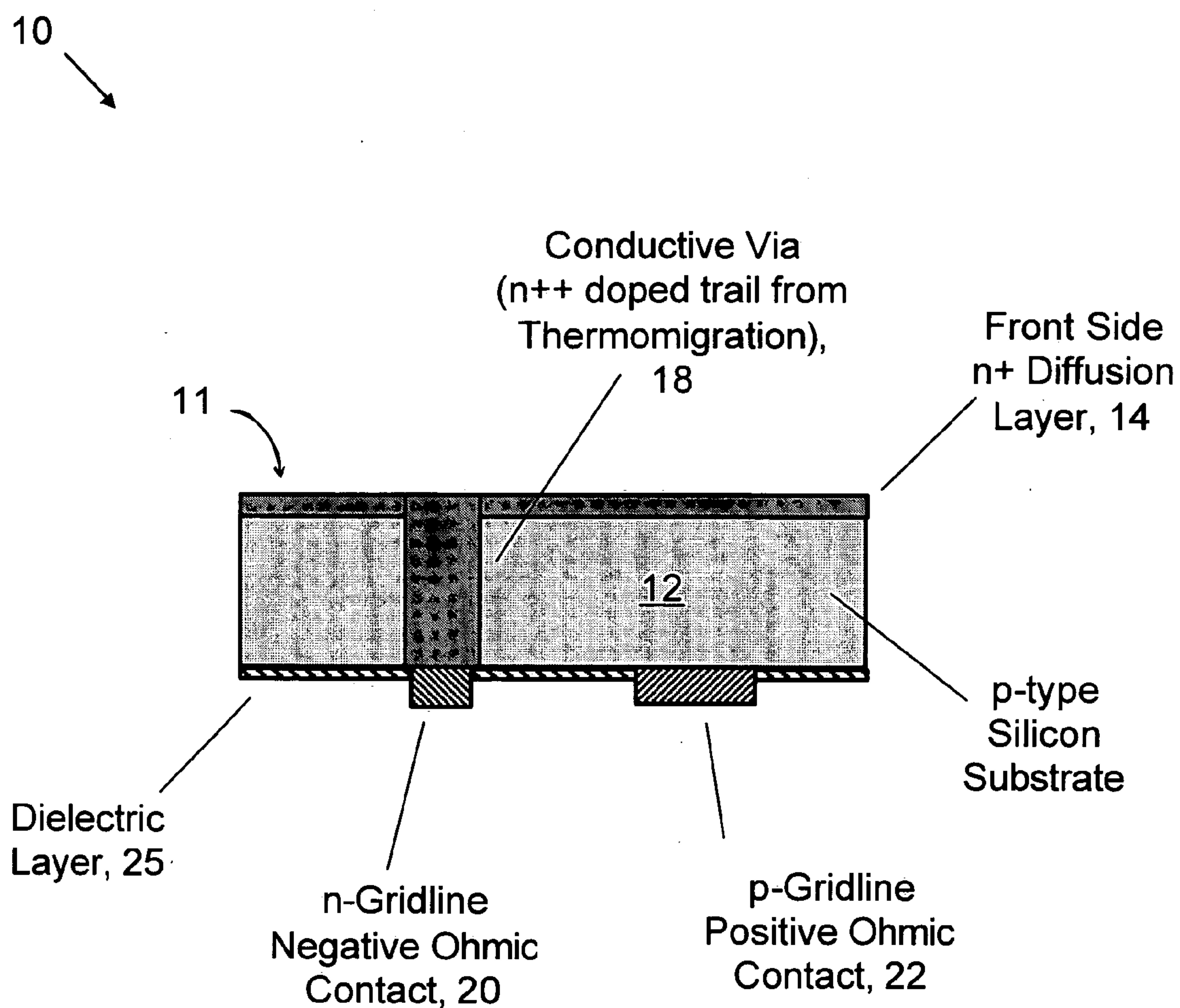


Fig. 1D



24

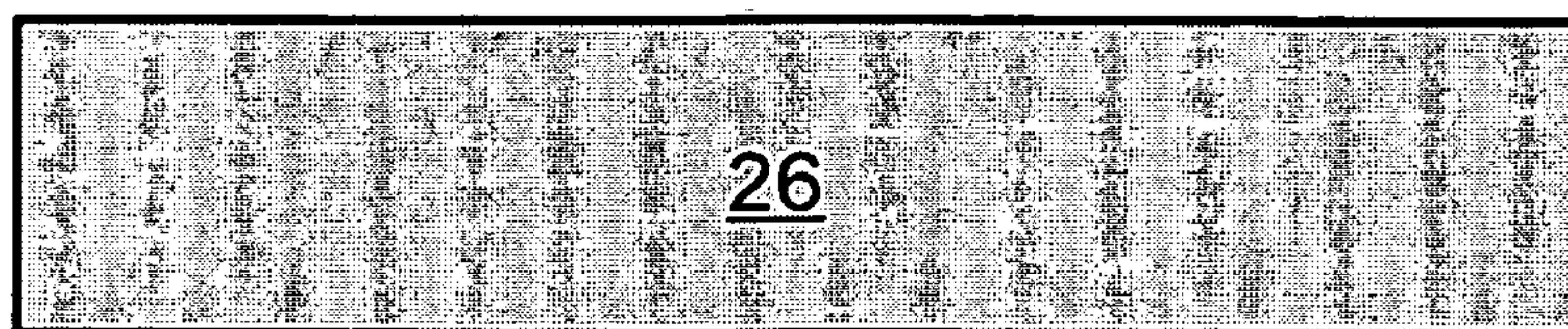
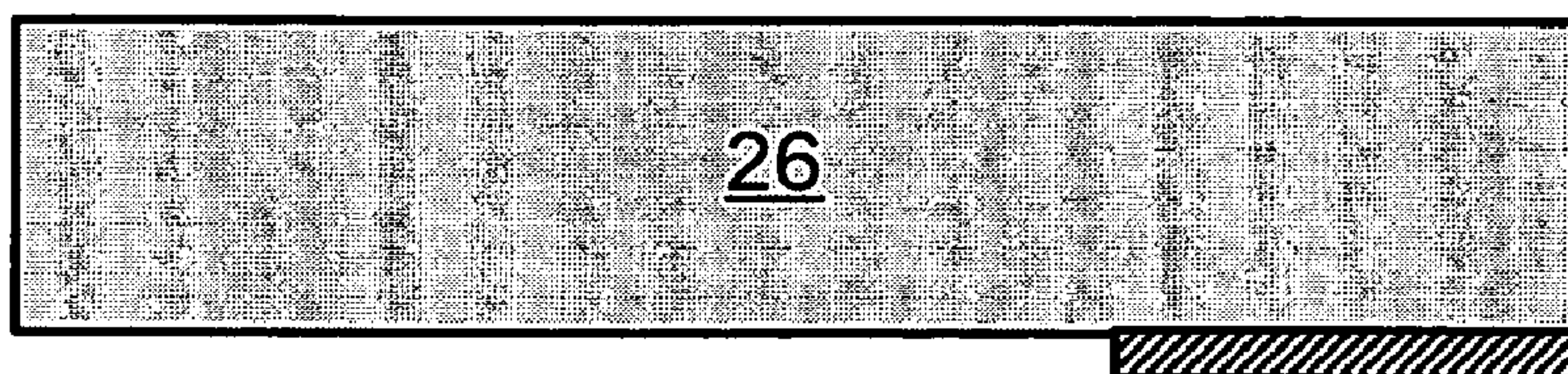


Fig. 2A

24

28



30

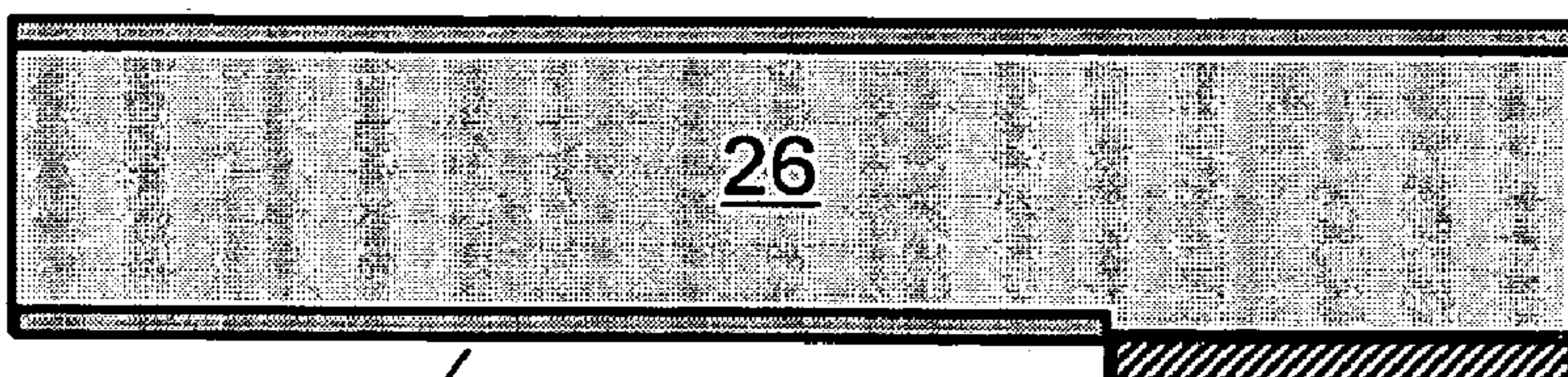
32

Fig. 2B

24

28

34



30

36

32

Fig. 2C

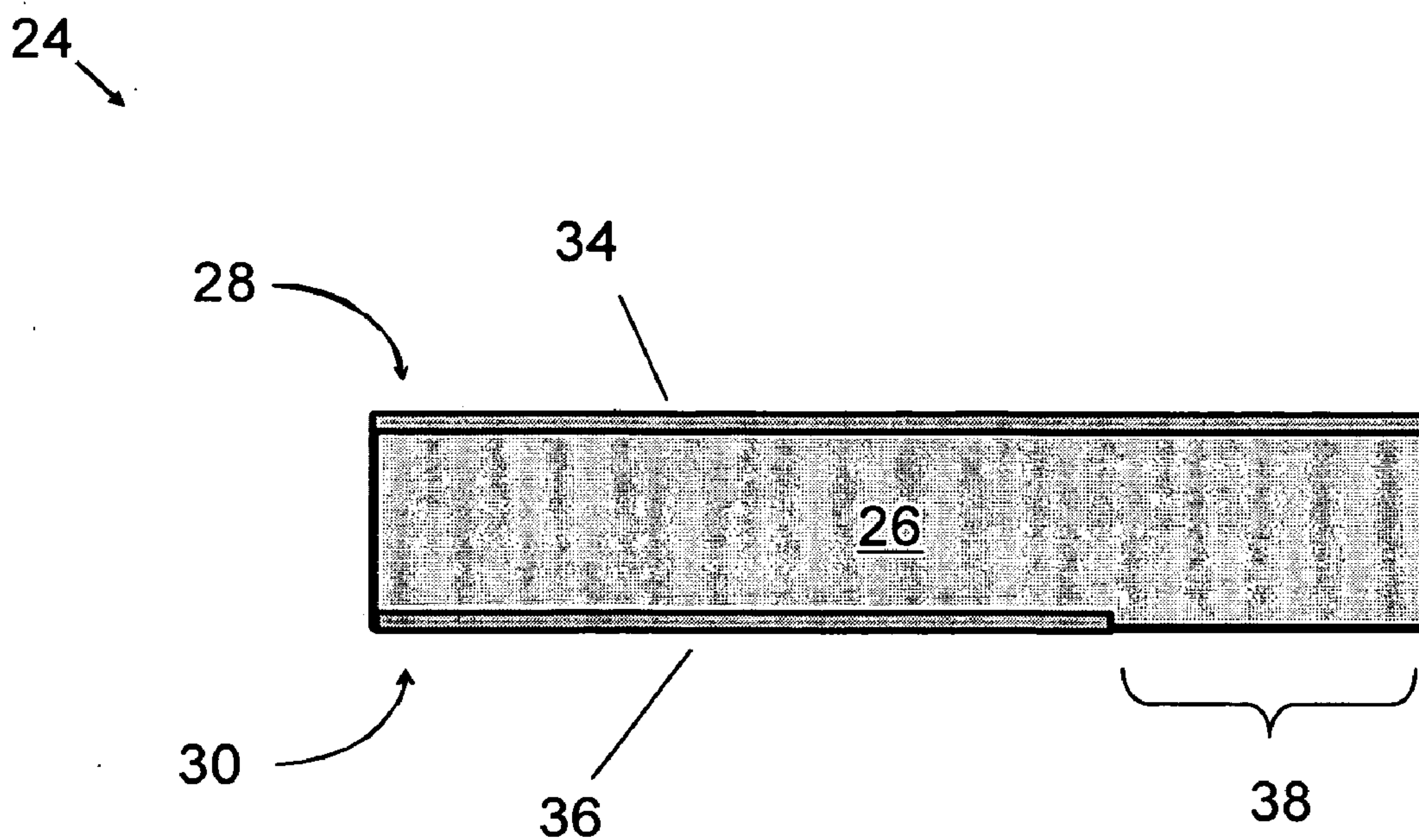


Fig. 2D

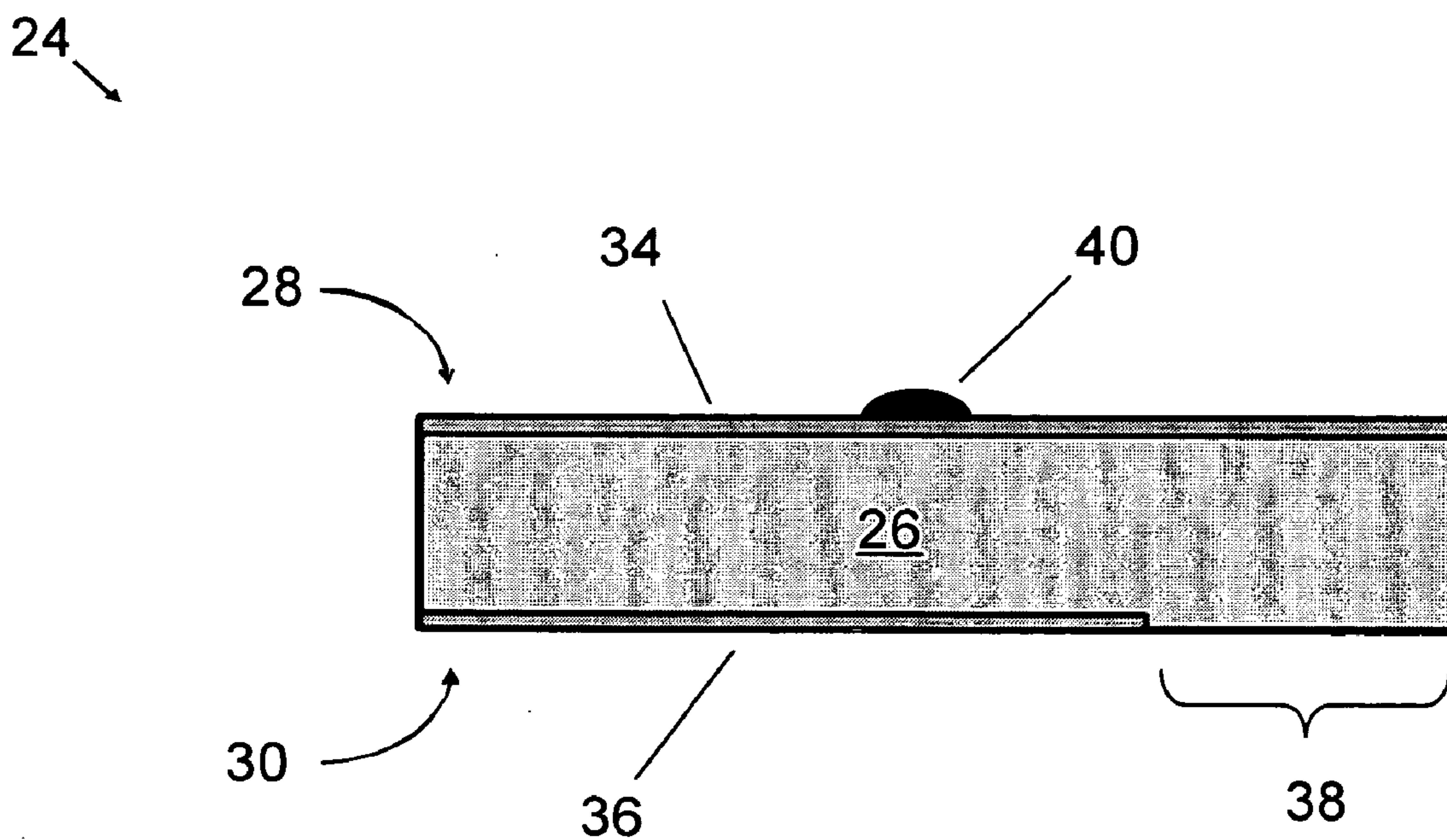


Fig. 2E



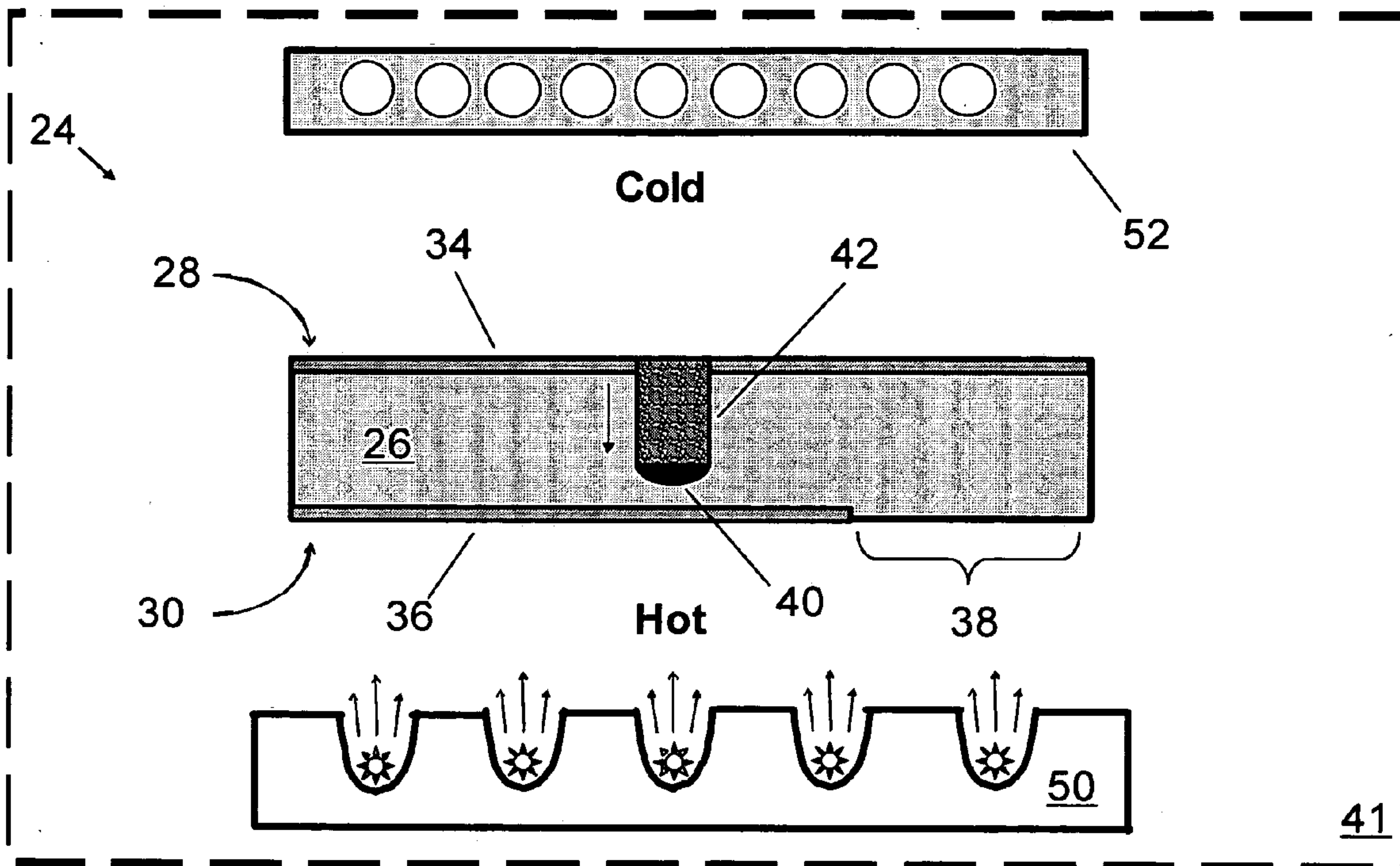


Fig. 2F



24 ↘

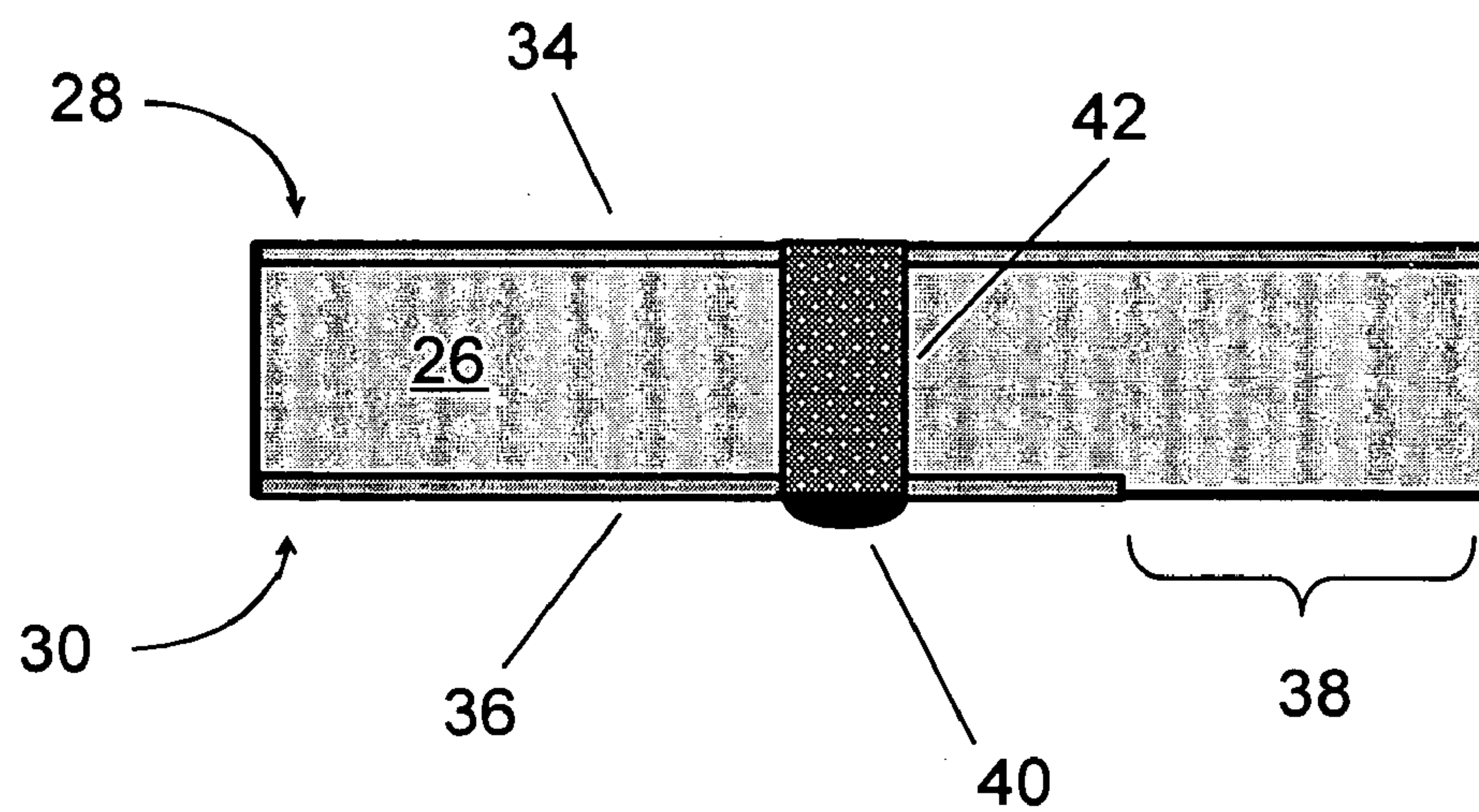


Fig. 2G

24 ↘

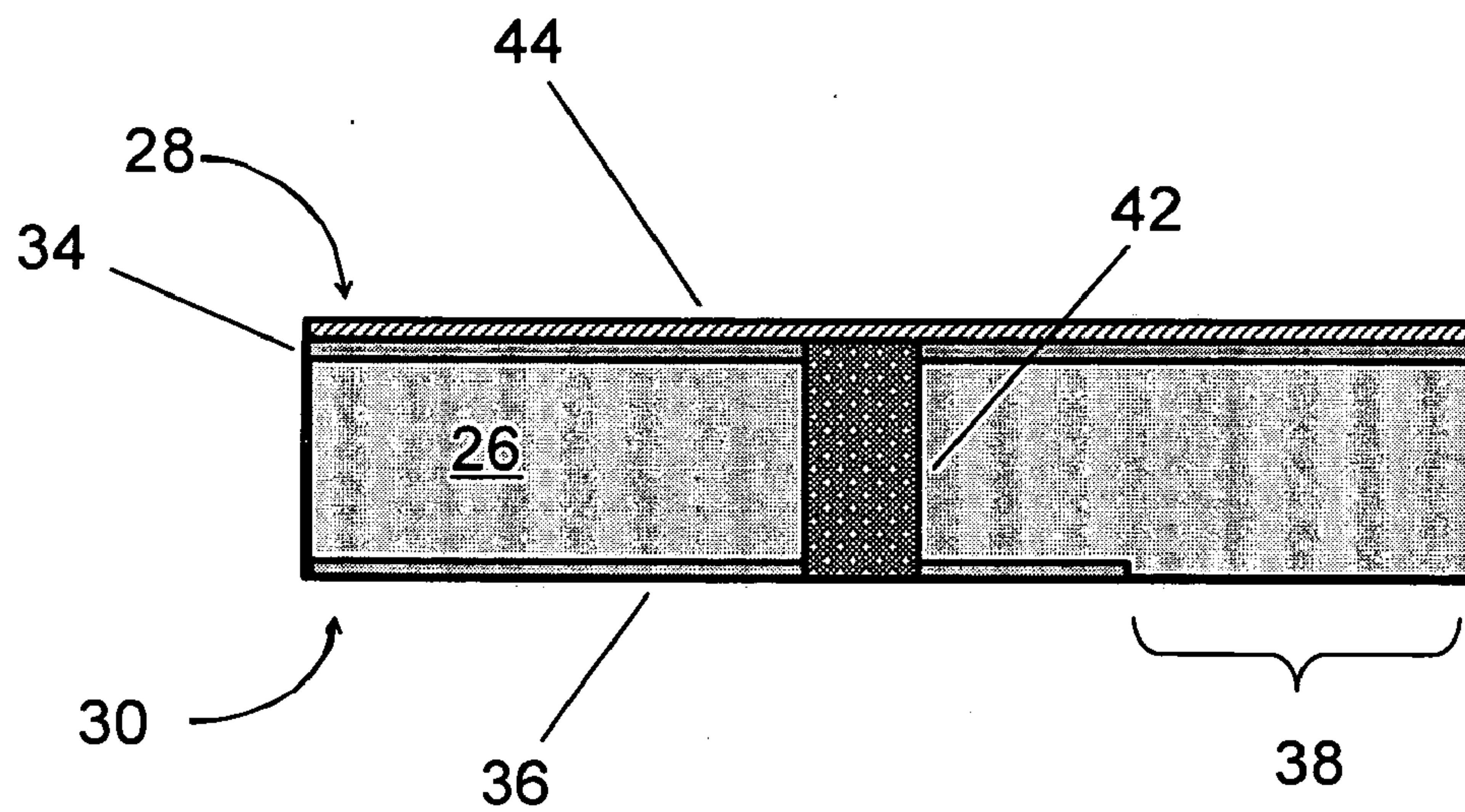


Fig. 2H



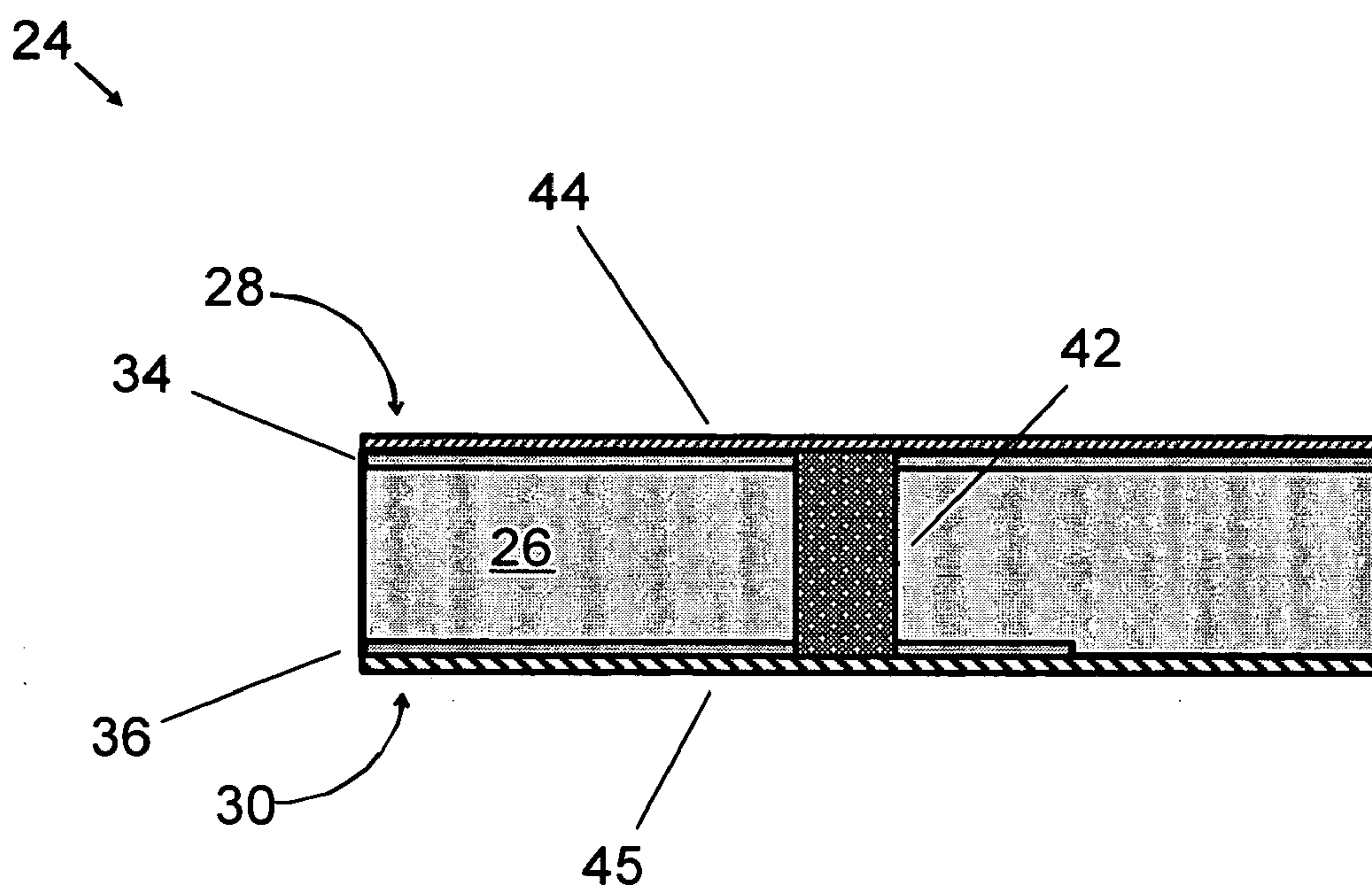


Fig. 2I

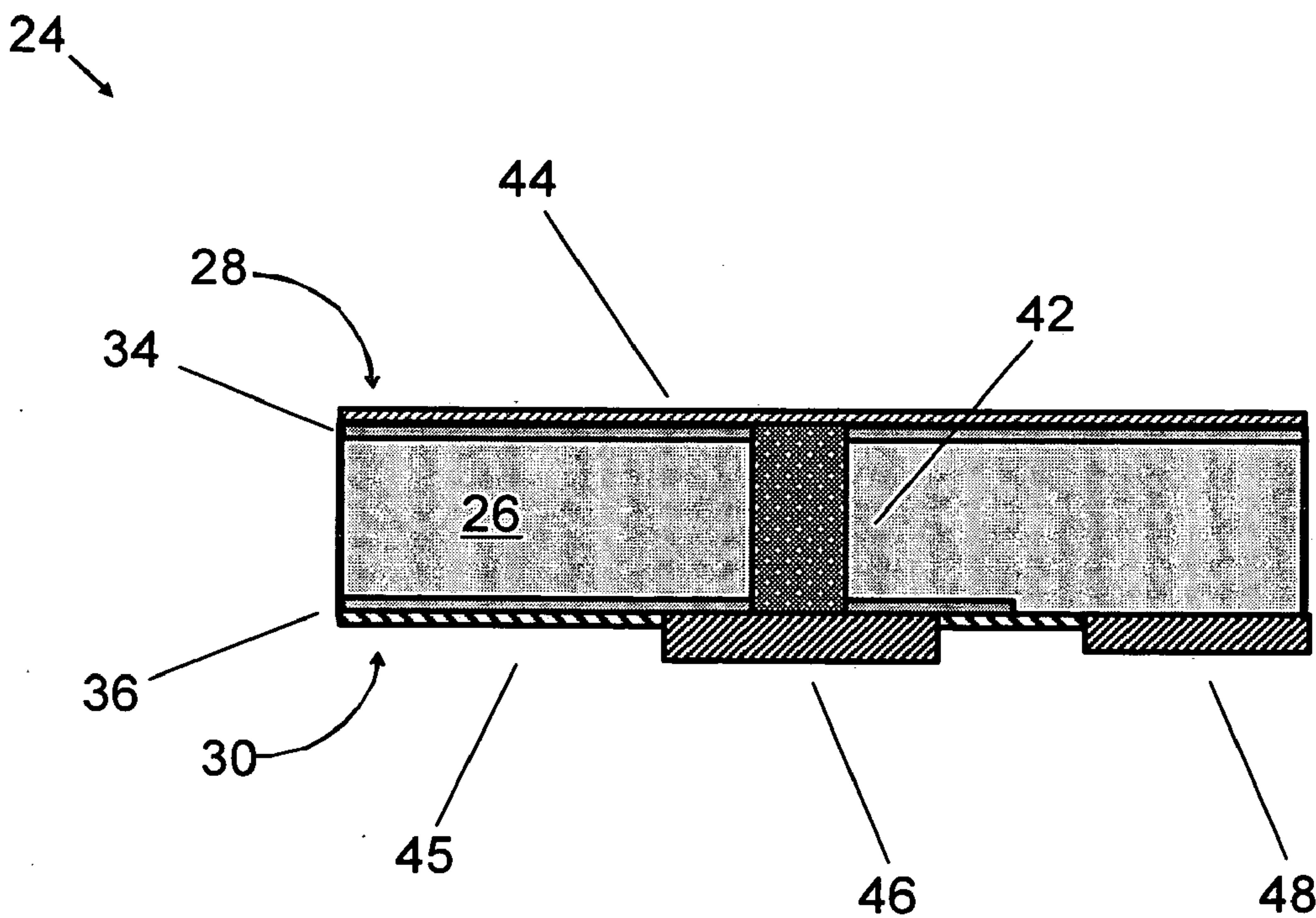


Fig. 2J



124

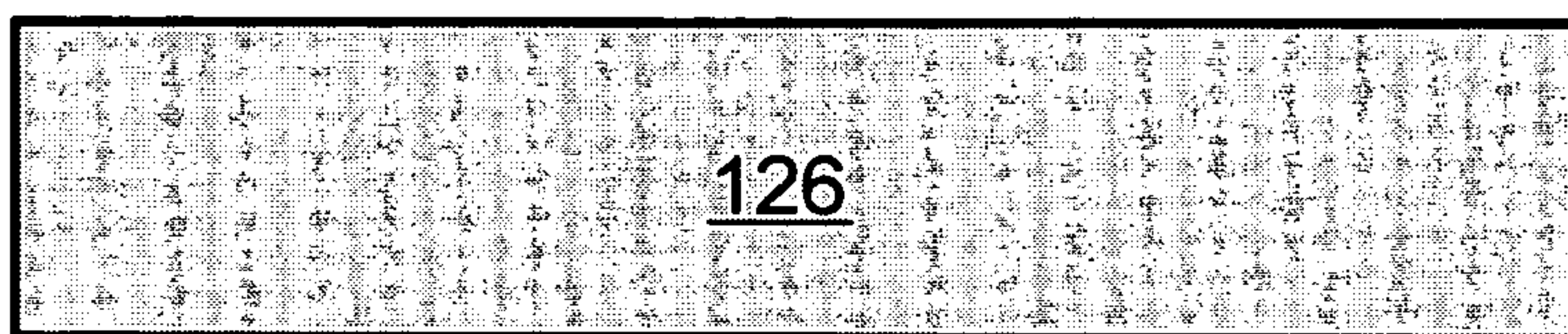


Fig. 3A

124

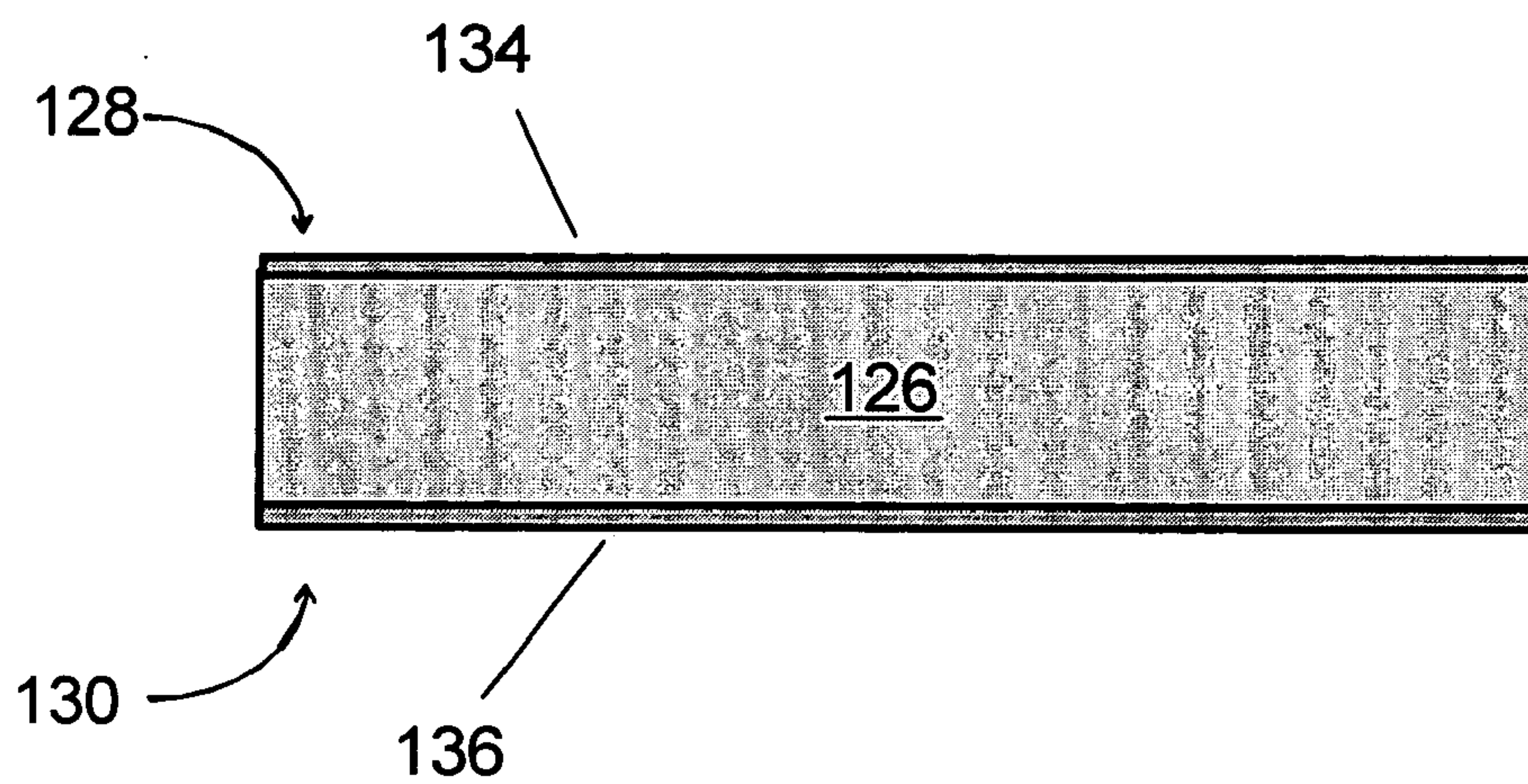


Fig. 3B

124

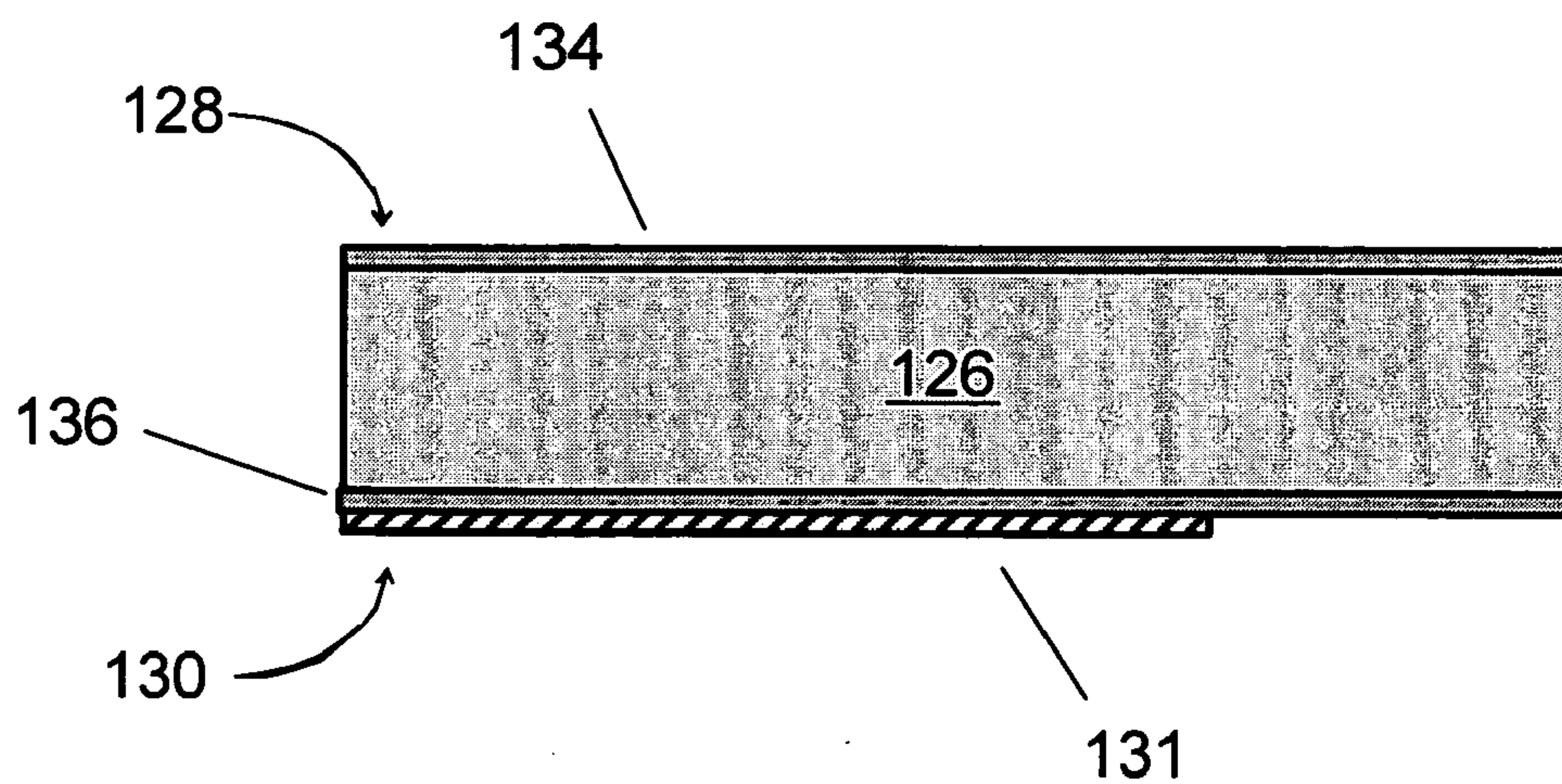


Fig. 3C



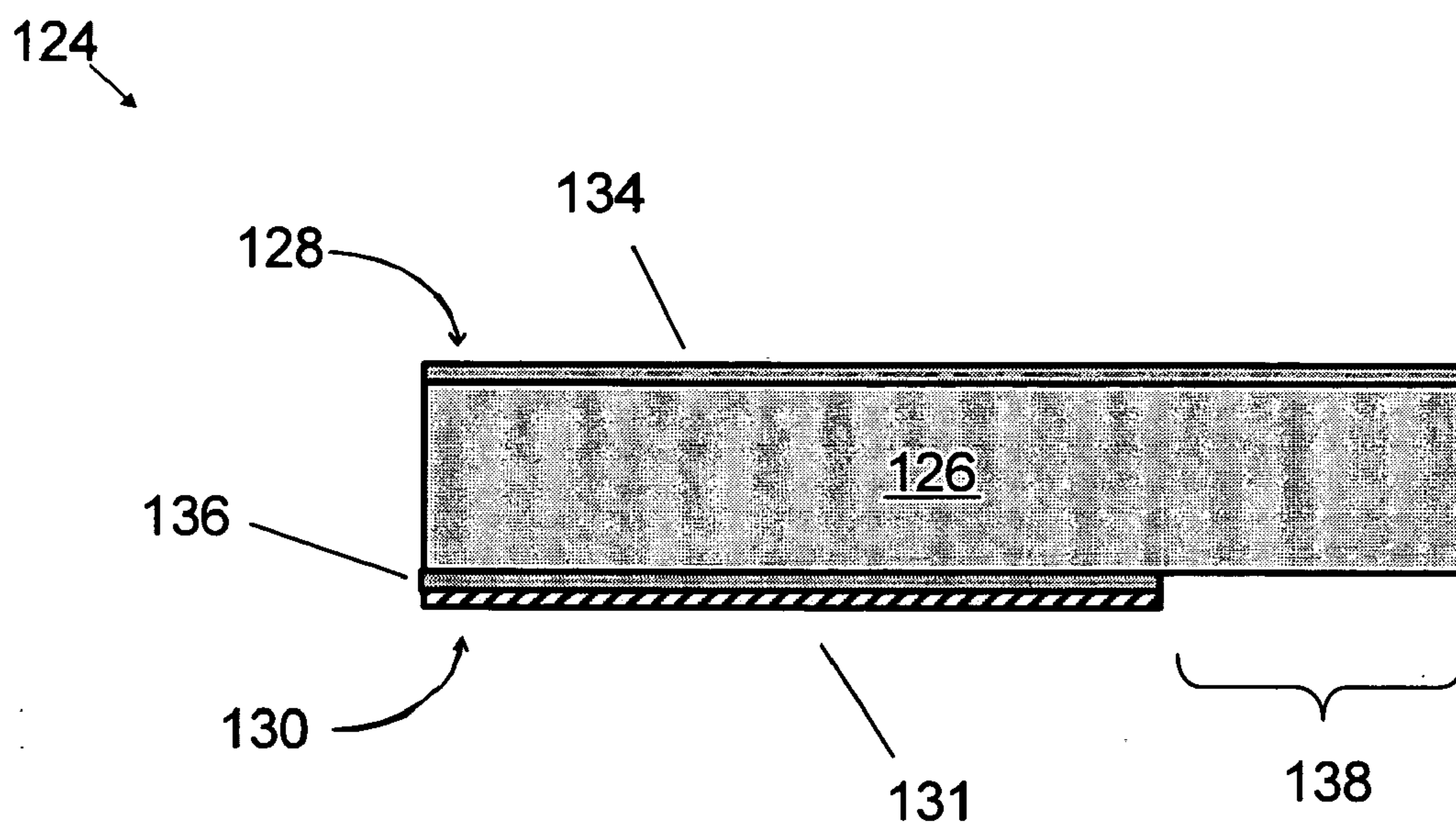


Fig. 3D

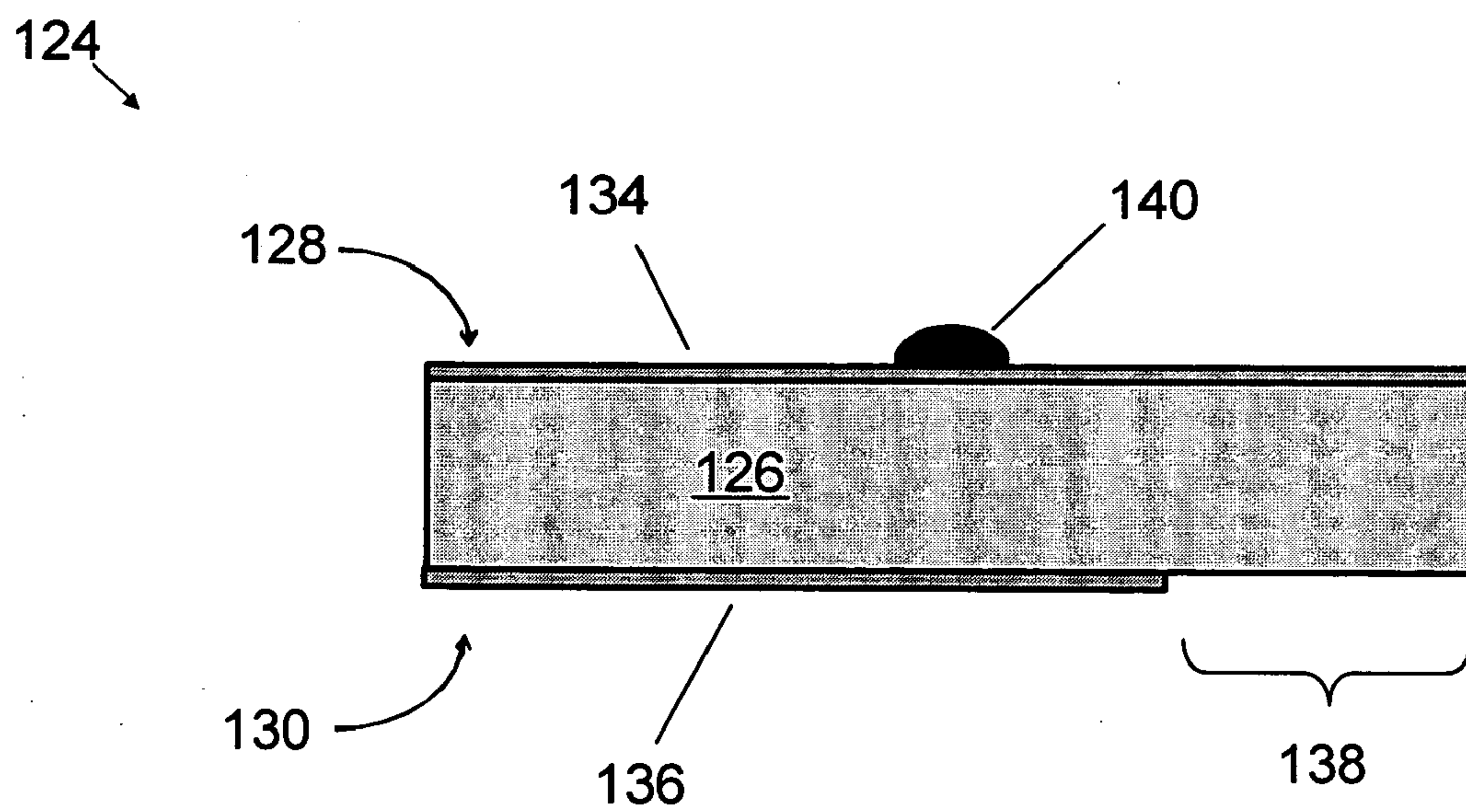


Fig. 3E



**BACK-CONTACTED SOLAR CELLS WITH  
INTEGRAL CONDUCTIVE VIAS AND METHOD  
OF MAKING**

CROSS-REFERENCE TO RELATED  
APPLICATIONS

[0001] This application is a continuation-in-part application of U.S. patent application Ser. No. 10/606,487, entitled "Fabrication of Back-Contacted Silicon Solar Cells Using Thermomigration to Create Conductive Vias", to Gee, et al., filed on Jun. 26, 2003, and a continuation application of International Patent Application Serial No. PCT/US2004/020370, entitled "Back-Contacted Solar Cells With Integral Conductive Vias And Method Of Making", to Gee, et al., filed on Jun. 24, 2004, and the specifications thereof are incorporated herein by reference.

FEDERALLY SPONSORED RESEARCH

[0002] The United States Government has rights in this invention pursuant to Department of Energy Contract No. DE-AC04-94AL85000 with Sandia Corporation.

BACKGROUND OF THE INVENTION

[0003] The present invention relates generally to photovoltaic solar cells and methods of making photovoltaic solar cells, and more specifically to back-contacted solar cells with an array of  $n^{++}$  conductive passages or vias integral to the p-type semiconductor substrate, preferably fabricated using a gradient-driven migration process, such as thermomigration or electromigration, to create the array of  $n^{++}$  conductive vias electrically connecting an  $n^+$  emitter surface on the front side of the cell to a grid of ohmic contacts located on the cell's back side.

[0004] Back-contacted silicon solar cells (photovoltaic cells) have several advantages compared to traditional silicon solar cells that have ohmic contacts located on both the front and rear surfaces. One advantage is that back-contacted cells have a higher conversion efficiency due to reduced (or eliminated) contact-obscuration losses (e.g., sunlight reflected from a front-side contact grid is unavailable to be converted into electricity). Another advantage is that assembly of back-contacted cells into electrical circuits is easier and cheaper because both polarity contacts are on the same surface (i.e., the back-side). As an example, significant cost savings compared to present photovoltaic module assembly can be achieved with back-contacted cells by encapsulating the photovoltaic module and assembling the solar cells into an electrical circuit in a single step. Another advantage of a back-contacted cell is better aesthetics by providing a more uniform appearance (e.g., an all-black surface). Aesthetics is important for some applications, like building-integrated photovoltaic systems (e.g., solar roof tiles), and photovoltaic sunroofs for automobiles.

[0005] An important issue for back-contacted silicon solar cells is identifying a cell design and fabrication process that are inexpensive to manufacture and that can use inexpensive, lower-quality silicon substrates. Solar cells that use inexpensive silicon substrates contain greater amounts of impurities and crystalline defects, which limit the internal collection depth of photo-generated carriers. Hence, silicon solar cells using inexpensive substrates generally have a carrier-collection junction (i.e., "emitter layer") on the front

surface, where most of the light is absorbed, in order to obtain a high collection efficiency of photogenerated carriers. For silicon solar cells, the bulk Si substrate is generally doped p-type and the emitter layer is generally a thin, heavily-doped,  $n^+$  layer that is formed in an "emitter diffusion" step by solid-state diffusion of phosphorus at elevated temperatures.

[0006] State-of-the-art back-contacted solar cells use an array of laser-drilled holes to effectively "wrap" the emitter layer from the front surface around to the back surface (hence, the name "Emitter Wrap Through", or EWT). The laser-drilled holes are closely spaced about 1-2 mm apart, and typically have a diameter of about 50-150 microns (after chemical etching). The emitter diffusion step (i.e., doping with phosphorus) dopes both the exposed exterior front and back silicon surfaces n-type (except for any masked areas), as well as doping the exposed interior silicon surfaces n-type (i.e., n-doped) that are located inside of the hollow laser-drilled holes. The interior n-doped surfaces of the holes form an electrically conductive channel or pathway (i.e., "via") that electrically connects the n-doped emitting front surface to the n-doped rear surface, thereby permitting negative ohmic contacts (i.e., current-collection grids) to be made on the rear surface. n-doping of the laser drilled holes also provides electrical insulation of the conductive via from the p-type bulk semiconductor. Efficient back-contacted solar cells using both photolithographically-defined and screen-printed metallizations have been demonstrated using laser-drilled holes diffused with phosphorus, i.e., in an EWT configuration, as disclosed in U.S. Pat. No. 5,468,652 to Gee, which is incorporated herein by reference. The back-contacted positive and negative grid lines are interdigitated and optimized to minimize electrical resistance and carrier recombination.

[0007] Disadvantages of an EWT design that uses laser-drilled holes to make conductive vias include the need for drilling a large number of holes (e.g., 100 holes/cm<sup>2</sup>), loss of structural integrity resulting from the large number of holes, and the added cost and manufacturing time of performing the laser-drilling step. Additionally, the conductivity of the laser-drilled vias is limited by the achievable concentration of n-type dopant, and by the depth of the emitter diffusion layer realized on the interior surfaces of the laser-drilled holes. In other words, the performance of laser-drilled/diffused EWT cells is limited by the need to perform a single heavy diffusion to achieve sufficiently high conductivity in the laser-drilled vias.

[0008] Thermomigration (i.e., Soret effect) is a gradient-driven migration process that refers to the movement of a liquid solute (e.g., drop, droplet, wire) through a solid host in the presence of a temperature gradient (i.e., thermal gradient). The physics of the process involves more-rapid dissolution of the solid host at the front (hot) surface of the liquid drop, which causes a supersaturation of the solute at the rear (cold) surface of the liquid drop where it is deposited. In other words, liquid droplets (typically, metals) migrate inside a solid host in the direction up the thermal gradient (migrating from cold to hot) because atoms of the solid host dissolve into the liquid at the hot interface of the droplet, diffuse across the droplet, and deposit on the cold interface of the droplet. The resulting flux of dissolved solid host atoms from the hot to the cold side of the liquid droplet causes the droplet to migrate in the opposite direction,



namely, towards the hot end of the host. For metallic droplets, the minimum temperature of the semiconductor substrate must be above the semiconductor/metal eutectic temperature for thermomigration to work.

[0009] Using the process of thermomigration, sheets, wires, or drops of a suitable metallic liquid can move through the bulk of a semiconductor material under the influence of a thermal gradient, leaving behind a trail comprising recrystallized solid host material doped with a solid solution of dopant material left behind by the passage of the liquid phase. Thermomigration can form conductive channels (vias) of heavily doped silicon if the liquid metal droplet contains (or is) a dopant having opposite polarity of the substrate. Thermomigration, also called temperature gradient or Thermal Gradient Zone Melting (TGZM), of fine droplets and planar zones has been shown to be a stable process when the dimensions of these zones are sufficient small. The TGZM process was first patented by Pfann in 1957. See also H. E. Cline and T. R. Anthony, *Journal of Applied Physics*, Vol. 47, No. 6, June 1976. Cline and Anthony have measured aluminum-rich liquid wires and dots/droplets migrating through n-type silicon at 1200° C. with an applied thermal gradient of about 500 C/cm at a velocity of about 1 mm/hour. In this experiment, the recrystallized silicon deposited behind the migrating aluminum-rich droplet was doped sufficiently high with a residual solid solution of aluminum (p-dopant) to convert the original n-type silicon matrix/host to p-type silicon inside of the recrystallized columnar/cylindrical droplet trail that was left behind. It is known that aluminum, gold, and gallium can be thermomigrated through silicon, germanium, or gallium arsenide.

[0010] Thermomigration has been used to fabricate p-n junctions in solar cells. See, for example, U.S. Pat. No. 3,936,319 to Anthony, et al.; U.S. Pat. No. 4,190,852 to Warner; and U.S. Pat. No. 4,173,496 to Chaing, et al. However, this technique has not been used to fabricate completely back-contacted solar cells, or to fabricate n-doped conductive vias in back-contacted solar cells.

[0011] In a gradient-driven transport process, such as thermomigration (or electromigration), a gradient in temperature (or electric field) determines the direction for transporting/migrating the solute material. In the fabrication of silicon solar cells, the direction of the thermal gradient is typically oriented across the thickness of the silicon substrate/wafer (i.e., in a direction perpendicular to the plane of the silicon substrate). Such a thermal gradient can be produced by heating one side of the substrate, rather than both sides (which would produce a uniform temperature).

[0012] In typical semiconductor production lines, the temperature of a silicon wafer sometimes needs to uniformly increase rapidly, and then held for a short period of time, e.g., 60 seconds, for annealing or diffusion treatments. This is often accomplished by using Rapid Thermal Processing (RTP) equipment, which typically consists of a double-sided bank of tungsten halogen quartz heating lamps that heat both sides of the wafer uniformly, so that there is essentially no temperature variation across the wafer or through its thickness. Unacceptably large temperature variations would create non-uniform annealing rates, diffusion rates, etc. and may result in poor reliability, reduced yield, etc. Hence, RTP equipment is carefully designed to heat the silicon wafers as

uniformly as possible, and to minimize any temperature gradients across the thickness of a wafer.

[0013] Electromigration is another type of gradient-driven migration process, similar to thermomigration that can be used to move metal droplets through a semiconductor material. For more details, see U.S. Pat. No. 4,377,423 to Anthony, which is incorporated herein by reference. In this process, an electric field gradient (potential) provides the driving force for moving liquid metal droplets through the thickness of a semiconductor material, such as liquid aluminum drops through silicon.

[0014] What is needed, therefore, is an economical and reliable process that uses thermomigration (or some other type of gradient-driven solute transport technique, such as electromigration) to create an array of closely-spaced n<sup>++</sup>conductive vias that electrically connect an n<sup>+</sup>emitter layer on the front surface of a solar cell to ohmic contacts located on the cell's back side, without the need for physical holes through the solar cell substrate. Against this background, the present invention was developed.

#### SUMMARY OF THE INVENTION

[0015] The present invention relates generally to methods of manufacturing photovoltaic solar cells, and more specifically to back-contacted silicon solar cells fabricated using a gradient-driven solute transport process, such as thermomigration or electromigration, to create an array of closely-spaced n<sup>++</sup>conductive vias that electrically connect a n<sup>+</sup>emitter layer on the front surface of a solar cell to ohmic contacts located on the cell's back side. The present invention further relates to photovoltaic silicon solar cells, and more specially to back-contacted silicon solar cells, wherein an array of closely-spaced n<sup>++</sup>conductive vias including a n<sup>++</sup>doped trail formed in the silicon structure electrically connect a n<sup>+</sup>emitter layer on the front surface of a solar cell to ohmic contacts located on the cell's back side.

[0016] Certain embodiments of the present invention use a gradient-driven migration process (e.g., thermomigration or electromigration) to create a conductive channel (i.e., via) in a single step, rather than a two-step process that laser-drills an array of holes followed by phosphorus doping to provide a conductive path. Simultaneous fabrication of an array of closely-spaced conductive vias using a gradient-driven migration process (as in the present invention) reduces the cost and time needed to fabricate a back-contacted solar cell, since multiple vias can be fabricated simultaneously (rather than waiting for each hole to be individually laser-drilled, one-at-a-time). The equipment for performing thermomigration is less expensive than the equipment used for laser drilling. Also, the use of thermomigration produces vias with higher conductivity, as compared to laser drilled-holes.

[0017] Further, a thermomigrated back-contacted cell can have a more optimally-doped front surface for higher conversion efficiency. In standard front-contacted cells, the front emitter must be doped heavily enough to achieve low contact resistance. Some photocurrent is lost in heavily doped emitters due to increased recombination losses in the emitter. The simplest process sequence for a back-contacted cell using an EWT geometry and laser-drilled holes uses a heavy emitter diffusion to minimize series resistance inside the holes and contact resistance to the grid. In a back-contact



cell using thermomigration vias, the front surface  $n^+$  diffusion and the conductive via doping can be performed in separate steps—so each step can be separately optimized. Hence, a more optimally-doped front surface comprising a lower doping concentration can be used for thermomigrated cells, which results in increased photocurrent collection.

[0018] Another advantage of thermomigrated vias is lower series resistance. A thermomigrated conductive via provides lower series resistance compared to diffused holes in the EWT cell because it is a solid cylinder or other solid structure that is doped, while the EWT cell only has a thin surface  $n^+$  diffusion in the walls of the laser-drilled holes. If the thermomigration metal is left in place after thermomigration, it yields a much lower contact resistance, as well. Further, if the thermomigrated via is a pattern of lines rather than holes, losses due to current flow in the emitter is reduced. Also, if the thermomigrated via pattern is a pattern of lines, the thermomigration metal on the rear surface may be left on the surface and used as the n-type grid.

[0019] Yet another advantage of the present invention is that  $n^{++}$  conductive vias including a  $n^{++}$  doped trail are formed in the p-type semiconductor substrate, such as a silicon structure, without the need for any hole or other gross physical alternation to the semiconductor substrate. Thus the  $n^{++}$  doped trail is formed within the structure of the semiconductor substrate.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The accompanying drawings, which are incorporated into and form part of the specification, illustrate various examples of the present invention and, together with the detailed description, serve to explain the principles of the invention.

[0021] FIG. 1A shows a schematic cross-section side view of a first example of a back-contacted silicon solar cell, according to the present invention.

[0022] FIG. 1B shows a schematic isometric view of the first example of a back-contacted silicon solar cell, according to the present invention.

[0023] FIG. 1C shows a schematic cross-section side view of a second example of a back-contacted silicon solar cell, according to the present invention.

[0024] FIG. 1D shows a schematic cross-section side view of a third example of a back-contacted silicon solar cell, according to the present invention.

[0025] FIGS. 2A-2I show a schematic cross-section side view of a first example of a sequence of process steps for fabricating a back-contacted silicon solar cell using a gradient-driven migration process, according to the present invention.

[0026] FIGS. 3A-3E show a schematic cross-section side view of a second example of a sequence of process steps for fabricating a back-contacted silicon solar cell using a gradient-driven migration process, according to the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

[0027] Note that in the drawings, the thicknesses of the various layers of insulating, semiconducting, and metallic

materials, and other dimensions, such as the width of contact pads, are not drawn to scale, but rather are shown schematically for purposes of illustration and easy identification.

[0028] In the specification and claims, processes referred to as “thermomigration” include any gradient-driven migration process, including thermomigration and electromigration.

[0029] FIG. 1A shows a schematic cross-section side view of a first example of a back-contacted silicon solar cell, according to the present invention. Back-contacted solar cell 10 comprises a p-type bulk silicon substrate 12; a front side  $n^+$  diffusion emitter layer 14 located on the front side 11 of substrate 12; a back side  $n^+$  diffusion emitter layer 15 located on the back side 13 of substrate 12; a n-gridline negative ohmic contact 20 located on the back side 13 of substrate 12, contacting back side emitter layer 15; a  $n^{++}$  conductive via 18 disposed through the thickness of substrate 12 that electrically connects front side emitter layer 14 to negative ohmic contact 20 located on back side 13 and a p-gridline positive ohmic contact 22 located on back side 13 that is electrically connected to p-type silicon substrate 12. Conductive via 18 also contacts back side emitter layer 15. Front side  $n^+$  diffusion emitter layer 14 may comprise a phosphorus  $n^+$  diffusion layer. In one embodiment, front side emitter layer 14 may be lightly n-doped, while back side  $n^+$  emitter 15 may be heavily doped. Alternatively, in another embodiment, both emitter layers 14 and 15 are n-doped approximately the same amount. Conductive via 18 may comprise a recrystallized  $n^{++}$  doped trail that has been formed after gradient-driven migration completely through substrate 12 of a solute material that is or contains  $n^{++}$  dopant material. In this context, “recrystallized” means a process of at least partial dissolution of a substrate, such as silicon, and at least partial regrowth of a crystalline structure, such as formed by thermomigration of a molten solute material through a substrate. The gradient-driven migration process may comprise thermomigration (e.g., TGZM), electromigration, or a combination of both. The direction of gradient-driven migration may be from the front side 11 towards back side 13, or, alternatively, may be from back side 13 towards front side 11. Both n-type and p-type ohmic contacts 20 and 22 are located on the back side 13 of substrate 12. Conductive via 18 is a solid member (e.g., cylinder, rod, plane) and is not a hollow, laser-drilled hole. A dielectric layer (not shown) may be added to back side 13 to electrically isolate n-grid 20 from p-type substrate 12 and from p-grid 22.

[0030] FIG. 1B shows a schematic isometric view of the first example of a back-contacted silicon solar cell, according to the present invention. The reference numbers are the same as in FIG. 1A. Back-contacted solar cell 10 comprises a closely spaced array of conductive vias 18, 18', etc. fabricated by a gradient-driven migration process. The spacing between adjacent conductive vias 18, 18', etc. can be from 1-2 mm, and the diameter of conductive vias 18, 18', etc. can be from 25-150 microns. n-gridlines 20, 20', etc. and p-gridlines 22, 22', etc. are interdigitated on back side 13, and optimized to minimize electrical resistance and carrier recombination. P-busbar 24 connects individual p-gridlines 22, 22', etc. An n-type busbar is not shown in this view.

[0031] FIG. 1C shows a schematic cross-section side view of a second example of a back-contacted silicon solar cell, according to the present invention. The reference num-



bers are the same as in **FIGS. 1A and 1B**. However, in this embodiment, there is no back side  $n^+$  diffusion emitter layer. Also, conductive via **18** is much wider than  $n$ -grid contact **20**, to prevent shorting between  $n$ -grid contact **20** and  $p$ -type substrate **12**. In this embodiment, conductive via **18** may comprise a wide line or stripe of metal (e.g., >100 microns), rather than a droplet.

[0032] There are several methods by which these back-contacted cells can be made, and variations of those examples specifically discussed herein are possible.

[0033] **FIGS. 2A-2I** show a schematic cross-section side view of a first example of a sequence of process steps for fabricating a back-contacted silicon solar cell **24** using a gradient-driven migration process, according to the present invention. In **FIG. 2A** a thin,  $p$ -type bulk silicon substrate **26** is provided. Then, the wafer is cleaned and etched. Next, in **FIG. 2B**, a patterned diffusion barrier **32** is created to mask off a portion of the back side **30** of substrate **26**. Diffusion barrier **32** may comprise an oxide layer that is screen-printed (e.g.,  $\text{SiO}_2$ ), or may comprise a deposited layer, such as  $\text{Si}_3\text{N}_4$  or other suitable material deposited by PECVD, APCVD, or other means, and subsequently patterned by screen printing a resist and performing an etch. Next, in **FIG. 2C**, a phosphorous diffusion step is performed (e.g.,  $\text{POCl}_3$ ), which creates a front side  $n^+$  emitter layer **34** and a back side  $n^+$  emitter layer **36**. The presence of diffusion barrier **32** prevents the underlying area of substrate **26** from being doped with phosphorus. Next, in **FIG. 2D**, diffusion barrier **32** is removed, for example, by performing a hydrofluoric acid etch. This exposes an undoped area **38** of  $p$ -type silicon substrate **26** that subsequently will be covered with an ohmic contact gridline.

[0034] Next, in **FIG. 2E**, metal carrier droplet **40**, which contains (or inherently is) an  $n$ -type dopant material, is deposited on top of front side  $n^+$  emitter layer **34**. Carrier droplet **40** may be deposited by a wide variety of deposition methods, including, but not limited to: screen printing, ink jet printing, evaporation, sputtering, CVD, PECVD, cold-spray deposition (kinetic deposition of metal powders), plasma-arc spray deposition, LIGA, electroplating, electroless plating, and combinations thereof. An array of closely-spaced droplets (see, e.g., **FIG. 1B**) may be simultaneously deposited. Optionally, a shallow "pit" or depression (not shown) for holding droplet **40** may be laser-drilled, chemically etched, or created some other way, prior to depositing droplet **40**. Then, the shallow pit may be filled with the solute metal by screen printing without using a screen, i.e., by using a squeegee to push metal-loaded paste across the surface, which fills in the shallow pits. Use of a shallow pit may help to improve the reliability of the subsequent thermomigration process by improving the wetting properties, and by holding and centering the melted metal droplet **40** in a well-defined depression. Otherwise, the molten droplet **40** could move around the surface a little before wetting and penetrating silicon substrate **26**. Optionally, a thin dielectric layer (e.g., PECVD  $\text{Si}_3\text{N}_4$ ) may be deposited on top of the as deposited droplet **40** (i.e., before starting the thermomigration process), in order to help stabilize the molten droplet; prevent evaporation of the droplet; and facilitate entrance of the molten droplet in the silicon substrate **12** (as well as serving later on as an anti-reflection coating). In an alternative embodiment, the thin dielectric layer may be deposited over the surface and in the shallow pits prior to

depositing the droplet **40**. In yet another alternative embodiment, a shallow groove or linear depression for holding a line or strip of carrier may be provided.

[0035] Next, in **FIG. 2F**, substrate **26** is placed in a specially-designed rapid thermal processor (RTP) **41**, where it is heated to a temperature sufficiently high to melt droplet **40**. RTP **41** also creates a temperature gradient through the substrate's thickness. Thermomigration is faster with larger thermal gradients and with higher average temperatures. A typical temperature gradient may be about  $50^\circ \text{C./cm}$ . This may be accomplished, for example, by heating back side **30** with a bank of tungsten halogen or plasma arc lamps **50** and by cooling the front side **28** by using a water or gas-cooled heat sink **52** with a blackened, radiation-absorbing surface. The temperature gradient created through the thickness of substrate **26** drives the movement of molten droplet **40** in a direction towards the hotter side (e.g., towards back side **30**) according to the process of thermomigration (or electromigration using an electric field gradient). The recrystallized, cylindrical zone **42** that forms after the passage of droplet **40** comprises a sufficiently high residual concentration of  $n^{++}$  dopant left behind in droplet's trail to make via **42** electrically conductive with respect to  $n$ -type emitter layers **28** and **30**, while also being electrically insulating with respect to  $p$ -type bulk silicon substrate **26**. Rapid thermal processor **41** may use a high power plasma arc lamp, such as an argon arc lamp manufactured by Vortek, Inc. of Vancouver BC, Canada, which produces an intense beam of light having a spectrum with a large percentage of UV/visible light, as opposed to a tungsten halogen lamp which produces mostly IR light. The large percentage of UV/visible light produced by an argon plasma arc lamp couples more efficiently into the silicon substrate (and, thus, heats it more rapidly and efficiently), because silicon is highly absorbing in the UV, but not in the IR, spectrum.

[0036] The thermomigration metal used for droplet **40** must dope the silicon  $n$ -type (e.g.,  $n^{++}$ ) in order to form a conductive channel between the phosphorus diffusion layers on the front and rear surfaces. Examples of suitable  $n$ -type dopant metals include phosphorus, arsenic, and antimony, and combinations or alloys thereof. These dopant metals can be used either in their elemental form, or can be combined, alloyed, or mixed with a carrier metal that forms an eutectic phase with silicon at relatively low temperatures. Examples of suitable carrier metals include silver, platinum, gallium, magnesium, indium, aluminum, tin, copper, and gold, and combinations or alloys thereof (e.g., silver/aluminum, silver/tin). Alternatively, ternary alloys may be used for carrier droplet **40**. For example, silver-gold-antimony and silver-tin-antimony may be used to dope silicon  $n$ -type. Silver-aluminum-antimony may be used to dope silicon either  $n$ -type or  $p$ -type, depending on the TGZM process temperature and droplet composition. Ag-10at % Sb-0at % Al at  $1200^\circ \text{C}$ . dopes silicon  $n$ -type. In general, however, the TGZM process should be practiced at a temperature greater than the temperature at which intermetallic compounds are formed between the material of the semiconductor body and either the dopant material and/or carrier droplet material.

[0037] For a semiconductor substrate made of germanium, examples of suitable  $n$ -type dopant metals include phosphorus, antimony, and arsenic. Examples of suitable carrier droplet metals include aluminum, gallium, lead, silver, cadmium, thallium, zinc, tin, gold, and indium. Additional



information about suitable dopantcarrier metal combinations can be found in U.S. Pat. No. 4,184,897 to Anthony, which is included herein by reference.

[0038] Next, in **FIG. 2G**, metal droplet **40** has thermomigrated completely through substrate **26** and re-emerged on the back side surface **30**. By penetrating through back side emitter layer **36**,  $n^{++}$ doped conductive via **18** thereby electrically connects front side emitter layer **34** to back side emitter layer **36**.

[0039] Next, in **FIG. 2H**, re-emerged droplet **40** is removed, e.g., by mechanical polishing. Alternatively, re-emerged droplet **40** can be left in place and not removed, where it can form part or all of a back side ohmic contact. Also, in **FIG. 2H**, a protective coating **44** of silicon nitride or other suitable protective material is deposited on the front side **28** of cell **24**, thereby covering emitter layer **34**. Silicon nitride coating **44** may be deposited, for example, by plasma-enhanced chemical vapor deposition (PECVD), or other techniques well-known in the art. Coating **44** may comprise a  $\text{SiN}_x$  antireflection (ARC) coating. Coating **44** can be used as an anti-reflection coating, and can also provide surface passivation and some passivation of bulk defects. Alternatively, layer **40** may comprise a  $\text{TiO}_2$  anti-reflection coating deposited by atmospheric-pressure CVD, spray pyrolysis, screen printing, or other techniques.  $\text{TiO}_2$  ARC films generally produce less efficient solar cells than PECVD  $\text{Si}_3\text{N}_4$ ARC films because the  $\text{TiO}_2$  films do not provide any passivation of surface or bulk defects.

[0040] Next, in **FIG. 2I**, an optional dielectric passivation layer **45** can be applied to the back side of cell **24**, prior to depositing the ohmic contacts, so as to prevent shorting or shunting between the contacts. An ideal surface passivation layer minimizes surface recombination, as well as surface conductance channels. Various dielectric layers with good surface passivation properties (e.g., deposited  $\text{SiN}_x$ , deposited  $\text{SiO}_2$ , or thermally grown  $\text{SiO}_2$ ) can be used for rear-surface passivation layer **45**. Note that passivation layer **45** may be patterned, or not, depending on the method subsequently used to fabricate the ohmic contacts (as described below).

[0041] Finally, in **FIG. 2J**, n-gridline negative ohmic contact **46** and p-gridline positive ohmic contact **48** are fabricated. These contacts are generally arranged in an interdigitated pattern, and may be applied by evaporation; screen-printing of pastes containing silver, aluminum, or silver-aluminum compounds; or other well-known techniques, such as electroless plating, etc. For example, screen-printed aluminum or silver/aluminum paste can be used to form the p-contacts **48** and screen-printed silver can be used to form the n-contacts **46**. After printing, the contacts can be co-fired in a belt furnace at approximately  $730^\circ\text{C}$ . to promote good contact to silicon. If passivation layer **45** has been previously applied prior to contact printing, and if passivation layer **45** has not been patterned, then it will be necessary to break through layer **45** in the areas where ohmic contacts need to be made to the underlying conductive surfaces. This can be accomplished, for example, by using a Ag-paste that includes some aggressive oxide frit particles to help etch through any surface oxides used for layer **45** and attach the Ag-particles to the underlying surface. Ag-paste vendors provide special compositions for firing a Ag-grid through a 70-nm thick SiN<sub>3</sub> layer. Use of such a special paste

composition may eliminate the need to mask or pattern rear-surface passivation layer **45**; however, this approach tends to limit the thickness of layer **45**.

[0042] The fabrication steps illustrated in the first example shown in **FIGS. 2A-2J** can be summarized as follows:

- [0043] 1. Provide thin p-type silicon substrate
- [0044] 2. Clean and etch silicon
- [0045] 3. Screen-print oxide for diffusion barrier
- [0046] 4. Phosphorus diffusion
- [0047] 5. Remove oxide (e.g., hydrofluoric acid etch)
- [0048] 7. Screen-print array of thermomigration metal droplets
- [0049] 8. Perform thermomigration in a special designed rapid thermal processor
- [0050] 9. Deposit silicon nitride by plasma-enhanced CVD on front surface for antireflection coating
- [0051] 10. Screen-print silver paste for negative-polarity n-contact
- [0052] 11. Screen-print silver paste for positive-polarity p-contact
- [0053] 12. Fire contacts for good contact to silicon
- [0054] 13. Test solar cell.

[0055] In the first example of a fabrication process illustrated in **FIGS. 2A-2J**, the direction of thermomigration for droplet **40** is from front surface **28** to rear surface **20** (i.e., from cold to hot). The choice of this direction is useful if the re-emerged droplet **40** is not removed and is used for an ohmic contact. However, if the re-emerged droplet is going to be removed, then it is possible to reverse the direction of thermomigration by creating a thermal gradient in the opposite direction. In this case, the rapid thermal processor is operated to make the front surface **28** hotter than the rear surface **30**. Also, the initial metal droplet **40** is deposited on the rear surface **30**. Therefore, thermomigration of droplet **40** is in the direction towards the hotter front surface **28**, and, eventually, droplet **40** re-emerges on to the front surface **28**, where it may be removed.

[0056] **FIGS. 3A-3E** show a schematic cross-section side view of a second example of a sequence of process steps for fabricating a back-contacted silicon solar cell **124** using a gradient-driven migration process, according to the present invention. In **FIG. 3A** a p-type bulk silicon substrate **126** is provided. Then, the wafer is cleaned and etched. Next, in **FIG. 3B**, a phosphorous diffusion step is performed (e.g.,  $\text{POCl}_3$ ), which creates a front side  $n^+$ emitter layer **134** and a back side  $n^+$ emitter layer **136**. No diffusion barrier is used in this second embodiment, unlike the first example shown previously in **FIGS. 2A-2J**.

[0057] Next, in **FIG. 3C**, a resist layer **131** is deposited (e.g., by screen printing) on a portion of the back side **130** of substrate **126**, and then dried. Resist layer **131** is patterned so that the area where the p-type ohmic contact subsequently will be placed is exposed.

[0058] Next, in **FIG. 3D**, the rear surface of substrate **126** is etched (i.e., chemical etched or plasma etched) to remove



that portion of the back side n<sup>+</sup>emitter layer **136** from the area **138** where the p-type ohmic contact subsequently will be placed.

[0059] Next, in **FIG. 3E**, the resist layer **131** is removed, thereby exposing the back side n<sup>+</sup>emitter layer **136**. Also, metal droplet **140** is deposited on top of front side n<sup>+</sup>emitter layer **134**, which will be thermomigrated later to form a conductive via. At this stage, the intermediate assembly shown in **FIG. 3E** is identical to that shown in **FIG. 2E**. As such, the remaining process steps are the same as shown and described in **FIGS. 2F-2J**.

[0060] The fabrication steps illustrated in the second example shown in **FIGS. 3A-3E** can be summarized as follows:

[0061] 1. Provide thin p-type silicon substrate

[0062] 2. Clean and etch silicon

[0063] 3. Phosphorus diffusion everywhere (no diffusion barrier)

[0064] 4. Screen-print resist on the back surface, except where the area where the p-type ohmic contact will be made

[0065] 5. Dry the resist

[0066] 6. Remove the n<sup>+</sup>diffusion emitter layer from the region of the p-contact area (chemical etch, plasma etch)

[0067] 7. Remove the resist layer

[0068] 8. Screen-print array of thermomigration metal droplets

[0069] 9. Perform thermomigration in a special designed rapid thermal processor

[0070] 10. Deposit silicon nitride by plasma-enhanced CVD on front surface for antireflection coating

[0071] 11. Screen-print silver paste for negative-polarity n-contact

[0072] 12. Screen-print silver paste for positive-polarity p-contact

[0073] 13. Fire contacts for good contact to silicon

[0074] 14. Test solar cell.

[0075] The present invention may be practiced with semiconductor substrates other than silicon or germanium, such as: indium gallium phosphide, gallium arsenide, indium antimonide, copper indium gallium diselenide, cadmium telluride, and zinc sulfide. Thus references herein to a "silicon" semiconductor substrate includes each of the foregoing.

[0076] The present invention may also be practiced with the use of metals that strongly reduce surface oxides added to the thermomigration alloy. Metals that strongly reduce surface oxides inherently serve to enhance surface wetting. Metals that may be so employed include Al and Mg.

[0077] The present invention may also be practiced with the use of a very thin layer of metal electrolessly plated onto the exposed Si surface prior to printing or other deposition of the thermomigration metal. A thin layer of electroless-plated metal serves to enhance wetting. Such metals can include, for example, Ni or Pd. In one embodiment using this method, the exposed Si surface is covered with a

patterned dielectric, wherein the dielectric is present only where the electroless-plated metal for surface wetting and the thermomigration metal is to be deposited. In yet another embodiment using this method, electroless plating, including optionally application of a patterned dielectric, may easily and readily be incorporated into processes wherein laser drilling, chemically etching or other means for putting pits or other depressions into the surface are employed. Thus the shallow pits or other depressions on the surface may be filled, partially or entirely, with a dielectric material, with a thin layer of electroless-plated metal added thereto, with the thermomigration metal droplet or line deposited on the electroless-plated metal.

[0078] The particular examples discussed above are cited to illustrate particular embodiments of the invention. Other applications and embodiments of the apparatus and method of the present invention will become evident to those skilled in the art. For example, thin lines or strips of metal, instead of small droplet, may be used to fabricate doped conductive vias using the process of thermomigration (or electromigration). Alternatively, a combination of lines and droplets (i.e., dots) may be thermomigrated (electromigrated). Alternatively, the thermomigration process can be repeated multiple times, each time adding additional carrier metal (e.g., lines or droplets). Alternatively, several closely-spaced lines (or droplets) may be thermomigrated in a same step, since the maximum practical line width of a single line (or, the maximum diameter of a droplet) that can be thermomigrated is limited by surface tension instability effects.

[0079] Those skilled in the art of silicon solar cell fabrication will appreciate that many variations in process steps can be used that are different from the examples and embodiments disclosed above, while still practicing the fundamental features of the present invention. For example, the thermomigration step may be performed before the phosphorus diffusion step.

[0080] It is to be understood that the invention is not limited in its application to the details of construction, materials used, and the arrangements of components set forth in the following description or illustrated in the drawings.

[0081] The scope of the invention is defined by the claims appended hereto.

What is claimed is:

1. A solar cell, comprising:

a substantially planar p-type bulk semiconductor substrate, having a front side and a back side;

a front side n<sup>+</sup>diffusion emitter layer disposed on at least a portion of the front side of the semiconductor substrate;

at least one negative ohmic contact disposed on the back side of the semiconductor substrate; and

at least one n<sup>++</sup>doped conductive path with a substantially solid cross-section and including the semiconductor substrate material, wherein the conductive path is disposed within and through the semiconductor substrate and electrically connects the front side n<sup>+</sup>emitter layer to the negative ohmic contact located on the back side of the semiconductor substrate.



2. The solar cell of claim 1 further comprising at least one positive ohmic contact located on the back side of the semiconductor substrate.

3. The solar cell of claim 1 wherein the at least one negative ohmic contact comprises a n-gridline negative ohmic contact.

4. The solar cell of claim 2 wherein the at least one positive ohmic contact comprises a p-gridline positive ohmic contact.

5. The solar cell of claim 1 wherein the front side n<sup>+</sup>diffusion emitter layer comprises a phosphorus n<sup>+</sup>diffusion layer.

6. The solar cell of claim 1 further comprising a n<sup>+</sup>diffusion emitter layer disposed over at least a portion of the back side of the semiconductor substrate.

7. The solar cell of claim 6 wherein the front side n<sup>+</sup>diffusion emitter layer is lightly doped, and the back side n<sup>+</sup>diffusion emitter layer is heavily doped.

8. The solar cell of claim 6, further comprising a passivation layer disposed on the back surface of the semiconductor substrate, and disposed in-between the positive and negative ohmic contacts.

9. The solar cell of claim 1 further comprising an anti-reflection coating disposed on the front surface of the semiconductor substrate, covering the front side n<sup>+</sup>diffusion emitter layer and conductive via.

10. The solar cell of claim 1 wherein the n<sup>++</sup>doped conductive path comprises one or more n-type dopant materials selected from the group consisting of phosphorus, arsenic, and antimony.

11. The solar cell of claim 1 further comprising an array of closely-spaced n<sup>++</sup>doped conductive passages.

12. The solar cell of claim 11 wherein the n<sup>++</sup>doped conductive passages are approximately circular in cross section.

13. The solar cell of claim 12 wherein the diameter of the approximately circular cross section of the conductive passages is from about 25 microns to about 150 microns.

14. The solar cell of claim 11 wherein the n<sup>++</sup>doped conductive passages are approximately rectangular in cross section, with a short axis and a long axis.

15. The solar cell of claim 14 wherein the length of the short axis of the approximately rectangular conductive passages is from about 25 microns to about 150 microns.

16. The solar cell of claim 14 wherein the length of the long axis of the approximately rectangular conductive passages is substantially longer than the short axis.

17. The solar cell of claim 14 wherein the long axis of each of the approximately rectangular conductive passages extends across more than one-half of a dimension of the substantially planar p-type bulk semiconductor substrate.

18. The solar cell of claim 11 wherein the spacing between adjacent conductive vias is from about 1 mm to about 2 mm.

19. The solar cell of claim 1 wherein the at least one n<sup>++</sup>doped conductive path is made by a gradient-driven migration process.

20. The solar cell of claim 19, wherein the gradient-driven migration process comprises a thermomigration process, an electromigration process, or a combination of both.

21. The solar cell of claim 1 wherein the substantially planar p-type bulk semiconductor substrate does not have connecting holes between the front side and the back side.

22. A process for fabricating a back-contacted semiconductor solar cell, comprising:

providing a p-type semiconductor substrate with a front surface and a back surface;

forming an n<sup>+</sup>emitter layer over at least a portion of the front surface and back surface of the p-type semiconductor substrate;

depositing n-type dopant solute material on a portion of one surface of the p-type semiconductor substrate;

migrating the n-type dopant solute material through the p-type semiconductor substrate, whereby one or more substantially solid n<sup>++</sup>doped conductive vias are formed that electrically connect the front surface n<sup>+</sup>emitter layer to the back surface n<sup>+</sup>emitter layer; and

providing one or more negative contact back surface ohmic contacts, wherein each negative contact back surface ohmic contact is electrically connected with at least one substantially solid n<sup>++</sup>doped conductive via.

23. The process of claim 22 wherein forming an n<sup>+</sup>emitter layer comprises diffusing phosphorus.

24. The process of claim 23 wherein forming an n<sup>+</sup>emitter layer comprises the steps of:

providing a patterned diffusion barrier covering an area where a p-type ohmic contact will be formed;

diffusing phosphorus into the front and back surfaces of the semiconductor substrate to form front side and back side n<sup>+</sup>emitter layers; and

removing the patterned diffusion barrier.

25. The process of claim 24 wherein providing a patterned diffusion barrier comprises screen-printing a patterned diffusion barrier.

26. The process of claim 24 wherein providing a patterned diffusion barrier comprises a thermally grown, nitride deposited, laser patterned or ink jet printed diffusion barrier.

27. The process of claim 22 wherein the n-type dopant solute material comprises a closely-spaced array of droplets or lines of solute material.

28. The process of claim 22 wherein migrating the n-type dopant solute material comprises thermomigrating or electromigrating the solute material in a thermal processor.

29. The process of claim 28, wherein the thermal processor comprises a bank of plasma arc lamps to heat one side of the semiconductor substrate.

30. The process of claim 22 further comprising, prior to depositing the array, forming one or more shallow indentations on the front surface of the semiconductor substrate in the location where the n-type dopant solute material is to be deposited.

31. The process of claim 30 wherein the one or more shallow indentations comprise pits or grooves and the n-type dopant solute material comprises droplets of solute material.

32. The process of claim 22 wherein providing one or more negative contact back surface ohmic contacts comprises screen-printing silver paste for an array of negative-polarity n-type ohmic contacts.

**33.** The process of claim 22 further comprising providing an array of positive contact back surface ohmic contacts.

**34.** The process of claim 33 wherein providing an array of positive back contact surface ohmic contacts comprises screen-printing silver paste for positive-polarity p-type ohmic contacts.

**35.** The process of claim 33 wherein providing an array of positive back contact surface ohmic contacts comprises forming positive contacts by alloying aluminum through the back surface n<sup>+</sup>emitter layer.

**36.** The process of claim 22 further comprising, after migrating the n-type dopant solute material, depositing an

anti-reflection coating on the front surface-of the semiconductor substrate, covering the front side n<sup>+</sup>emitter layer and the conductive vias.

**37.** The process of claim 22 further comprising, prior to providing one or more negative contact back surface ohmic contacts, depositing a dielectric passivation layer on the back side of the semiconductor substrate.

**38.** The process of claim 37 wherein the passivation layer is patterned to not cover the areas where ohmic contacts are to be applied.

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