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(54) Title: APPLICATION OF ELECTRICAL CONDUCTORS OF A SOLAR CELL

(57) Abstract: A method is disclosed for applying an electrical conductor to a solar cell, which comprises providing a flexible membrane with a pattern of groove formed on a first surface thereof, loading the grooves with a composition comprising conductive particles. The composition is, or may be made, electrically conductive. Once the membrane is loaded, the grooved first surface of the membrane is brought into contact with a front or/and back of solar cell. A pressure is then applied between the solar cell and the membrane so that the composition loaded to the grooves adheres to the solar cell. The membrane and the solar cell are separated and the composition in the groove is left on the solar cell surface. The electrically conductive particles in the composition are then sintered or otherwise fused to form a pattern of electrical conductor on the solar cell, the pattern corresponding to the pattern formed in the membrane.

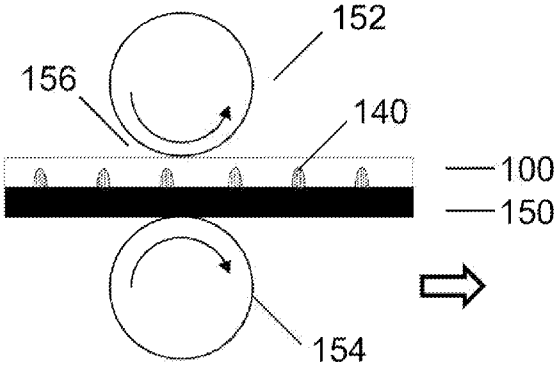


FIG. 1C

APPLICATION OF ELECTRICAL CONDUCTORS OF A SOLAR CELL

FIELD

The present invention relates to applying a pattern of electrical conductors to a solar cell.

BACKGROUND

Known methods of forming conductors on solar cells suffer from several disadvantages, amongst them the limitation that they place on line resolution and exact placement. Often, the techniques are cumbersome, can only be implemented using batch processing and when used to apply conductors to opposite sides of a solar cell, each side has to be processed separately.

SUMMARY

With a view to mitigating at least some of the foregoing disadvantages, there is provided in accordance with a first aspect of the present disclosure a method of applying a pattern of electrical conductors to a substrate formed by a surface of a solar cell, which method comprises:

a) providing a flexible membrane,

b) forming a pattern of grooves in a first surface of the membrane, the pattern corresponding at least partially to a desired pattern of electrical conductors to be applied to the substrate,

c) loading into the grooves a composition that includes, as composition components, electrically conductive particles and an adhesive, said loading being performed in one or more sub-steps such that on completion of the loading step the composition substantially fills the grooves, level with the first surface of the membrane, and parts of the first surface between the grooves are substantially devoid of the composition,

d) contacting the membrane with the substrate with the first surface of the membrane facing the substrate,

e) applying pressure to the membrane to cause the composition loaded into the grooves in the first surface of the membrane to adhere to the substrate,

f) separating the membrane from the substrate to transfer the composition from the grooves in the first surface of the membrane to the substrate, and

g) applying sufficient energy to sinter the electrically conductive particles in order to render electrically conductive the pattern of composition transferred to the substrate from the grooves.

When forming a pattern of conductors, a liquid carrier may be added to the components of the composition to form a wet composition having the consistency of a liquid or a paste. The liquid carrier can consist of an organic solvent or of an aqueous solvent. A wet composition wherein the liquid carrier comprises at least 60wt.% of water can be termed an aqueous or water-based composition, whereas a wet composition wherein the liquid carrier comprises at least 60wt.% of organic solvents can be termed a solvent-based composition.

A doctor blade may be used during the step of loading, to press the composition into the grooves and wipe away the composition from the parts of the substrate between the grooves. The relative flexibility and/or hardness of the tip of the squeegee or blade contacting the first surface of the membrane to load the compositions applied thereon within the grooves may be selected and adapted to the consistency/viscosity of the composition being loaded, the dimensions of the grooves to be filled, the force being applied to "wipe" the composition within the pattern and like considerations readily appreciated by the skilled person. The liquid carrier may then be driven off by application of heat or vacuum to leave the dried composition coating the first surface of the flexible membrane or the selected regions therein.

Driving off of the liquid carrier (*e.g.*, the liquid being removed by evaporation) tends to cause shrinkage of the composition remaining in the grooves. It is noted that while the loading step (described as step c) in the afore-mentioned method) may include only a single filling of the grooves, it may optionally comprise a plurality of sub-steps, such as repeated filling sub-steps, with optional sub-steps of liquid removal (*e.g.*, by drying) and cleaning there-between (*e.g.*, by wiping). Such sub-steps may need to be repeated until the dry composition substantially fills the grooves, level with the first surface of the membrane. If the loading step is carried out by repeated cycles of filling, and/or drying, and/or cleaning, the last step would leave the spaces between the grooves on the first surface of the membrane substantially devoid of the composition.

By substantially devoid, it is meant that residual composition in the space in between the grooves, if any, is in an amount/distribution insufficient or too scarce to significantly mask the surface of the solar cell following transfer. The spaces between the grooves are substantially devoid of composition if 2% of less of their area comprises trace amounts of

electrically conductive particles, or less than 1%, or less than 0.5% or less than 0.1%. Such trace amounts of compositions can be detected and estimated by routine image analysis.

When the loading of the grooves is carried out in several steps, the relative proportions of the components of the composition may be varied between filling steps. In the first step or steps, the adhesive may only serve to bond the electrically conductive particles to one another but in the last step the adhesive can be relied upon additionally to cause adhesion of the composition to the substrate. For this reason, the proportion of adhesive in the composition may optionally be increased at least in the last filling step.

Additionally and alternatively, the type of adhesive agent may be modified in between filling steps, the adhesive agent of the last filling step being more potent and/or in higher amount than the adhesive or earlier steps, "potency" relating to the ability to adhere to the substrate. In some embodiments, an adhesive coating may be further applied over the filled grooves of the flexible membrane.

The composition with a lower amount of adhesive (and/or a less potent one, which can then be considered as a binder) and a higher amount of electrically conductive particles may be called the metal paste, whereas the composition with a higher amount of adhesive (and/or a more potent one), appropriate for the adhesion of the dried composition to the substrate, may be called the adhesive paste. The term "paste" is not meant to indicate any particular viscosity, or solid content, however less viscous compositions may understandingly require more evaporation of the carrier. The composition which may be optionally added to cover the filled grooves of the membrane to further facilitate subsequent adhesion to a substrate may be called an adhesive coating.

Alternatively, and additionally, each filling step can be performed with a different type of wiper (*e.g.*, squeegee or doctor blade) each adapted to the composition being loaded within the grooves and/or to the loading conditions.

While a properly applied doctor blade or squeegee may provide the desired result of leaving the non-grooved portions of the membrane's first surface sufficiently clean of the composition, different steps may optionally and/or additionally be taken to achieve such goal, including, by way of example, rubbing, wiping, brushing and the like, in order to remove the composition left on the surface between the grooves, so as to complete the step of loading. Such cleaning may take place between filling sub-stages, or only prior to the completion of the loading step, after the last filling sub-step took place and optionally before the application

of an adhesive coating, if applied to the membrane following loading. The optional cleaning is preferably carried out with a cleaning device adapted to the composition to be cleaned and to the membrane.

Any cleaning step, if performed, should not affect the surface of the membrane in a manner that would significantly reduce or prevent subsequent contact with the substrate. It is to be noted that the cleaning sub-step can be performed either before or after the drying of the compositions. If a cleaning sub-step is performed after a drying sub-step, then a cleaning liquid may, if desired, be further applied to the cleaning device and/or to the surface to be cleaned.

For instance, cleaning can be performed by a blade wiper positioned downstream of the filling device (*e.g.*, upstream of a squeegee or doctor blade loading the composition within the grooves). The cleaning blade can have the same orientation as the loading blade with respect to the membrane, or can form an opposite angle. The cleaning can alternatively be performed using a cleaning roller having a soft wiping surface. If the cleaning is performed following a drying step, a cleaning liquid can be used to facilitate the displacement of the cleaning device over the surface of the membrane. Such a cleaning liquid, if used, can also facilitate the dislodgment of dry composition residues, if any in the spaces between the grooves. In the afore-provided illustrative examples, the cleaning liquid could be applied downstream of a cleaning blade or serve to impregnate the wiping surface of a cleaning roller. The cleaning liquid is selected so as not to affect the compositions already loaded and/or dried within the pattern of grooves. For instance, the cleaning liquid can be a solvent compatible with the flexible membrane and incompatible with the composition liquid carrier.

The grooves of any desired pattern can be characterized, for instance, by their cross-section profile, by their top view shape, by their dimensions, by their distance from one another and such factors described in more detail below. The grooves of a pattern need not be identical and any first groove may differ from any second groove. Moreover, in some embodiments, an individual groove may also vary along its own length. For instance, from a top view perspective, a segment of a contiguous groove may form a straight delineation and another segment a curved one, or a first segment may have a first width and a second segment a second width and the like variations. From a cross section view, an individual groove may have a first profile in a first segment and a second profile in a second segment and/or a first set of dimensions in a first segment and a second set of dimensions in a second segment of the groove. By way of non-limiting example, an individual groove may comprise a first segment

having a triangular or trapezoidal profile of a first height / depth and a second segment having a semi-elliptic or semi-circular profile of a different second height / depth. A flexible membrane harboring such non-identical grooves, where an individual groove may consist of relatively shallow trench segments and relatively deeper indentations which may alternate along the length of the groove the deeper indentations forming, following transfer, higher spots of conductive material, or contact pads, which may serve to interconnect adjacent patterns that may be formed in the direction perpendicular to the plane of the substrate or to connect a pattern of electrically conductive lines to an external circuitry (*e.g.*, to a battery able to store the electrical energy harvested by the solar cell).

The membrane in some embodiments is sufficiently flexible at operating temperature (*e.g.*, at ambient room temperature *circa* 23°C) to facilitate patterning of the flexible membrane, filling of the grooves with any of the compositions as herein taught, drying of the compositions, or any other required processing, release of the dried compositions from the membrane upon contacting with the substrate, and/or separation of the membrane from the substrate. While in some embodiments, the flexible membrane may be preformed and provided as such (*e.g.*, in rolls or sheets), the flexible membrane may alternatively be cast from suitable materials (*e.g.* thermoplastic polymers that solidify upon cooling or photopolymers that cure upon exposure to radiation which can be referred herein as plastics polymers) to form a membrane as part of the process. Formable plastics polymers that can be embossed or cast are known to the skilled persons.

Flexible membranes made from such polymers are preferably sufficiently non-elastic to maintain the contour of the grooves (and patterns) to be formed thereupon and the shape of the compositions being filled therein. On the other hand, the membranes are preferably flexible enough to conform to the surface of the substrate, so as to permit a sufficiently intimate contact for transfer of the composition lines. A membrane having a relatively smooth surface can be desired for similar reasons of improving interfacing during the process (*e.g.*, with a squeegee filling the grooves, with the substrate, *etc.*). Advantageously the mean roughness *Rz* of the first surface of the flexible membrane is of 1 μm or less, 500 nm or less, 250 nm or less, or 100 nm or less. Other desirable mechanical properties can be readily understood, so as to render the membranes compatible with the method (*e.g.*, stretch resistant, stress resistant, heat resistant, radiation resistant, and the like) and with the compositions used therein (*e.g.*, chemically resistant, chemically inert, *etc.*)

Flexible membranes with low surface energy can be used in the method disclosed herein, membranes including thermoplastic polymers selected from cyclic olefin copolymer (COC), polypropylene (PP), polyethylene (PE), and thermoplastic polyurethane (TPU) being particularly suitable.

Flexible membranes may be formed of a single layer comprising one or more of suitable plastics polymers, in particular one or more of the afore-mentioned thermoplastic polymers. Alternatively, the flexible membrane can be formed of two or more distinct layers. For instance, by way of non-limiting example, the membrane can comprise a first support layer predominantly providing mechanical integrity and/or strength (*e.g.*, ability to substantially retain its dimensions during the process) of the membrane, a second layer sufficiently deformable so as to permit formation of grooves and a third layer "sealing" the intermediate patternable core of the membrane, improving for instance the adhesion of the membrane to the substrate ahead of transfer of the pattern and subsequent separation of the membrane or any other desirable property which may be preferred for the method according to the present teachings (*e.g.*, providing sufficient toughness to maintain the pattern as desired). All such layers are preferably flexible so as to provide the desired flexibility of the overall membrane formed thereby. In such embodiments, where the membrane is formed from two or more layers, the layer opposite the support layer constitutes the first surface of the membrane due to contact the surface of the substrate during the transfer step.

The transfer of the dried compositions from the flexible membrane to the substrate upon application of pressure (*e.g.*, in the range of from about 0.1 kgF/cm^2 to about 50 kgF/cm^2) can optionally be conducted at elevated temperatures. Such transfer temperature may depend on the flexible membrane and on the substrate to be so contacted. It may also depend on the compositions loaded within the grooves and how temperature may promote their release from the flexible membrane and/or their adhesion to the substrate. The transfer temperature can be, for instance, of at least 60°C, at least 80°C, at least 100°C or at least 120°C; and optionally of at most 200°C, at most 180°C, at most 160°C or at most 140°C. In some embodiments, the pressure is applied at a transfer temperature in the range of 130-140°C.

In some embodiments, the transfer temperatures are achieved by jointly heating the substrate and the membrane, for instance by contacting them between two rollers, at least one of the cylinders being heated to a temperature allowing their rapid attaining of the desired transfer temperature. In other embodiments, the transfer temperatures are achieved by heating solely the substrate, while the membrane remains or is maintained at ambient temperature.

The substrate can be heated by any suitable method, such as by conduction (*e.g.*, passing over a hot plate), by convection (*e.g.*, using a hot air flow), by radiation (*e.g.*, using an IR lamp) or by combination of such heating means.

In some embodiments, the temperature is decreased after pressure is applied to effect proper contact and before the membrane is peeled away to effect transfer of the content of the grooves to the substrate. At this intermediate stage, the membrane is said to be "substrate attached" or the substrate "membrane attached", even though this attachment is temporary until separation takes place. The cooling can be effected by conduction (*e.g.*, passing the substrate attached membrane over a cold surface), by convection (*e.g.*, blowing air optionally cooled towards the substrate attached membrane) or by combination of such cooling means.

The substrate is selected and adapted to the intended use of the pattern transferred thereto, such selection being known to the skilled person. The substrate can be rigid or flexible, made-up of one or more layers of materials, serve for transfer on one or more of its sides, can be doped or undoped, and the like. By way of non-limiting example, a substrate suitable for the preparation of a solar cell can be a rigid wafer or a flexible film. The substrate may be a face of a solar cell made of inorganic materials, such as mono or multi-crystalline silicon (mono c-Si or multi c-Si), amorphous silicon (a-Si), gallium arsenide (GaAs), poly-silicon (p-Si), and any other like substrate used in solar cells, or of organic materials, such as flexible polymers.

It will be appreciated that the present method, relying on a flexible membrane for the formation of a desired pattern, can be particularly advantageous when the solar cell substrate is not planar. Substrates that can be bent, folded and even wrapped around objects, as may be desired to achieve certain applications, can be contacted in one step by a membrane comprising the desired pattern. For example, assuming an object requiring a board to fold at an angle between a left panel and a right panel of the same board, current being able to flow from one end to the other, present technologies may require the separate preparation of each panel, their assembly and possibly even the need for an intermediate connecting panel or circuitry. In contrast, the present method may permit the continuous contacting of the left panel with the corresponding part of the pattern on the flexible membrane and of the right panel with its respective pattern, the intermediate "angle" area between the left and right panels (and corresponding left and right parts of the pattern) providing for an uninterrupted circuitry bridging the two.

Further steps may depend on the intended use of the metal pattern.

When used in the production of solar cells, the substrate may be a semiconductor wafer. In such embodiments, the composition advantageously may include a glass frit and subsequent to the composition being sintered by heating to render it electrically conductive, the substrate and the composition may be fired to cause the conductors to fuse with the substrate.

In other aspects, set forth in Claims 27 to 29 of the appended claims, the invention provides a membrane for the manufacture of a solar cell and solar cells produced by methods of the invention. Such membranes and solar cells can be characterized by various features, illustrated herein in more details in connection with the diverse embodiments of the method, as herein taught.

BRIEF DESCRIPTION OF THE DRAWINGS

Implementation of the present disclosure will now be described further, by way of example, with reference to the accompanying drawings, in which:

Figures 1A to 1D are sections showing simplified process steps in forming a pattern of lines of a composition containing electrically conductive particles on a membrane and then transferring the pattern to a substrate;

Figure 1E depicts a simplified diagram of a process to implement the process of Figures 1A to 1D;

Figure 2A is a perspective view of the process step shown in Figure 1A providing an example of how the line pattern may be designed to form a continuous membrane having discrete spaced patterns, each intended for application to a separate respective substrate, and each pattern defining a set of parallel conductors connected to one another by transverse bus bars;

Figure 2B and 2C are respectively enlarged views of the circles designated B and C in Figure 2A showing the grooves in cross section;

Figure 3A is a section through a membrane showing how a single composition may be applied for forming the lines of composition within grooves in the membrane;

Figure 3B is a section through a membrane showing how two distinct compositions may be consecutively applied in the groove for forming the lines of composition in the membrane;

Figure 3C is a section through a membrane showing how a release layer may first be applied to assist in separation of the composition lines from the membrane;

Figure 3D is a section through a membrane showing how an adhesive coating may be applied to cover the entire surface of the membrane to assist in the transfer of the lines of composition from the membrane to the substrate;

Figures 4A to 4C show how an electrode, such as the back electrode of a solar cell by way of example, may be formed and applied to a large surface;

Figure 5A schematically illustrates an exemplary metallic pattern as generated by the present method;

Figure 5B schematically illustrates an exemplary cross section through a protruding die rule, which is similar in shape to a cross section through a transferred contact line before and after sintering and comparable to a negative image of a cross section through a groove;

Figure 5C is a perspective micrograph taken by confocal laser scanning microscopy of a groove of a flexible membrane, the groove being filled with a composition including electrically conductive particles;

Figure 5D is a perspective micrograph taken by confocal laser scanning microscopy of a contact line transferred from a groove of a flexible membrane to a substrate; and

Figure 6 schematically illustrates an exemplary cross-section of an apparatus for filling a plurality of groove sets with respective compositions.

DETAILED DESCRIPTION

The ensuing description, together with the figures, makes apparent to a person having ordinary skill in the pertinent art how the teachings of the disclosure may be practiced, by way of non-limiting examples. The figures are for the purpose of illustrative discussion and no attempt is made to show structural details of an embodiment in more detail than is necessary for a fundamental understanding of the disclosure. For the sake of clarity and simplicity, some objects depicted in the figures may not be drawn to scale.

For brevity and clarity, the description is generally directed to forming a pattern as shown in Figure 2A (enlarged views of which are shown in Figures 2B and 2C), by way of illustrative example only. The skilled in the art would readily understand that the pattern

formed by grooves, and ensuing corresponding conductors pattern may take any form, and is a matter of technical choice dictated by the matter at hand.

Flexible Membrane Patterning

In **Figure 1A**, there is shown a membrane **100**, made of a plastics material, that is passed through a nip between a cylindrical pressure roller **104** and a die roller **102**. The die roller **102** can be formed of a cylinder from the smooth surface of which there project rules **106** and **108**. The manner in which the die roller **102** is formed is not of fundamental importance. One method of its manufacture may be by etching a smooth cylinder and an alternative would be to mount an embossing shim (typically made of nickel or chrome) with protruding rules **106** and **108** around a cylinder. While not shown in the figure, the flexible membrane **100** can be formed of one or more layers of distinct flexible materials.

Rules **106** are parallel to the circumference of die roller **102** and are aligned with each other along the axis of the die roller so as to form upon contacting the facing surface of the membrane, grooves parallel to the direction of movement of the membrane. Only one such rule can be seen in the schematic cross-section of Figure 1A. Rules **106** need not follow the entire circumference of the die roller, their length being adjusted to the desired length of the longitudinal lines in the grooves pattern. Rules **108** are parallel to the axis of die roller **102** and can form upon contacting the facing surface of the membrane **100**, grooves transverse to the direction of movement of the membrane, and optionally orthogonal to the longitudinal grooves formed by rules **106**. Rules **108** need not extend along the entire length of the die roller, or width of the membrane, their length being adjusted to any desired number of longitudinal lines to be traversed in the grooves pattern. The lengths of rules **106** and **108** may also take into account the dimension of the intended substrate and margins that may be required to surround any particular pattern. Though rules **106** and **108** are illustrated as straight lines, it is readily understood that a die roller **102** may carry rules forming any other desired shape.

The edges or profile of the rules can have any desired shape, typically regular, allowing for the transfer of the composition lines from the membrane to a substrate, and therefore have desirably a tapering form. Such a profile is schematically illustrated by a semi-ellipse in Figures 1A-1D. The edges of rules **106** can be, by way of example, trapezoidal, that is to say that the rules may have upwardly tapering sides and a flat top. The width of the base of the trapeze is herein denoted W_B, the width of the flat top w_T, and the height between the two, h, as will be discussed in more details with reference to Figure 5A. Rules **108** may have edges

similarly shaped to those of rules **106**, but this need not necessarily be the case. For example, rules **108** may be formed from an assembly of protrusions rather than from a single shape, as previously exemplified by a trapeze for rules **106**. Rules **108** can for instance be formed by a strip of mesh material. For the manufacturing of solar cells, wherein rules **108** may serve for the later formation of bus bars, the width of the mesh stripe can be larger than the width of the base of rules **106**. Generally the number of rules **108** is smaller than the number of rules **106** for the metal patterns applied in the depicted example of electrodes for a solar cell.

Though in the following, the terminology assigned to trapezoidal cross sections shall be used, rules may have any different tapering shape satisfying similar ranges. The top edge of a rule may come to a point if the rule cross section is a triangle, a semi-circle or a semi-ellipse, and the like. The width of the base of the rules may depend on its function. Widths of up to a few millimetres can be suitable for bus bars, and even wider rules may be suitable for solar cell back side electrodes, if such are prepared using a grooved membrane. For longitudinal lines, base widths of 50 micrometers (μm) or less are preferred, a W_B in the range of 10-40 μm, or 10-30 μm, or 10-20 μm, or even 5-20 μm, being particularly desired. The width of the top of the rule can also depend on function, and be approximately commensurate with the base width, though typically smaller. For longitudinal lines, top width of 40 μm or less are preferred, a w_T in the range of 5-25 μm, or 5-15 μm, or 10-20 μm, being particularly desired. The height of the rules h generally does not exceed 50 μm, a h in the range of 25-40 μm, or 25-30 μm, or 15-25 μm, being particularly desired. It can be appreciated that the aspect ratio (ASP) between the height h of a rule **106** and its base width W_B can be in the range of about 5:1 to about 1:5, an ASP between 3:1 and 1:1, between 2:1 and 1:2, or between 1.75:1 and 1:1.75, or between 1.5:1 and 1:1.5, optionally of about 2:1, 1.5:1 or at least 1:1, being preferred.

Additionally, the pattern can be characterized by the distance d between the facing edges of adjacent grooves. Typically, such distance is no less than 100 μm. In some embodiments the distance between parallel segments of adjacent grooves d is at least 150 μm, at least 200 μm or at least 300 μm. For longitudinal lines, the maximal distance between two grooves may depend on the intended use and/or the desired efficiency. For instance, for the preparation of solar cells d is at most 2,000 μm, at most 1,500 μm, at most 1,000 μm, or at most 500 μm. It is to be noted that the dimension of the grooves and of the lines resulting from any particular rules, are not necessarily identical to the dimension of the original rule.

Such variations may depend on the membrane being used and on other variables of the process. Advantageously, such variations do not exceed 25% of the original dimensions.

Yet, the present method allows transferring to the substrate metal lines having a relatively high aspect ratio, generally supporting lower resistance. Taking for illustration, a metal trace having a width of 25 μm, clearly a line having a height of 50 μm, namely an *ASP* of 2:1, would have lower resistance than a line having an height of only 5 μm, namely an *ASP* of 1:5, all other parameters (*e.g.*, metal line composition) being similar.

The die roller **102**, though typically significantly more intricate and/or with rules having smaller dimensions, may be formed in the same way as used in producing dies for creasing or cutting cardboard. As the membrane **100**, passes through the nip between the pressure roller **104** and the die roller **102**, grooves or indentations **110** are formed in the upper surface of the membrane. The rules **106** and **108** are designed to form a groove pattern in the membrane that corresponds to the pattern of the electrical conductors to be applied to a substrate, which may be an insulator or a semiconductor. Though in the present figure, and as shown more clearly in Figure 2A, two sets of rules are illustrated for the formation of a depicted groove pattern in the membrane, this is not limiting, as different applications may require only one set or more than two sets of rules, as relevant to the desired patterns.

Moreover, though the patterning element is illustrated as a rotating die roller **102**, alternatively shaped assemblies of rules may be suitable to form grooves as above described. The formation of grooves in the membrane can be, for instance, achieved by plates. If the process is carried by passing the membrane through fixed stations, such a groove forming station and a groove filling station to load the compositions, lengths of slack membrane between the stations can permit the process to be performed continuously. As sub-steps of the loading step may be repeated, there might be more than one filling station wherein the compositions may be applied and dried, each station can be operated under different conditions, in particular when the compositions being loaded within the grooves differ from one repeat to another.

In addition to embossing the pattern of grooves within a preformed flexible membrane of one or more layers, the membrane can be cast from a relatively viscous yet fluid state material, the grooves being formed prior to the hardening of the film. The pre-hardened material can be referred to as “pre-membrane” material. For instance, the membrane can be formed by extrusion of pre-membrane material through a nozzle having on at least part of its

contour protrusions able to yield the corresponding grooves in the film as it hardens. Similarly to the process described in Figure 1, a fluid of pre-membrane material can be cast through a smooth slot and the grooves formed by a rotating die roller or by plates carrying the desired pattern of rules. Depending on the materials being used, the hardening of the relatively fluid pre-membrane material into a flexible membrane with a pattern of grooves according to the present teachings can be achieved by cooling the film and/or by curing it. Such processes of cold / hot embossing and UV-embossing are known.

The pre-membrane material can for instance be a UV-curable material, which can be cast, by way of example between a rotating die roller and a transparent counter surface (*e.g.*, pressure roller) allowing to UV-cure the film as it passes at the nip where the grooves or indentations are being formed. The pre-membrane polymer or blend thereof can be cast as a single self-supporting layer or can be cast to form a patternable layer (*e.g.*, made of CPP) upon a relatively less deformable support layer (*e.g.*, a PET film).

Optionally, the grooves may be formed by a directed laser beam. In such embodiments a laser beam is directed at desired locations of the membrane, to ablate portions of the membrane, or to heat it causing shrinkage. Furthermore, the grooves may be formed by one or more punches applying pressure to the membrane.

Figure 1E is a simplified flow diagram depicting process steps in applying a pattern of electrical conductors to a substrate which may in turn form a solar cell. The process begins by providing a suitable flexible membrane **305** and forming a pattern of grooves **310** in a first surface of the membrane, the pattern corresponding at least partially to the desired pattern of electrical conductors to be applied to the substrate. The grooves are then loaded **315** with a composition that includes electrically conductive particles and an adhesive. The loading step, which includes filling the grooves with the desired composition then optionally drying it and/or cleaning the space in-between the grooves, can be repeated until the dried composition essentially levels with the surface of the membrane. The membrane is then contacted **320** with the substrate and pressure is applied **325** between the membrane and the substrate, to cause the composition loaded into the grooves in the first surface of the membrane to adhere to the substrate. The membrane is then separated **330** from the substrate to transfer at least some, and preferably substantially all, of the composition from the grooves in the first surface of the membrane to the substrate, and sufficient heat or other form of energy is applied to sinter or otherwise fuse **335** the electrically conductive particles in order to render electrically conductive the pattern of composition transferred to the substrate from the grooves.

The loading step, which includes filling the grooves with the desired composition(s), may also include substantially drying or otherwise stabilizing the composition(s). Such steps can be repeated until the sufficiently dried composition is essentially level with the surface of the membrane. The loading step may also include one or more cleaning steps, which may be performed simultaneously with, or separately from, the one or more filling steps by the likes of a doctor blade, a squeegee, a wiper, and the like. Alternatively or additionally, the first surface of the membrane may be wiped brushed, or otherwise cleaned.

From the perspective view of **Figure 2A**, it may be seen that the membrane may be a continuous membrane on which the same groove pattern is applied repeatedly. The pattern may comprise parallel lines extending parallel to the length of the membrane, these longitudinal lines being formed by circumferential rules **106** on the die roller **102**, as well as transverse bus bars, which are formed by rules **108** extending axially on the surface of the roller **102**. An enlarged cross-section view of a few exemplary rules **106** is shown in Figure 2B. Helical rules (not shown) on the die roller **102** may be used to form diagonally extending grooves, likewise relatively curved connecting rules may serve to join the linear ones so far described, thereby enabling any desired pattern of conductors to be formed. Though for simplicity of illustration, the rules **106** or **108** are shown has having same length among their group, this need not be the case (see **520** and **530** in Figure 5A by way of example).

The Flexible Membrane

As explained, it is required of the membrane that it should not have the resilience to return to its original shape after passing through the nip, beneath plates, or after the grooves are being formed in any desired manner. The membrane may suitably be formed of one or more plastics polymers, in particular thermoplastic polymer(s) selected from the group comprising cyclic olefin copolymer (COC), ethylene-vinyl acetate (EVA), polyamide (PA), polycarbonate (PC), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polyurethane (TPU), polyvinyl chloride (PVC), and substituted versions thereof. But it may alternatively be formed of different polymers, or of non-plastics materials, such as photopolymers, that can be hardened after grooves have been pressed into any of them. It is desirable for the membrane to be sufficiently flexible to permit it to be coiled. It is also important that the membrane would be sufficiently flexible to be peeled away from a contacting surface (*e.g.*, of a substrate).

It should be stressed that the above described method of forming a membrane having a groove pattern is not fundamental to the invention. Any membrane formed by extrusion,

stamping or machining may be used, so long as it is pliable, and preferably flexible, and is capable of maintaining accurate grooves of the desired depth, width and cross section (*e.g.*, a trapezoidal or triangular cross section), the grooves being shaped and spaced as desired within the pattern.

The membrane can be supplied in sheets or as a continuous web. The dimensions of the membrane are not limiting, but need preferably be commensurate with the patterning element and the intended substrate. For instance, the width of a membrane may approximately correspond to the length of die roller **102** in its axial direction, while the length of the membrane, if provided as individual sheets, the length being parallel to the direction of movement, is typically a low multiple of the roller circumference. The thickness of the membrane exceeds the height of the rules (*i.e.*, the depth of the grooves) and is generally in the range of 20-100 μm. If the membrane if formed by more than one layer of polymers, its thickness can be in the range of 20-150 μm, each layer being individually in the range of 0.5-100 μm. For instance, a support layer (*e.g.*, made of PET) can have a thickness of 8-75 μm, a patternable / deformable layer (*e.g.*, made of CPP) can have a thickness of 10-75 μm, and a protective sealing layer optionally furthering future proper contact with the substrate (*e.g.*, made of ethylene vinyl acetate copolymer resins, such as commercialized as Elvax®) can have a thickness of 0.5-5 μm.

It is noted that patterns generated by one cycle of the die roller may suffice to the preparation of a plurality of end products, even if the lamination contact of the membrane to the desired substrate is performed in parallel and/or in series on an area corresponding to a number of such end-products.

If desired, the surface properties of the flexible membrane may be modified (*e.g.*, by physical or chemical treatment) to improve the suitability of the membrane for application of any following material. For instance, if the flexible membrane is made of an hydrophobic polymer and the compositions to be subsequently applied may not sufficiently wet it or otherwise interact therewith, then a modification of the polymer surface, or part of it such as a selective modification of the grooves wall surface, may be performed. The surface can be treated (*e.g.*, corona treatment or chemical treatment with wetting improving agents) in order to improve the wettability of the flexible membrane or of its grooves, so that it becomes relatively more hydrophilic. The compositions may also include agents improving their wetting of the membrane. The membrane, or part thereof, and the interfacing compositions

are sufficiently wettable or wetting, accordingly, if their contact is intimate enough to prevent undesired entrapment of air bubbles of a size and/or in an amount and/or at a density which may weaken the resulting pattern. Preferably, optimal wetting of the flexible membrane by any composition interfacing therewith result in a subsequently dried layer of the composition being substantially continuous and/or devoid of air bubbles.

Compositions for the Patterns of Conductive Lines

After the groove pattern has been formed in the membrane **100**, the next step in the process is to fill the grooves with a composition that contains electrically conductive particles, for instance silver, and an adhesive, such as a hot melt polyamide (if transfer is performed at elevated temperature). This loading step is shown in **Figure 1B** where the membrane **100** passes between a pressure roller **132** and a blade or scraper **130** that squeezes the composition **120** into the grooves **110** to fill grooves in the manner shown to the right of the blade **130** in **Figure 1B**, a filled groove being shown as **140**. An enlarged cross-section view of exemplary grooves **110** before their loading is shown in Figure 2C.

In the following, the proportion between various compounds or agents forming a composition can be provided in weight per weight (w/w) or volume per volume (v/v) ratio, or percentage of the composition, part thereof, or even with respect to a single other constituent, which percentage can be denoted wt.% and vol.%, respectively.

The particles (whether of metal or of adhesive, such as glass frits) may have any shape, for instance form regular or irregular spherical beads / flakes / rods and the like, preferably the individual particles of metals are devoid of cavities that may prevent proper sintering or firing at a later stage. The maximum dimension of the particles should be smaller than the groove minimal size in any of its axis / dimension. (*e.g.*, the particles are in the order of a few microns, commonly not exceeding 10-20 μm, and often significantly smaller). Too large particles may not pack satisfactorily within the groove, depending on their shape, such deficient packing reducing or preventing the formation of adequately conductive lines. Though smaller particles are easier to pack in the groove, excessively small particles may not be beneficial. First, they may undergo uncontrolled sintering at temperatures relatively lower than the sintering temperature of larger particles (*e.g.*, at transfer temperature of about 135°C). Such premature sintering of particles that are too small may subsequently affect transfer of the paste (hampering flow) and its interfacing with the substrate. Second, the increased surface area of numerous small particles may require the presence of additional

adhesive, which may in turn affect the rheology of the composition and the workability of the paste. Furthermore the increased presence of adhesive may interfere with sintering (affecting prospective conductivity). Hence particles having a maximum dimension of at least 200 nm; and optionally at most 10 μm, are preferred. In some embodiments, the electrically conductive particles have a maximum dimension in the range of 0.5-5 μm or 1-3 μm. Populations of particles heterogeneous in size, though not essential for certain shapes, may improve the packing within the grooves, resulting in packing having less inter-particular voids. Such packing facilitates sintering and if needed firing, and can improve the conductivity of the finished sintered / fired line.

Information about particle size is generally provided by the suppliers, and may be determined by routine experimentation using, Dynamic Light Scattering (DLS) techniques by way of example, where the particles are approximated to spheres of equivalent scattering response and the size expressed as hydrodynamic diameter. Dimensions of particles may also be estimated by microscopic methods and analysis of images captured by scanning electron microscope (SEM), transmission electron microscope (TEM), focused ion beam (FIB), and/or by confocal laser scanning microscopy techniques. Such methods are known to the skilled persons and need not be further detailed. As particles typically have different sizes in different directions, unless perfect spheres, the longest dimension in the largest plane projecting from the particle is considered for simplicity. When the particles are globular or near spherical, the "longest dimension" is approximately their diameter which can be estimated by DLS methodology. In such a case, the hydrodynamic diameter of 90% of the population of the particles, but more typically of 50% of the population, can serve to assess the size of the particles. In other words, and depending on shape, the particles can be characterized by their longest length $\boldsymbol{L}$, by their thickness, by their hydrodynamic diameters at D_V90, D_V50, D_N90 or D_N50.

As used herein, the term "electrically conductive particles" encompasses particles made of any conductive material, including metals, metal oxides, metal salts, organo metals, alloys and conductive polymers, as well as any electrochemically compatible combinations of the foregoing (*e.g.*, a mixture of two metals, aluminum and silver). By electrochemically compatible, it is meant that any conductive material of any layer is chemically inert with respect to any other conductive material of the same layer, or of other layers when the loading of the grooves is done by repeated filling sub-steps. In particular none of the materials are deleterious to the intended effect, more specifically not affecting the electrical conductance

and/or conductivity of the ultimate conductive lines that can be obtained by the present method, nor their ability to properly attach to the substrate in due time.

Metals can be selected from the group comprising aluminum, copper, gold, silver, tin, nickel, platinum, zinc; and alloys can be selected from the group comprising bronze, brass and palladium/silver. Organo-metals can be selected from the group comprising copper(II) formate ($C_2H_2CuO_4$), copper(II) hexanoate ($C_{12}H_{22}CuO_4$), copper(I) mesitylene ($C_9H_{11}Cu$), vinyltrimethylsilane Cu(I) hexafluoro-acetylacetonate, silver neodecanoate ($C_{10}H_{19}AgO_2$), precursors, hydrates and/or salts thereof.

In addition to electrically conductive particles, the composition **120** includes an adhesive. Different types or amounts of adhesives may be used depending on the elected method step and the ultimate substrate. Broadly, the adhesive may be one or more of a) an organic binder sufficient to maintain the cohesivity of the electrically conductive particles but insufficient to provide enough adhesion to the substrate (a "poor adhesive"), b) an organic adhesive additionally adequate to provide the desired adhesion to the substrates (a "potent adhesive"), and c) glass frits, which may be deemed an inorganic adhesive, when the method is used at elevated temperatures into glass and/or glass-receptive substrate, such as for the preparation of solar cells. In the event a first composition lacks a potent organic adhesive of type (b), then a second composition enriched with a suitable adhesive is consequentially used, as will be described in more details with reference to **Figure 3**. Though classified as adhesive, being a fundamental activity of the inorganic glass frits, such compounds may fulfill additional roles in the manufacturing of solar cells, as known to the skilled persons.

Adhesive compounds can be, for instance, pressure sensitive adhesives, if transfer is performed only under pressure, or heat sensitive adhesives (*e.g.*, hot melt adhesives), if transfer conditions further include elevated temperatures. The hot melt adhesives can be polymers having a softening point in the range of relevance to transfer, for instance between 60°C and 180°C. A softening temperature in such range can optionally be achieved by mixing an adhesive agent having a relatively higher softening point with a plasticizer able to reduce such phase transition temperature. Softening temperatures of polymers are provided by their suppliers, but can be assessed by routine experimentation according to methods known to the skilled persons, for instance by using Differential Scanning Calorimetry (DSC).

The adhesive is compatible with other components of the composition (*e.g.*, the electrically conductive particles, the glass frits, when present, and the carrier) and the process conditions, for instance, providing for a suitable flowability of the composition within the

grooves and/or excess removal from membrane surface, being non-brittle to maintain pattern integrity or being sufficiently "heat resistant" till sintering of electrically conductive particles to remain in an amount maintaining adequate shape. The adhesive should preferably have a relatively low adhesion to the flexible membrane (*e.g.*, only sufficient for the composition, wet or dry, to remain within the grooves during manufacturing and handling, but to be releasable from the membrane when it is peeled off from the substrate after lamination). On the other hand, the adhesive should preferably have a relatively high adhesion to the receiving substrate (*e.g.*, allowing for the transfer of the metal pattern to the substrate). Advantageously, adhesives having a low ash content are expected to facilitate metal sintering, improving conductivity (optionally after firing). Adhesives having an open time sufficiently long to allow proper transfer of metal pattern to the substrate, following its optional heating to an elevated transfer temperature, while being sufficiently short to maintain the desired shape (structural integrity of the pattern lines) following transfer, are considered suitable. It is to be noted that open times of less than a few seconds, one second, hundreds or even tens of a millisecond are preferred.

Exemplary organic adhesives can be polyamides, including, for instance, commercially available hot melt polyamide adhesives Uni-Rez® 147, Uni-Rez® 2620 and Uni-Rez® 2720 (formerly of Arizona Chemical, now of Kraton Corporation, USA), Macromelt® 6211, Macromelt® 6238, Macromelt® 6239, and Macromelt® 6264 (Henkel, Germany), Versamid® 744 and Versamid® 754 (Gabriel Performance Products, USA); terpene phenolic resins, such as Sylvaprint® 3523 and Sylvaprint® 7002 (Arizona Chemical, USA); hydrogenated Rosin, such as Foral™ AX-E (Eastman Chemical Company, USA); ethylene-vinyl acetate (EVA) copolymers, including, for instance, commercially available Elvax® 40W of E.I. du Pont de Nemours and Company, Inc.; or ethyl cellulose polymers, including, for instance, commercially available Ethocel™ std 4, 7, 10 or 20 of The Dow Chemical Company.

Glass frits suitable for solar cells are generally made of the following glasses: i) Lead oxide (PbO) based glasses, usually lead borosilicate glass: $PbO - SiO_2 - B_2O_3$; ii) Bismuth oxide (Bi_2O_3) based glasses, usually bismuth borosilicate glass: $Bi_2O_3 - SiO_2 - B_2O_3$; and iii) Tellurium oxide (Tl_2O) based glasses.

Each of the above glasses may also contain one or more of the following: aluminum oxide (Al_2O_3), bismuth oxide (Bi_2O3), boron oxide (B_2O_3), lead oxide (PbO), molybdenum oxide (MoO_2), silicon oxide (SiO_2), tellurium oxide (Tl_2O), tungsten oxide (WO_3), and zinc oxide (ZnO).

A suitable amount of electrically conductive particles (including glass frits when present) is 30-95 vol.% with respect to all solids (*e.g.*, electrically conductive particles, adhesives and glass frits, if present), more preferably 65-90 vol.% for the metal paste and more preferably 50-70% vol.% from all solids for the adhesive paste. The amount of glass frits, when present, is generally 0.5-15 vol.% of the electrically conductive particles, preferably in the range of 1-5 vol.%.

A suitable amount of adhesive: 5-70 vol.% with respect to all solids (*e.g.*, electrically conductive particles and adhesives, including glass frits, if present), preferably within 30-50 vol.% of solids for the adhesive paste, and preferably within 10-35 vol.% of solids for the metal paste.

Optional plasticizers can be phthalates, phosphates, glycerides, and esters of higher fatty acids and amides. For example, when needed, a plasticizer can be one or more of the group comprising dibutyl sebacate, butyl stearate, glycol esters of coconut oil fatty acids, butyl ricinoleate, dibutyl phthalate, castor oil, butyl stearate, diphenyl phthalate, dicyclohexyl phthalate, and dioctyl phthalate. If present, a plasticizer can be found at 5-30 wt.% with respect to the adhesive.

The electrically conductive particles and adhesives can be mixed in a liquid carrier, to form the composition **120** that is used to fill the grooves **110**. Preferably, the amount of carrier should be sufficiently low to shorten the time needed to eliminate it when drying the composition. On the other hand, the amount of carrier need be sufficient to provide suitable flowability to the composition, allowing the composition to fill the grooves relatively rapidly and excess thereof to be removed relatively easily from the surface of the membrane. Typically, the liquid carrier is present in the composition in the range of 30-80 vol.% of the total paste.

The liquid carrier may be aqueous, organic, or consist of mixtures thereof. Organic solvents are preferably volatile and can, for example, be selected from the group comprising linear or branched C1-C7 alcohols and C1-C7 alkyl acetates, any such solvent preferably being of high purity of 95% or more, typically above 98%. Such alcohols can be one or more of methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, pentanol, hexanol and heptanol. Such alkyl acetates can be one or more of methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, pentyl acetate, hexyl acetate and heptyl acetate.

As explained, the composition **120** may be applied in consecutive steps, the elimination of the liquid carrier in between such steps resulting in relative shrinkage of the dried composition as compared to the wet composition.

It is to be understood that intermediate drying of the composition during first fillings providing for a partial filling of the grooves need not necessarily be as extensive as the drying performed subsequent to the last filling step. As used herein, a "dried" or "substantially dried" composition may retain residual amount of liquid carrier, as long as such presence does not hamper the structural integrity of the patterned conductor lines so dried or any other aspect of the process. A composition comprising less the 5vol.%, and preferably less than 2vol.% or even less than 1vol.% can be considered "dried".

Once the dry composition substantially fills the grooves (see, **140** in Figure 1B or any of **140a-d** in Figure 3) and levels with the first surface of the membrane, the flexible membrane bearing metal pattern is ready for further processing, which however need not be performed by the same entity, nor in temporal proximity to the filling step. In such case, the steps preceding and following the contacting of the first surface of the membrane with the solar cell substrate can be temporally separated.

For instance, once a length of membrane has been made by its manufacturer, it may be packaged and sent to an end user who will use the membrane to form conductors on solar cell. The membrane may be packaged in coils. To prevent the composition from adhering to the opposite side of the membrane when it is coiled, the second surface of the membrane may have "non-stick" properties with respect to the first surface of the membrane. Alternatively, a protective sheet, preferably having a release surface (*e.g.*, hydrophobic), may be applied to the membrane to be peeled away from it prior to the next step in the process.

Figure 1C shows the next step (which can be performed by the same or a different entity) in which the membrane **100** is brought into contact with the substrate **150** and the two are passed through a nip **156** between two pressure rollers **152**, **154** to cause the composition **140** within the grooves of the membrane to adhere to the surface of the substrate **150**. At least one of pressure rollers **152** and **154** can be heated to a temperature typically in the range of 60-200°C to further facilitate the transfer. In such a case, the transferring composition may also be called a molten paste. This step may also be referred to as the lamination stage.

Last, in **Figure 1D**, a portion of the membrane **100** of which the composition was already brought into contact with the substrate **150** is pulled away from the substrate **150** in

the general direction of the arrow **160** while the membrane **100** continues to be held against the substrate **150** by a roller **170** at the point of separation, so as to peel the membrane **100** at a known region away from the substrate leaving lines **140'** of the composition adhering to the substrate **150**.

These lines **140'** may not yet be electrically conductive but the electrically conductive particles in the composition may be sintered, fused, or otherwise transformed into a conductive state. Different sintering methods exist, including thermal sintering, light induced sintering, microwave sintering, electrical sintering and chemical sintering, the elected sintering method being dependent upon the compositions and preferred process conditions. These may in turn be dictated by the intended end product. Generally sintering is performed by the application of heat to form a conductor pattern matching the pattern on the die roller **102** of Figure 1A.

If the conductive pattern is applied to a semiconductor wafer (*e.g.*, a polished or unpolished, doped or undoped, silicon wafer optionally having an anti-reflective coating), as is common in the production of certain solar cells, merely placing electrical conductors over the surface of the semiconductor would not suffice to achieve the desired electrical connection. In such an embodiment, the composition preferably additionally contains a glass frit and is fired to cause the conductor pattern to fuse with the substrate. The molten glass etches the dielectric layer of the semiconductor wafer, while allowing metal ions (*e.g.*, silver) to migrate through it to the substrate (*e.g.*, a silicon wafer or thin-film), producing a conductive path between the surface metal pattern and the wafer underneath the dielectric or passivation layer, if one exists. Such firing may be carried out separately, or merely as an extension of the step utilized to sinter the electrically conductive particles. The temperatures and times required for the fusing of the conductors to a semiconductor substrate are however different from those needed for mere sintering. For instance, sintering of the electrically conductive particles may be carried out at a sintering temperature in the range of from about 100-150°C to about 800°C, whereas firing through the composition pattern so as to form electrical contact with the substrate can be performed at a firing temperature in the range of from about 500°C to about 900°C, the firing temperature being greater than the sintering temperature.

During the filling of the grooves **110** in the membrane **100** with composition **120**, the composition may optionally be rendered more flowable by addition of a solvent, which as above-detailed may be an aqueous or an organic solvent. In such a case, the composition may

shrink as it dries and will not totally fill the grooves. **Figure 3A-3D** schematically show optional steps to solve, and optionally utilize, such phenomenon.

In Figure 3A, the grooves are filled with a unique composition **210**. Such substantially complete loading of the groove by any composition may result from consecutive filling of the grooves, the volume of which reduces with each drying of each applied volume of the same composition. When the dried composition **210** is level with the surface of the membrane **100**, the structure shown as **140a** is formed. The number of consecutive filling cycles necessary to entirely fill a groove may depend upon the composition, the groove dimensions and the process operating conditions, but typically do not exceed five cycles, three or four cycles being preferred.

The effect of the composition **210** shrinking away from the surface of the membrane **100** upon drying, is better seen in **Figure 3B**, in which the dip left by composition **210**, applied and dried in a first step, is filled in a second step, which in the depicted example utilizes a second composition **220**. This may be repeated as necessary to ensure that the grooves **110** are eventually filled to substantially the level of the surface of the membrane **100**. When the dried composition **220** is substantially level with the surface of the membrane **100**, the structure shown as **140b** is formed.

When successive steps and/or cycles are performed to fill the grooves, the constituents of the composition may vary between steps/cycles. In essence, only the last applied composition is required to have sufficient adhesiveness to adhere to the substrate while in earlier steps the adhesive is only required to hold the electrically conductive particles together. Additionally, and alternatively, the electrically conductive particles, or blends thereof, used for each composition of each filling repeat may differ from filling to filling. Therefore, while in **Figure 3A**, the composition **210** may comprise a relatively potent adhesive, being the sole composition forming the filled groove **140a**, in **Figure 3B**, composition **220** would have to satisfy this purpose. Composition **210** in the latter figure may therefore comprise either a “poor adhesive” binder or a potent adhesive.

In **Figure 3C**, a release coating **230** that separates easily from the membrane **100** is used to line the grooves before they are filled with a composition containing electrically conductive particles, to form the filled groove cross-section shown at **140c**. Of course, this could alternatively be a multi-layer structure having additional further composition layers with a higher concentration of adhesive by way of example, such as the composition **220**. Hence, in

some embodiments the conductive lines that can be obtained by the present method may have a multi-layered structure.

A release coating **230** may consist of a relatively diluted polymer, in an organic solvent (*e.g.*, a C1-C7 alcohol such as butanol). The "release" polymer has poor adhesion to the surface of the membrane and preferably has a relatively low ash content, allowing for its substantially complete elimination (*e.g.*, by combustion) at a later stage, if it is transferred with the metal lines. In some cases, the polymer of the release composition can be compatible (*e.g.*, adhesion wise) with the compositions to be poured thereupon. Thus, the release composition, once dried, may either remain attached to the grooves' walls or transfer with the composition lines.

The "release" polymer can be, for example, a water-insoluble ethylcellulose polymer or a water soluble cellulose ether, depending on the preferred vehicle of such a release coating. The polymer concentration typically does not exceed 10 wt.%, compositions consisting of 5wt.% or less being favored. As other compositions, the release composition can be applied to fill the grooves with a squeegee, the organic solvent being eliminated by drying. In view of the low polymer content, a dried release composition generally forms upon the walls of the grooves as a film of 1-2 μm or less. If desired, a second layer of release composition can be similarly applied.

The release coating **230** may for example consist 5wt.% water-insoluble ethyl cellulose (such as available as Ethocel™ Std 100, of The Dow Chemical Company) in 1-butanol (Sigma Aldrich). Alternatively, if aqueous compositions are preferred, the release coating may consist of 10 wt.% water soluble cellulose ether (such as available as Methocel™ E15, of The Dow Chemical Company) in deionized water.

It is to be noted that when the compositions used for the loading of the grooves, as well as for the optional pre-coating with a release coating and/or post-coating with an adhesive coating are all aqueous (*e.g.*, water constituting at least 60wt.% of a liquid carrier of the composition), it can be desirable to treat the flexible membrane (generally hydrophobic) to facilitate its even wetting by these compositions. Such a treatment, which can be achieved by corona, can be preferably performed once the release coating, if present, has been applied and dried within the grooves, but can also be performed, if at all, before the application of a release coating.

Figure 3D shows an optional structure **140d** that in addition to the composition **210** filling the grooves has an adhesive coating **250** that covers the entire surface of the membrane. The adhesive coating **250** is intended to assist in the transfer the composition from the grooves to the substrate. The surface of the substrate can be, if desired, subsequently washed with a solvent to remove the adhesive from all the areas where it is exposed and does not lie beneath the lines of composition. In most cases, however, removing the adhesive coating by the use a solvent may prove unnecessary as it will be burned away upon sintering (and/or further firing) of the metal lines transferred to the substrate.

Though the structure **140d** is shown in **Figure 3D** as comprising a single composition **210**, it may be formed from of multiple layers as described with reference to **Figure 3B** and **Figure 3C**.

An adhesive coating **250** may consist of the same potent organic adhesives as previously mentioned (but be devoid of glass frits), such adhesives being now dispersed or dissolved in a carrier that would not negatively affect the structural integrity of the dried compositions filling the grooves. The amount of adhesive polymer in such an inert carrier can be in the range of 5-50 wt.% of the adhesive coating composition. The "inert" carrier can be at least one of the organic solvents previously detailed, the volatility of such solvents shortening the time such compositions may affect the previously applied and dried compositions. Subsequent to its drying, the adhesive coating should preferably have a thickness in the range of 0.2-3 μm.

The adhesive coating **250** may for example consist of 5wt.% polyamide hot melt adhesive (Uni-Rez® 2720), 15wt.% butanol (Sigma Aldrich) and 80wt.% pentyl acetate (Sigma Aldrich). Alternatively, if aqueous compositions are preferred, the adhesive coating may consist of 5 wt.% water soluble adhesive made of poly(2-ethyl-2-oxazoline) (such as available as Aquazol® 5, by Polymer Chemistry Innovations), 1wt.% cosolvent, such as butanol, 0.25wt.% of a first wetting agent, such as a silicone surfactant (as BYK®-349 by BYK), 0.075wt.% of a second wetting agent, such as a silicone surfactant (as BYK®-333 by BYK) in deionized water.

Other Electrodes

The processes as described above are better suited for forming thin conductors but when coating a large surface with an electrode is desired, such as the back electrode of a solar cell by way of example, the process can be considerably simplified as shown in **Figures 4A** to **4C**.

In **Figure 4A**, a doctor blade having a rounded tip is pressed against the membrane **100** as it passes between a pressure roller **402** and the doctor blade **400**. An excess of composition **404** is applied to the membrane **100** upstream the doctor blade **400** and its thickness is reduced uniformly as it passes beneath the doctor blade. The thickness can be set by varying the radius of curvature of the tip of the doctor blade **400** and the applied pressure. The excess composition need not be applied along the entire length of the doctor blade or the doctor blade may be optionally "segmented" the composition being layered within a desired portion of the membrane. The composition **404** can then be dried.

The membrane **100** carrying dried composition **404** is then pressed against the substrate **150** as shown in **Figure 4B** by passing it through the nip between two pressure rollers **406** and **408** and the membrane **100** can be peeled away from the substrate **150** as shown in **Figure 4C** to leave a coating of the composition **404** on the substrate. Pressure rollers **406** and **408** can be further heated to facilitate the transfer of compositions including an adhesive having a softening point at transfer temperature. This coating of dried composition **404** can then be sintered (*e.g.*, heated) to render it conductive onto the substrate **150** and if necessary fired to form the back electrode of the solar cell. A suitable solar cell back electrode may not only be fused to the wafer as previously explained, but can also create a highly doped layer (*e.g.*, aluminum doped) on the silicon substrate. Such highly doped layer, called a back scattering field (BSF), can improve the energy conversion efficiency of the solar cell. Such considerations are known to the skilled persons, who can accordingly formulate composition **404** following principles previously detailed for composition **120**.

It will be appreciated that the laminating steps shown in **Figure 1C** and **Figure 4B** can be carried out at the same time. This enables a large area back electrode to be applied to a semiconductor wafer at the same time as a conductive grid pattern is applied to its front surface. The sintering and fusing of the composition on both sides of the wafer may then be conducted at the same time.

Back electrodes can alternatively be applied to the opposite side of the substrate by any method conventionally used in the industry of relevance, for instance by screen printing. Such method may be used directly on the back side of the substrate, but preferably may serve to apply a layer of compositions of the present disclosure on a flexible membrane allowing the concomitant transfer of "front" metal pattern and "back" electrode according to the above-detailed method. If forming the back electrode on a membrane, gravure printing can be additionally considered to form the layer of composition on the membrane.

Example of Solar Cell

A conductive metal pattern was prepared according to the above principles, schematically summarized in **Figure 5A**. In the figure, a metal pattern **500** is illustrated. Such a pattern can be "negative", below the surface of the membrane when the dried compositions substantially fill the grooves, or "positive" protruding above the substrate (*e.g.*, wafer surface) after transfer. The longitudinal grooves of metal lines **510** result from rules **106** (see, **Figure 1A** or **Figure 2A-2B**), whereas transverse grooves or metal lines (*e.g.*, bus bars) are shown as **520**, if "uninterrupted" traversing all longitudinal lines of the metal pattern, or **530**, if traversing only a subset of lines **510**. In any event, transverse grooves or lines **520** and **530** result from rules **108** (see, **Figure 1A** or **Figure 2A**). The longitudinal lines due to collect the current generated by the intended photovoltaic cell may also be referred to as grid lines or fingers.

The flexible membrane used in the present example was a cast polypropylene film (50 μm thick CPP; RollCast™ 14 of R.O.P. Ltd). It was patterned with a rotatable die **102** wherein a nickel shim provided for a series of about 85 rules **106** for the formation of the longitudinal grooves. The edges of rules **106** were trapezoidal, as shown in **Figure 5B**, with a base having a width W_B of 20 μm, a flat top having a width w_T of 12 μm, and a height h of 32 μm. The distance d between adjacent rules was of 1.8 mm. The length of each rules along the circumference of the roller **102** was set to be compatible with the solid support to which the metal pattern would be transferred (including "margins" in between patterns, if desired).

The grooves so formed (having a base W_B of about 25 μm, a top w_T of 12 μm and a depth (height *h)* of about 25 μm, the distance between the facing edges of two adjacent grooves being of about 1,775 μm) were filled with a release composition consisting of 5wt.% Ethocel™ Std. 100 (The Dow Chemical Company) in 1-butanol (Sigma Aldrich). The composition was applied to the patterned membrane using a doctor blade (MDC Longlife Multiblade, Daetwyler) positioned at an angle of 65-70° to the surface normal. The stainless steel beveled blade had a width of 20 mm, a thickness of 0.2 mm, a bevel angle of 3°, a bevel length of 2.7 mm and a tip radius of 18 μm. The force used was of 3N/cm. The doctor blade was parallel to the axis of rotating die **102**, perpendicular to the grooves generated by rule **106**, and in relative motion with the flexible membrane, the moving direction being parallel to lines **510**. The membrane was then heated with a hot air gun until the release composition became a substantially dry film. The heating / drying temperature was selected to prevent

membrane deformation (<70°C for CPP). In the present example, the release composition was applied in a single step.

After the formation of a thin release film coating the walls of the grooves, a metal paste was loaded within the grooves. The metal paste included a) silver particles (1-3 μm beads) and lead oxide based glass frits (1-3 μm chunks), the foregoing constituting about 60 vol.% of the solids, glass frits being present at approximately 3-5 vol.% of the electrically conductive particles; b) a polyamide adhesive, Uni-Rez® 2720 or Uni-Rez® 147, constituting about 40 vol.% of the solids; and pentanol, constituting 40 vol.% of the total paste. When converted to wt.% of the total composition, such metal paste was composed of 87.3-88.7 wt.% silver particles, 1.3-2.7 wt.% glass frits, 6 wt.% adhesive and 4 wt.% carrier.

Each loading step of the metal paste was followed by a substantial elimination of the organic carrier and drying of the composition with a hot air gun. It typically took three passes to fully fill the grooves, level with the surface of the flexible membrane.

If an additional adhesive coating layer was desired, it was applied by a 6 μm wire bar, the dried adhesive coating having a thickness of less than 2 μm. The adhesive coating applied in some experiments included 10wt.% of Uni-Rez® 2720, in a mixture of solvents consisting of butanol and pentyl acetate (at a weight per weight ratio of 1:5). Alternative adhesive coatings were prepared using additional polyamide hot melt adhesives including Uni-Rez® 2620 of Kraton Corporation, USA, Macromelt® 6211, Macromelt® 6224, Macromelt® 6238 and Macromelt® 6239, of Henkel, Germany, and Versamid® 744 and Versamid® 754 of Gabriel Performance Products, USA. 10wt.% of each polyamide hot melt adhesive was mixed with 90wt.% of organic solvents. The Macromelt® and Versamid® polyamide adhesives were blended in propylene glycol methyl ether (such as commercially available as Dowanol™ PM from the Dow Chemical Company). The Uni-Rez® 2620 and Uni-Rez® 2720 polyamide adhesives were applied in further additional solvents, each having been blended in (a) 90wt.% butanol, (b) 90wt.% pentanol, (c) 15wt.% butanol and 75wt.% amyl acetate and (d) 15wt.% pentanol and 75wt.% amyl acetate; all solvents being supplied by Sigma-Aldrich at purity level of at least 95%. All afore-said adhesive coating compositions based on polyamide hot melt adhesives were found satisfactory for the transfer of patterns from the membrane to the substrate.

In an additional series of experiments, different adhesive polymers were tested and found similarly suitable. The three further alternative adhesive coatings consisted of (a)

20wt.% of a fully hydrogenated gum Rosin (Foral™ AX-E by Eastman Chemical Company) in 80wt.% Dowanol™ PM, and (b) 10wt.% of a terpene phenolic resin (Sylvaprint® 3523 or Sylvaprint® 7002 by Arizona Chemical) in 90wt.% Dowanol™ PM.

Figure 5C shows a micrograph picture taken by confocal laser scanning microscope showing a groove of a flexible substrate filled with metal paste (see for example **140** in **Figure 1A**). As can be seen, the groove is substantially filled to the level of the surface of the flexible membrane, while the areas surrounding it are substantially free of dried composition. For such picture, an adhesive coating was omitted.

The flexible membrane including the patterned grooves filled with dry composition was contacted with a textured boron-doped silicon wafer having a phosphor doped emitter side and an anti-reflective coating of silicon nitride. Such wafers may assume a variety of sizes (*e.g.*, 156x156 mm or 125x125 mm) and thicknesses (*e.g.*, in the range of 150-300 μm), the ones used in the present example having a square shape of about 156 mm side and a thickness of about 200 μm. The membrane was pressed against the wafer at a pressure of 6Kg/cm^2, by passing through a nip **156** at a speed of 5 cm/s. Pressure rollers **152** and **154** were heated to about 130-140°C. The adhesive coating, if any, flowed into the Si wafer surface texture, to which it adhered after cooling of the wafer back to about ambient temperature. The CPP membrane was then peeled off the wafer, while the coating layer of adhesive and the metal pattern transferred to the wafer and remained thereon following the removal of the membrane. The transferred metal patterns were sintered and fired at a temperature profile reaching a peak temperature of about 750°C in a solar belt furnace Despatch CDF-SL. The patterns so treated were at a temperature of 700°C or higher typically for at least 5 to 20 seconds, before being cooled back to ambient temperature.

The contact resistance (*Rc*) of the resulting conductive lines was measured with the Transfer Length Method (TLM). *Rc* values were between 0.05 to 0.1 Ωcm, values below 0.2 Ωcm being considered highly satisfactory, representing a loss of efficiency of less than 0.1% as compared to an optimal contact having a null *Rc*.

Figure 5D shows a micrograph picture taken by confocal laser scanning microscope (LEXT OLS4000 3D of Olympus Corporation) showing a contact line made of metal paste (as filled in the groove shown in **Figure 5C**) transferred to a wafer (see for example **140'** in **Figure 1D**) and sintered as above-described. As seen from the figure, the sintered metal line substantially retained the shape of the rules defining the grooves wherein it was prepared.

It is an advantage of the process of the present disclosure that the conductors can be very narrow (*e.g.*, ~20-25 μm or less, half or less than typical art values), while retaining a sufficient height, as can be assessed by a relatively high aspect ratio, *ASP* being about 1:1 in the present example.

A solar cell was similarly prepared, using the same membrane and pattern of grooves, by replacing the above described non-aqueous compositions by aqueous ones. The release coating was prepared using a release composition including 10 wt.% Methocel™ E15 (The Dow Chemical Company) in deionized water. The release composition was twice applied and dried, following which the grooved side of membrane was exposed to close corona treatment (BD-20AC Laboratory Corona Treater, by Electro-Technic Products).

A water-based metal paste was then loaded within the grooves. The metal paste included a) silver particles (1-3 μm beads) and lead oxide based glass frits (1-3 μm chunks), the foregoing constituting about 60 vol.% of the solids, glass frits being present at approximately 3-5 vol.% of the electrically conductive particles; b) a poly(2-ethyl-2-oxazoline) adhesive, Aquazol® 5, constituting about 40 vol.% of the solids; and deionized water, constituting 40 vol.% of the total paste. When converted to wt.% of the total composition, such metal paste was composed of 87.3-88.7 wt.% silver particles, 1.3-2.7 wt.% glass frits, 6 wt.% adhesive and 4 wt.% carrier. The aqueous metal pasted was loaded in six filling / drying steps.

Finally, a water based adhesive coating was applied to the entire surface of the loaded membrane. The aqueous adhesive coating consisted of 5 wt.% Aquazol® 5 (a poly(2-ethyl-2-oxazoline) by Polymer Chemistry Innovations), 1wt.% butanol, 0.25wt.% BYK®-349 and 0.075wt.% BYK®-333 (both wetting agents by BYK), all in deionized water.

Light Reflective Grid Lines

When considering the particular use of the present method for the preparation of a flexible membrane used for the manufacturing of solar cells, optional additional steps may be further implemented. As known to persons skilled in the fabrication of photovoltaic devices, a recurrent problem is the trade-off between the number and size of the grid lines and the reduction in the amount of photo-current that can be generated due to their shading.

The shading of the light collection surface of such devices by the grids of conductive lines (fingers and bus lines) may amount to up to about 5 to 10% of the surface which can impair the resulting efficiency of photovoltaic conversion. Light incident upon the conductive

lines may reflect back to the environment, this energy being lost for the unobstructed light collecting areas adjacent to the grid lines. Proper selection of the rules forming the groove profile within the flexible membrane (hence affecting the resulting contour and size of the conductive lines that can be prepared therein) may reduce such shading. For instance, the shape of the rules (and conductive lines which may result therefrom) may enhance or facilitate the reflection or redirection of impinging light onto the non-obstructed photovoltaic light harvesting surface of the future substrate (the "active area"), thus decreasing the effective optical shading of the grid. For similar reasons, it is expected that fingers and bus lines having a relatively smooth surface provide for a higher reflectivity / lower light diffusivity than otherwise similar conductive lines having a relatively rougher surface. A lower diffusivity of the conductive lines when their slopes would otherwise suitably redirect the incident light to the active area (*e.g.*, forming an angle of 45° or more) of the light harvesting substrate may also decrease the shading effect of the grid, a higher portion of incident light being properly redirected. Conversely, conductive lines having shapes and/or slopes which would otherwise reflect incident light away from the available substrate area may benefit from a higher diffusivity which may increase the amount of light being redirected to the photovoltaic surface free of grid lines. Preferably, the shape, size and/or spacing of the rules / grooves / conductive lines facilitate or enhance redirecting the light to active areas in response to a wide range of incident light angles. However, the ability to utilise light incident from a wide range of angles may not be essential if solar panels including such cells are equipped with a tracking mechanism following the movement of the sun, limiting the ranges of incident light angle that would impinge on the conductive lines and maintaining sufficient active area of photovoltaic surface as day proceeds.

The volume bounded by any pair of reflective grid lines may be considered to act as a light funnel which may reduce the effect of actual shading, by increasing the exposure of the photovoltaic area free of grid lines to light, enhancing the efficiency of the solar cell or of a solar panel formed by an interconnected plurality of such cells. The shape of this "funnel" is derived from the shapes of the conductive lines bordering it and the profile of their reflective surfaces. As above explained, the faces of a conductive line may have a range of light reflective or diffusive properties, while remaining suitable for their intended use. Thus the terms "reflective surface(s)" or "reflective face(s)" of a grid line do not intend to limit such surfaces to ideal mirror-like walls.

It can be theoretically demonstrated, using principles of ray optics, that for many illumination conditions, the higher the angle between the reflective surface of the grid lines and the solar cell surface (0° being parallel to the wafer surface and 90° being perpendicular) the higher the amount of light that may be reflected back to the solar cell non-obstructed area. Taking for example an ideal mirror-like inversed V shaped grid line having substantially smooth and perfectly specular reflective faces essentially lacking any diffusive reflection forming an angle of less than 45° with the solar cell light harvesting surface, an incident light beam perpendicular to the solar cell surface will be reflected back (*e.g.*, to the air), and will not contribute to photovoltaic conversion and current generation, resulting in effective optical shading that is equivalent to the geometrical shading. In contrast, a similarly shaped line having ideally reflective mirror-like faces forming an angle of more than 45° will totally reflect an incident perpendicular light beam to the solar cell surface, resulting in null effective optical shading.

The above depicts a very particular situation and when calculating light losses for standard solar cell operation conditions, the following factors should be considered:

1. The losses should be integrated for various light incident angles, and intensities, according to the illumination conditions as day or seasons proceed.

2. The solar cells are usually encapsulated (*e.g.*, in glass and adhesive) for protection, which encapsulating material(s) may change the optical light path and intensity of the incident and reflected beams. Light beams might be reflected from the grid surface to the protective capsule – air interface, go through total internal reflection and be redirected to the solar cell surface.

3. The surface of the lines of the solar grid is seldom ideally smooth and light is usually reflected in a diffusive way. The spatial distribution and intensity of the diffracted light at the various incident angles may depend on the roughness of the surface

The theoretical light loses considering the above factors can be calculated by ray optics, suggesting that the effective optical shading can be reduced as the angle of the faces of the conductive lines with respect to the solar harvesting surface is increased. For faces forming an angle greater than 45°, the effective optical shading is of less than 30% of the actual geometrical shading for totally diffusive surface (Lambertian surface), such shading decreasing as the angle increases. When diffusivity of the lines surfaces is decreased (*e.g.*, by reducing roughness / increasing smoothness), the effective optical shading can be further

decreased, down to 0% for ideal mirror-like surfaces as previous explained. Any of the above approaches to reduce shading of the conductive lines, including by selecting a favorable profile to the lines and/or, depending on the angle formed by the reflective surface, by increasing reflectivity of incident light towards the active area of the harvesting substrate and/or by decreasing diffusivity of the light away from the wafer active area is desirable to increase the photovoltaic conversion efficiency of a solar cell prepared using a flexible membrane according to the present teachings.

Based on the above principles, a rule / groove / conductive line can suitably have a trapezoidal profile, preferably with a small flat top width w_T to lessen light loss (*e.g.*, having a w_T of 5 μm or less) or have a triangular profile. The base for such profiles can advantageously have a width W_B between about 10 μm and about 25 μm. When the grid is to be used in association with a suitable protective case which may redirect at least some of the light back to the active light harvesting area of a solar substrate, the angle between the face of the line and the substrate (represented by α in Figure 5B) can be at least 25°, at least 30°, at least 40°, at least 45°, at least 50°, at least 60°, or at least at least 70°. In absence of further encapsulation, the faces of the conductive lines are preferably relatively poorly or essentially not diffusive, the total lack of diffusivity afforded by mirror-like surfaces being particularly advantageous. In such case, the angle between the faces of such highly specular reflective / poorly diffusive lines and the substrate can be at least 60°, at least 65°, or at least 70°. Whether or not encapsulated, the angle between the face of such a conductive line and the substrate is of at most 85°, at most 82.5°, at most 80°, at most 77.5°, or at most 75°. Advantageously, the angle formed by the face of the conductive line and the substrate is between 60° and 85°, or in the range of 65° to 82.5° or 70° to 80°. When the conductive lines are to serve in applications other than the preparation of solar cells, in particular with light reflective faces, additional angles between the substrate and the face of the line raising therefrom can be suitable. Hence, in some embodiments, this angle can be within the range from 20° to 90°.

It will be appreciated, that while the angle formed by a side of the groove with respect to the surface of the membrane can be designed to be constant until the apex of a cross-section profile of the groove in the flexible membrane before loading, such angles may mildly vary during the process, in particular once the conductive pattern is transferred to its substrate and sintered thereon to form an end-product solar cell. For example, assuming a groove having a triangular cross-section profile, the faces of the triangle forming *ab initio* an angle of 45° with

the surface of the membrane, a conductive line of a solar cell resulting from such a groove might have a less perfect triangular profile. Considering only half of its profile, from the base of the solar cell substrate to the top of the conductive line, the angle in a first segment can be either less than 45°, the profile of the line having an initial shallow slope, or on the contrary forming an angle of more than 45°, the profile of the line having an initial "stair" slope, such angles further varying as the half profile of the line reaches its apex. The profile can be mildly convex or concave, or with alternating convex, concave and straight segments. To take into account the profiles of the resulting conductive lines, which may form a variable angle as considered at different points along the slope formed between the basis and the top of the line, it can be preferred to consider the average of the angle as the mean of $\tan^{-1}$ of the profile slope (=derivative) at each sub-segment along the tapering face. Such value can also be referred to as the averaged slope. Using such method, and assuming that in the afore-detailed illustrative example, the angles of the triangularoid shape do average to 45°, even if fluctuating below and above this value along different sub-segments, then the averaged slope of the half-profile would be of 1.

Hence in some embodiments, the averaged slope of one side of a conductive line elevating from the base of the solar cell substrate to the apex of the line (*i.e.* a tapering face) can be of at least 0.50 (~26°), at least 0.75 (~37°), at least 0.85 (~40°), or at least 1 (45°), or at least 1.15 (~49°), at least 1.3 (~53°), at least 1.5 (~56°), or at least 1.7 (~60°). In some embodiments, the averaged slope is of at most 8 (~83°), at most 6 (~80°), at most 4 (~76°) or at most 2 (~63°)

In addition, and alternatively, to the selection of a more favorable shape for the cross-section of a conductive line, a light modifying coating can be applied to the conductive lines in a manner similar as described for the optional release layer. As used herein, the term "light modifying" relates to any type of coating that may reduce shading or increase photovoltaic harvesting and conversion. The coating may perform any of the following: increase smoothness or decrease roughness of the conductive line, increase reflectivity of incident light towards the active area (whether directly or indirectly as a result of an optional protective case) or decrease the diffusivity of the light away from the active area.

Briefly, a reflectivity-enhancing or diffusivity-reducing composition including a light reflective material is used to coat the walls of the grooves, so that upon transfer to the substrate, the transferred lines are coated with a thin layer of the reflective material, so as to reduce or prevent shading.

Example of Pattern with Light Reflective Faces

The flexible membrane used in the present example was the above-mentioned cast polypropylene film (50 μm thick CPP; RollCast™ 14) patterned with a rotatable die **102** the profile of rules **106** being trapezoidal, with a base having a width W_B of 20 μm, a flat top having a width w_T of 12 μm, and a height h of 32 μm. Such profile provides for grooves having inclined walls ideally forming a steep angle of about 83° with the surface of the film, however as the actual dimensions of the cross section of a resulting groove and subsequent longitudinal line mildly diverge yielding measurements closer to a base width W_B of 25 μm, a top width w_T of 12 μm and a height h of 25 μm, the angle between the reflective surfaces and their substrate is in fact of about 75°. Such angle, calculated based on the sizes achieved within the flexible membrane, may slightly decrease following subsequent steps of lamination, sintering and firing.

The grooves so formed, being separated from one another by a distance d of about 1.8 mm, were filled with a release composition consisting of 5wt.% Ethocel™ Std. 100 in 1-butanol, applied to the patterned membrane and subsequently dried as described above.

After the formation of a thin release film coating the walls of the grooves, a layer of nano silver ink containing about 40 wt.% silver beads having a particle size of less than 100 nm was deposited within the grooves. Non-limiting examples of suitable nano silver inks include Nano silver ink Metalon® JS-A101 and JS-A102 from NovaCentrix® and there are numerous commercially available sources of metal nano inks having average particle size (*e.g.*, z-avg particle size as determined by DLS) between about 40 nm and 200 nm or between about 30 nm and 100 nm that can be suitable. The nano silver ink was deposited on top of the release film already coating the grooves with a doctor blade by the same method as described above and dried for approximately 10 minutes with a hot air gun to form a thin nano silver layer.

To the grooves now thinly coated with a release film contacting the flexible membrane and a nano silver layer, the core of the conductive line was added. The interior of the line was prepared as above-detailed by 3 steps of metal paste deposition followed by the application of an adhesive coating layer. The filled grooves were transferred to the Si wafer by lamination, sintered and fired in the same way described for previous example.

A control was similarly prepared, lacking the nano silver layer. The fired grid of the lines having the nano silver layer displayed a lower light diffusivity as compared to the grid

prepared without the nano silver ink layer. Such findings were established by independent trained observers by tilting at least five grids of each type against a constant light source, the relative diffusivity of the grids being ranked in a blinded manner. It was therefore assumed that the nano silver layer enhanced the smoothness / decreased the roughness of the exterior faces of the conductive lines, an hypothesis confirmed by microscopic study of the reflective faces of the lines using a confocal laser scanning microscope (Olympus® LEXT OLS4000 3D).

While in the present example, the nano silver ink was applied to the grooves after the formation of a release layer, this earlier step is not deemed essential and a suitably formulated ink may satisfactorily achieve release of the conductive lines from the flexible membrane upon future lamination. It is believed that in addition to the above-exemplified silver, metal nano inks including aluminum, chrome, cobalt, copper, gold, indium tin oxide, molybdenum, nickel, palladium and platinum may similarly increase grids' reflectivity (or decrease their diffusivity). While the material improving the reflectance of the faces of the lines can be a conductive metal, alloy or metal oxide, this is not essential, the reflective enhancing layer, if applied, predominantly serving to reduce the shading and improve the efficiency of a resulting solar cell, the ability of the line to conduct electrical current being predominantly provided by its core.

The light reflective material can be made of silver nano particles. It can be present in the reflective composition in amount of 1 to 20 vol.%. Once dried, the light reflective coating may have a thickness in the range of 0.2 to 10 μm.

Plurality of Sets of Grooves

In the embodiments of the invention previously detailed, there was described a flexible membrane in which one pattern of grooves was formed, then loaded with the compositions of interest ahead of lamination upon the substrate of choice for transfer of the pattern of dried composition thereto. If distinct patterns (*e.g.*, having different shapes, different dimensions, different profiles, different compositions and the like differences) are to be formed on a same substrate, the method according to the present teachings may be suitable. For example, a first membrane with a first pattern can be applied on a first surface of the substrate, while a second membrane with a second pattern can be applied on a second surface of the substrate. The first and second surface of the substrate can be on the same side of the substrate, typically in non-overlapping areas, but can also be on opposite sides. Moreover, each pattern in each membrane may be loaded with same or different compositions.

By way of example, in a solar cell the conductive lines of the light harvesting side (the solar face) can be formed by transfer of a first pattern of a first composition from a first membrane and the back electrode can be formed by transfer of a second pattern of a second composition from a second membrane. Preferably, the distinct patterns are concomitantly transferred during the lamination step in which pressure is simultaneously applied on both membranes each facing its respective face of the substrate.

Distinct patterns which are to be transferred to a same side of a substrate can advantageously be obtained using a single membrane as explained in the following. **Figure 6** represents a membrane having a plurality of sets of grooves, each filled with a different material. Such membrane may be utilized for providing differing patterns of materials on the substrate. By way of example, the first pattern may provide for the formation of the bus bars, while the second pattern may permit the preparation of the finger grid lines. In such case, while the two patterns may even intersect in some areas, the compositions of the first and second pattern can differ, for instance, in the amount of glass frits. In this illustrative example, while the compositions of the second pattern due to form the grid lines would include glass frits to properly electrically contact the substrate in the finished solar cell, the compositions of the first pattern due to form the bus lines would not need as high amounts of glass frits. In some embodiments, the compositions serving for the preparation of the bus lines may even be devoid of glass frits, as such lines are mainly used to interconnect the grid lines rather than electrically connect the substrate.

In Figure 6 a groove pattern symbolized by groove **110A** is embossed into membrane **100A**. The first groove pattern is then filled by a first composition **120A**, with the aid of a doctor blade **130A**, the action of which being backed by pressure roller **132A**, or by any other desired method. As described in more detail above, such as in relation to Figures 1A-1D, and 3A-3D, a plurality of filling steps may be utilized and a plurality of filling and/or drying stations and/or doctor blades may be utilized (not shown). Similarly, a cleaning station may be optionally included, so as to facilitate the removal of composition in the spaces between the grooves.

Once the grooves of the first pattern are filled as shown by way of example by **140A**, **140B**, **140C**, *etc.* a second set of grooves symbolized by groove **112** is formed in the membrane. The second set of grooves is then filled by a second composition **120B** utilizing doctor blade **130B**, the action of which being backed by pressure roller **132B**, or any other desired method. As the grooves of the first pattern **140A**, **140B**, **140C** are already filled, the

second composition **120B** is applied to the grooves of the second pattern. The second sets of grooves may be filled by a single or a plurality of filling steps, doctor blades, flowing aids and like, until a desired level of fill **142** is achieved. Thus the membrane may carry a plurality of groove patterns and each of the groove patterns may utilize a composition providing a desired set of characteristics. While in this figure, the two patterns of grooves are respectively illustrated by grooves **110A** and **112**, which may seem parallel one to the other in the represented view, this need not be the case and the grooves of one pattern may assume any desired position and orientation with respect to the grooves of the second pattern.

Figure 6 also shows that different methods may be utilized to form the grooves. While the first set of grooves is depicted as being formed by embossing by die roller **102A** (**104A** representing a corresponding pressure roller), the second set of grooves are formed utilizing an alternative method symbolized by the numeral **150**. Such groove forming device may be one of many devices, ranging from a dedicated punch to a laser source for selectively ablating parts of the membrane **100A** or in certain cases for causing membrane shrinkage by heating. Alternatively, the pattern of grooves can be formed on a flexible membrane by a patterning technique, such as photolithography.

Once the membrane grooves are filled with various compositions, an adhesive coating may be applied, as illustrated by **250** seen for example in Figure 3D, and the membrane may be brought into contact with the substrate for transferring the patterned compositions thereto, as described above.

It will be readily appreciated that the present method may facilitate proper registration between various patterns and the substrate. The patterns can be separated from one another on the flexible membrane in a manner that may further facilitate such registration.

Figure 1E depicts several dashed line elements which reflect process steps directed to producing a membrane with a plurality of compositions, for later transfer to a substrate. After the first pattern grooves are filled **315**, an additional set of grooves is produced **340** on the membrane by any desired manner. The second set of grooves is then loaded **345** with a second composition (the loading being optionally performed in repeated cycles of filling and drying a set of compositions which differ from the composition or set of compositions used to fill the grooves of previous pattern). Those process steps for patterns other than the first pattern may be repeated any desired number of times, as shown by dot-dashed line **355**. Once all desired patterns have been formed in the membrane and loaded with the desired pastes of materials, the process continues **350** to contacting the membrane and subsequent transfer of the

materials to the substrate (which involves steps such as previously described **320**, **325**, and **330**), the final step **335** being adapted to sinter the materials of all transferred patterns. In some embodiments, the steps of the process are not performed in a continuous manner nor necessarily by the same entity. In certain embodiments, material may not be completely sintered, and in some embodiments temperatures and other environmental conditions are adjusted to prevent damage to the numerous compositions.

In the description and claims of the present disclosure, each of the verbs, "comprise" "include" and "have", and conjugates thereof, are used to indicate that the object or objects of the verb are not necessarily a complete listing of members, components, elements, steps or parts of the subject or subjects of the verb.

As used herein, the singular form "a", "an" and "the" include plural references and mean "at least one" or "one or more" unless the context clearly dictates otherwise.

Positional or motional terms such as "upper", "lower", "right", "left", "bottom", "below", "lowered", "low", "top", "above", "elevated", "high", "vertical", "horizontal", "backward", "forward", "upstream" and "downstream", as well as grammatical variations thereof, may be used herein for exemplary purposes only, to illustrate the relative positioning, placement or displacement of certain components, to indicate a first and a second component in present illustrations or to do both. Such terms do not necessarily indicate that, for example, a "bottom" component is below a "top" component, as such directions, components or both may be flipped, rotated, moved in space, placed in a diagonal orientation or position, placed horizontally or vertically, or similarly modified.

Unless otherwise stated, the use of the expression "and/or" between the last two members of a list of options for selection indicates that a selection of one or more of the listed options is appropriate and may be made.

In the disclosure, unless otherwise stated, adjectives such as "substantially" and "about" that modify a condition or relationship characteristic of a feature or features of an embodiment of the present technology, are to be understood to mean that the condition or characteristic is defined to within tolerances that are acceptable for operation of the embodiment for an application for which it is intended, or within variations expected from the measurement being performed and/or from the measuring instrument being used. Furthermore, unless otherwise stated the terms used in this disclosure should be construed as having tolerances which may depart from the precise meaning of the relevant term but would

enable the invention or the relevant portion thereof to operate and function as described, and as understood by a person skilled in the art.

Certain marks referenced herein may be common law or registered trademarks of third parties. Use of these marks is by way of example and shall not be construed as descriptive or limit the scope of this disclosure to material associated only with such marks.

While this disclosure has been described in terms of certain embodiments and generally associated methods, alterations and permutations of the embodiments and methods will be apparent to those skilled in the art. The present disclosure is to be understood as not limited by the specific examples described herein.

CLAIMS

1. A method of applying a pattern of electrical conductors to a substrate formed by a surface of a solar cell, which method comprises:

a) providing a flexible membrane,

b) forming a pattern of grooves in a first surface of the membrane, the pattern corresponding at least partially to a desired pattern of electrical conductors to be applied to the substrate,

c) loading into the grooves a composition that includes, as composition components, electrically conductive particles and an adhesive, said loading being performed in one or more sub-steps such that on completion of the loading step the composition substantially fills the grooves, level with the first surface of the membrane, and parts of the first surface between the grooves are substantially devoid of the composition,

d) contacting the membrane with the substrate with the first surface of the membrane facing the substrate,

e) applying pressure to the membrane to cause the composition loaded into the grooves in the first surface of the membrane to adhere to the substrate,

f) separating the membrane from the substrate to transfer the composition from the grooves in the first surface of the membrane to the substrate, and

g) applying sufficient energy to sinter the electrically conductive particles in order to render electrically conductive the pattern of composition transferred to the substrate from the grooves.

2. A method as claimed in claim 1, wherein the composition loaded into the grooves comprises, as an additional composition component, a liquid carrier to form a wet composition, and wherein the step of loading comprises performing, at least once, a filling cycle that includes the steps of:

(i) applying an excess of the wet composition to the whole of the first surface of the membrane,

(ii) removing excess wet composition from the first surface to leave the wet composition substantially only within the grooves in the first surface of the membrane, and

(iii) substantially drying the wet composition within the grooves by removing the liquid carrier to leave dried composition,

steps (i), (ii) and (iii) being repeated, as necessary, until dried composition substantially fills the grooves, level with the first surface of the membrane.

3. A method as claimed in claim 2, wherein the membrane is cleaned to remove composition from parts of the membrane between the grooves either before or after step (iii) of at least the last filling cycle.

4. A method as claimed in claim 2 or claim 3, wherein the relative proportions of the components of the composition are varied between filling cycles.

5. A method as claimed in any one of claim 1 to claim 4, wherein a release coating is applied to the grooves of the membrane and dried thereon, prior to loading of the composition into the grooves.

6. A method as claimed in claim 5, wherein the release coating is formed only on the walls of grooves.

7. A method as claimed in any one of claim 1 to claim 6, further comprising, prior to step c), and optionally after the application of a release coating, the steps of:

A. applying a light modifying coating to the first surface of the membrane,

B. wiping the first surface to leave the coating substantially only within the grooves, and

C. drying the light modifying coating, before or after the wiping of the first surface, to leave the dried light modifying coating only on the walls of grooves.

8. A method as claimed in any one of claim 1 to claim 7, wherein prior to contacting said membrane with said substrate according to step d), an adhesive coating is applied to the first surface of the membrane so as to coat any composition present in the grooves, said adhesive coating being dried prior to contacting the substrate.

9. A method as claimed in any one of claim 1 to claim 8, wherein the grooves of the pattern are substantially identical with one another.

10. A method as claimed in any one of claim 1 to claim 8, wherein at least two grooves in the pattern, or two different segments of the same groove, differ from one another in depth and/or width.

11. A method as claimed in any one of claim 1 to claim 10, wherein the substrate comprises a semiconductor wafer, and wherein at least one of the compositions being loaded in one or more sub-steps of the step of loading includes a glass frit, as an additional composition component, the substrate and the composition being heated, following step f), to cause the composition to fuse with the substrate.

12. A method as claimed in claim 11, wherein the heating of the substrate and the composition, to cause the composition to fuse with the substrate, occurs prior to the step g) of sintering the electrically conductive particles of the composition.

13. A method as claimed in claim 11, wherein the heating of the substrate and the composition, to cause the composition to fuse with the substrate, occurs subsequent to the step g) of sintering the electrically conductive particles of the composition.

14. A method as claimed in any one of claims 1 to 13, wherein the flexible membrane is selected from a preformed membrane of plastics polymer and a cast plastics polymer.

15. A method as claimed in claim 14, wherein the plastics polymer is a thermoplastic polymer, selected from the group consisting of cyclic olefin copolymer (COC), polyethylene (PE), polypropylene (PP), thermoplastic polyurethane (TPU), and combinations thereof.

16. A method as claimed in claim 15, wherein the preformed membrane consists of at least two layers, at least one of the layers comprising the thermoplastic polymer.

17. A method as claimed in any one of claim 1 to claim 16, wherein the first surface of the flexible membrane has a mean roughness *Rz* of 1 μm or less, of 500 nm or less, of 250 nm or less, or 100 nm or less.

18. A method as claimed in any one of claim 1 to claim 17, wherein the particles of electrically conductive material are made of compounds selected from the group consisting of metals, alloys, organo-metals, conductive polymers, precursors thereof, salts thereof and combinations thereof.

19. A method as claimed in any one of claims 1 to 18, wherein the adhesive is at least one of a) an organic binder, b) an organic adhesive, and c) glass frits.

20. A method as claimed in claim 19, wherein the organic adhesive is a pressure or heat sensitive adhesive.

21. A method as claimed in any one of claim 1 to claim 20, wherein step e), at which pressure is applied, is performed at a temperature in the range of from 60°C to 200°C.

22. A method as claimed in any one of claim 1 to claim 21, wherein the pattern of grooves in the flexible membrane is formed by a complementary pattern of rules on a patterning element, the flexible membrane and patterning element being in relative motion during patterning, the patterning element optionally being a die roller and the flexible membrane further optionally being a continuous membrane.

23. A method as claimed in any one of claim 1 to claim 22, wherein the composition is sintered in step g) at at least one temperature in the range of from 150°C to 800°C.

24. A method as claimed in any one of claim 1 to claim 23, wherein the grooves form contiguous or distinct straight or curved lines, at least a portion of each line having a tapering cross section profile selected from a triangular, trapezoidal, polygonal, semi-circular, or semi-elliptic profile, any of the profiles having at least a base width W_B and a height h, the dimensionless aspect ratio ASP between the height and the base width being in the range of 5:1 to 1:5, 3:1 to 1:2, 2:1 to 1:1 or 1.75:1 to 1:1.75.

25. A method as claimed in claim 24, wherein a tapering face of the cross section profile (a) forms an angle with the first surface of the membrane of at least 30°, at least 40°, at least 45°, at least 50° or at least 60°, and optionally of at most 90°, at most 85° or at most 80°; and/or (b) has an averaged slope of at least 0.75, at least 1, or at least 1. 3, and optionally of at most 8, at most 4 or at most 2.

26. A method as claimed in any one of claim 1 to claim 23, wherein at least one of the grooves is formed by a patterning element selected from a punch or a laser beam or by a patterning technique including photolithography.

27. A flexible membrane suitable for applying a pattern of electrical conductors to a substrate formed by a surface of a solar cell, the flexible membrane being prepared by the method of any one of claim 1 to claim 26.

28. A flexible membrane suitable for applying a pattern of electrical conductors to a substrate formed by a surface of a solar cell, the membrane having a first surface that includes a pattern of grooves, the grooves being loaded so as to be substantially level with the surface of the membrane with a composition that includes electrically conductive particles and an adhesive, the composition being adapted to become electrically conductive upon

sintering by application of energy thereto, and ungrooved parts of the first surface being substantially devoid of the composition; the membrane being such that upon pressing the membrane and the substrate against one another, the composition in the grooves adheres more strongly to the substrate than to the membrane, and such that subsequent separation of the membrane from the substrate results in the composition remaining on the substrate in a pattern mirroring that of the grooves.

29. A solar cell having a pattern comprising a pattern of electrical conductors applied on a light harvesting side thereof, wherein at least part of the electrical conductors fulfil one or more of the following:

a) the electrical conductors have a cross-section profile wherein W_B represents a width of a base of said profile, the base contacting the light harvesting side of the solar cell, h represents an orthogonal distance between the base and a top point of the profile (also termed the height of the profile), and ASP represents an aspect ratio between the height of the profile and the base width ($ASP = h / W_B$), wherein:

i. W_B is at least 5 μm, or at least 10 μm and at most 50 μm, or at most 40 μm, or at most 30 μm, or at most 20 μm;

ii. h is at least 3 μm, at least 5 μm, at least 10 μm, at least 15 μm or at least 20 μm and at most 80 μm, at most 60 μm, at most 50 μm or at most 40 μm; and

iii. ASP is at least 1:2, at least 1:1.75, at least 1:1.5, or at least 1:1 and at most 3:1, at most 2:1 or at most 1.5:1;

b) the cross-section profile of the electrical conductors has at least two sides rising from a base of the profile, wherein an average of a slope along half of the width of the basis, as assessed by the tangent value of the angles formed between at least one of the two sides and the base of the profile, is at least 0.85, or at least 1, or at least 1.15, or at least 1.3 and at most 6, at most 4 or at most 2;

c) the electrical conductors consist of one or more sintered electrically conductive materials;

d) a cross-section slice of the electrical conductors perpendicular to the light harvesting side of the solar cell comprises two or more layers of different sintered materials, the layers optionally following the profile of the cross-section of the conductors; and

e) the electrical conductors have an external surface, the external surface having light reflective properties.

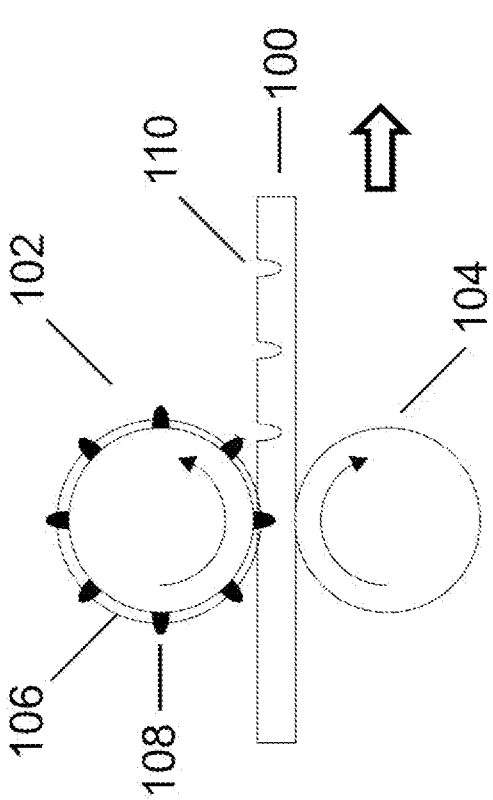


FIG. 1A

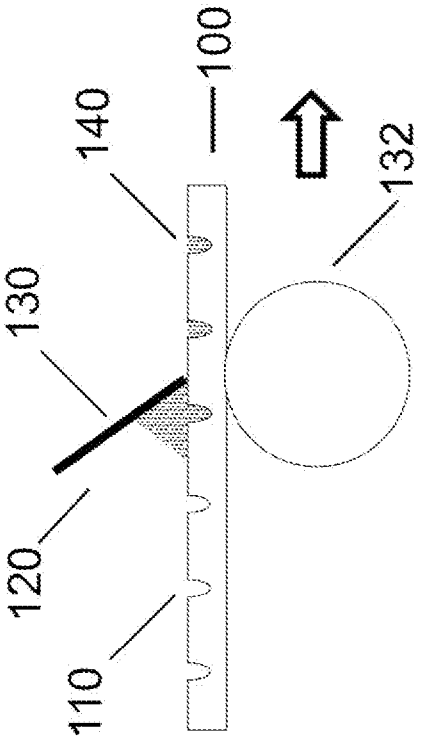


FIG. 1B

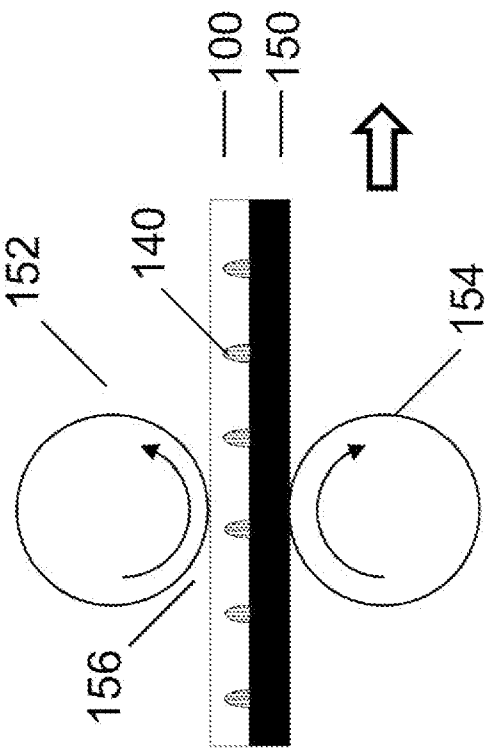


FIG. 1C

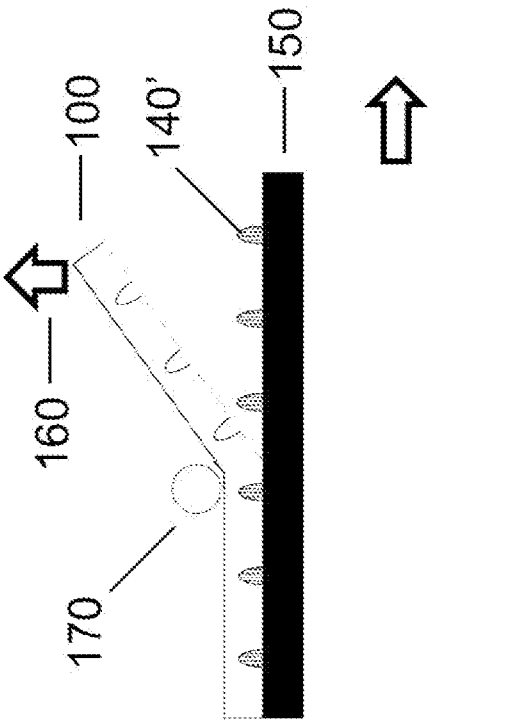


FIG. 1D

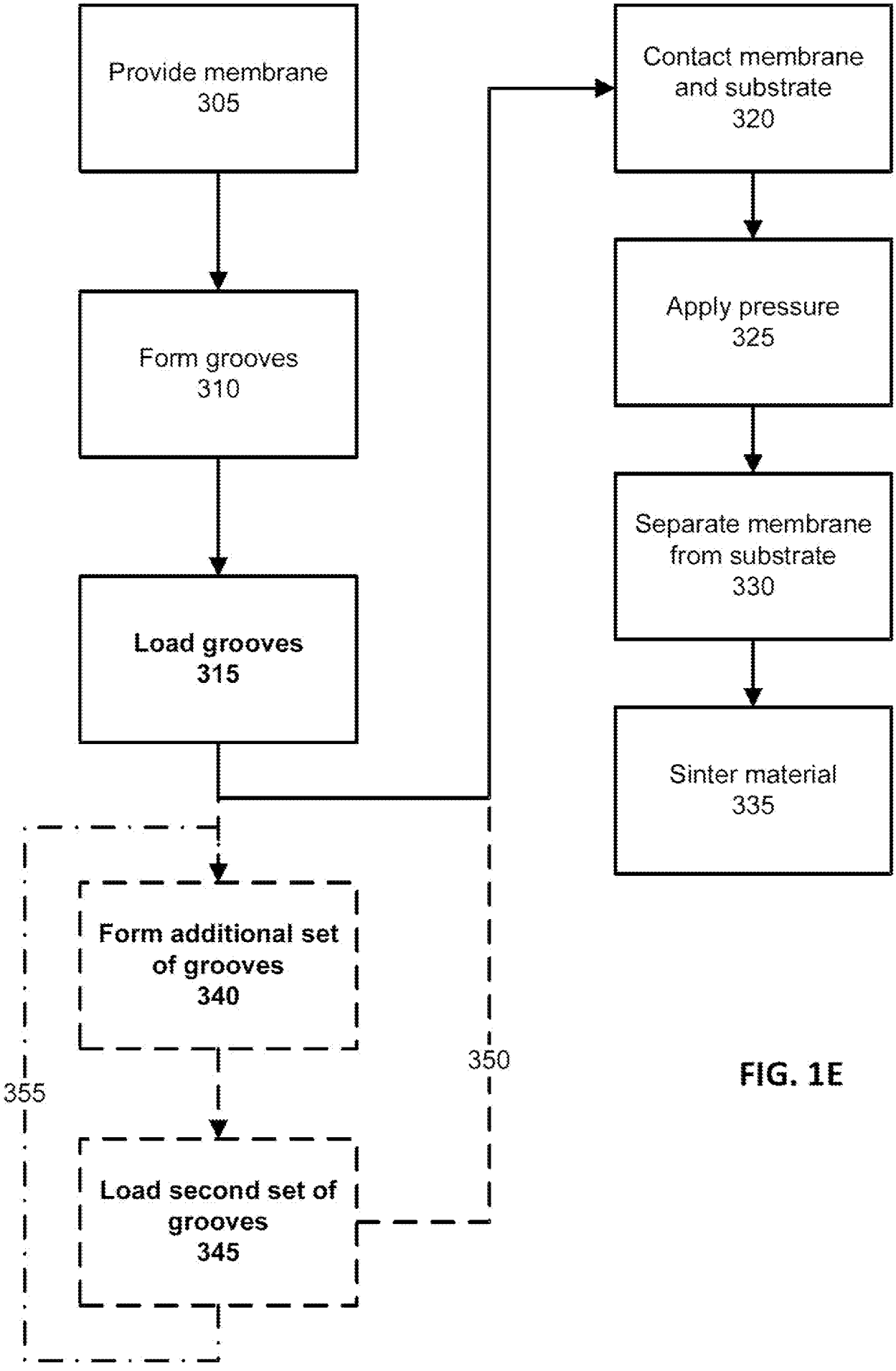

Provide membrane
305
Form grooves
310
Load grooves
315
Form additional set of grooves
340
Load second set of grooves
345
355
350
Contact membrane and substrate
320
Apply pressure
325
Separate membrane from substrate
330
Sinter material
335

FIG. 1E

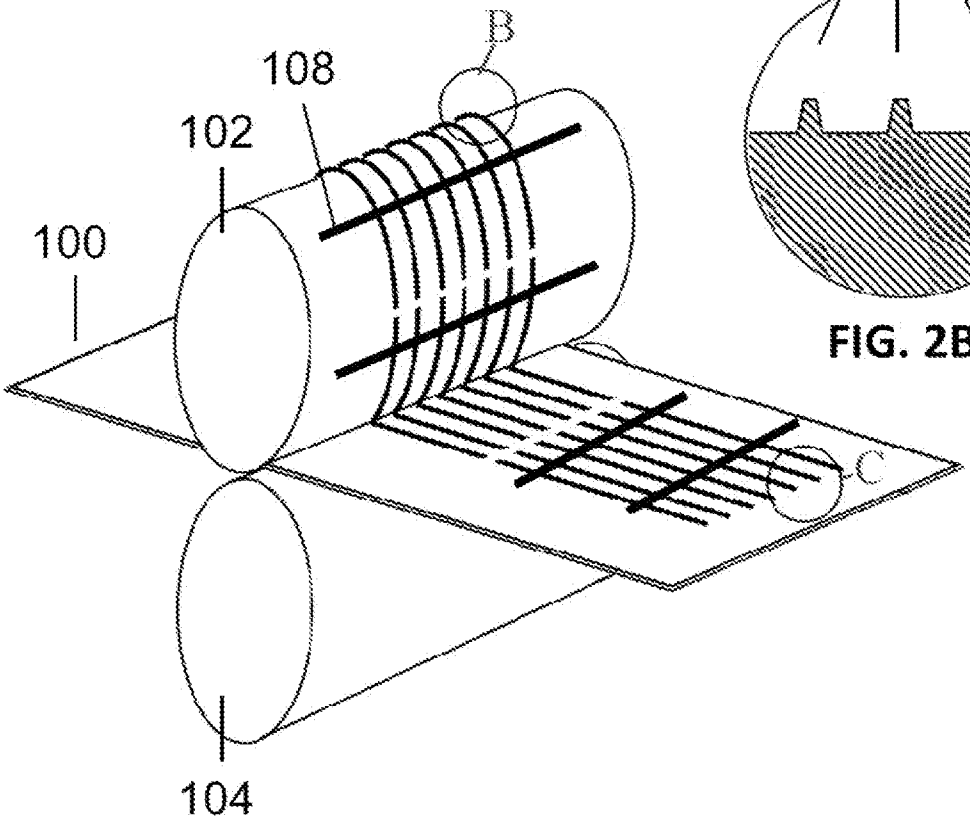


FIG. 2A

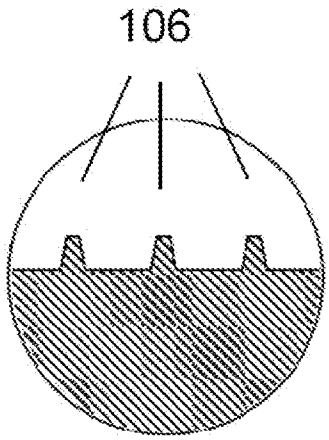


FIG. 2B

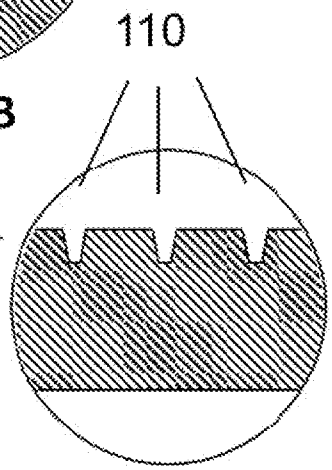


FIG. 2C

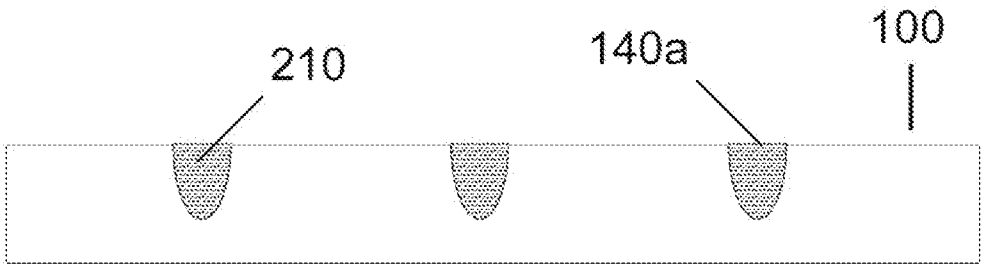


FIG. 3A

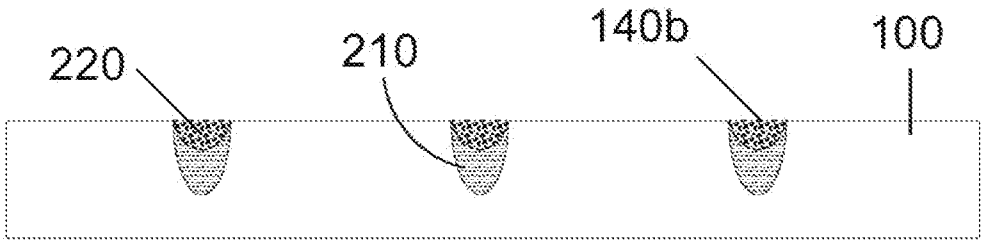


FIG. 3B

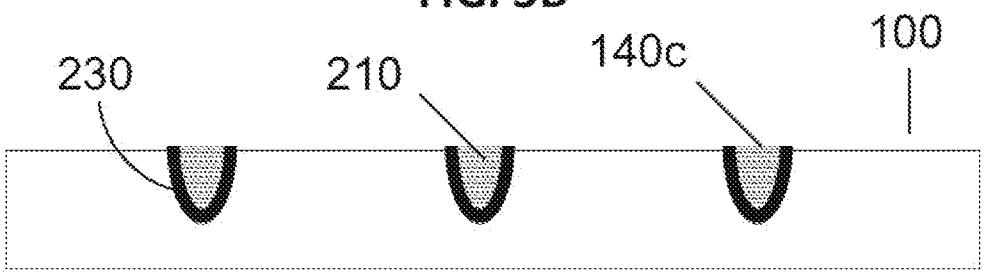


FIG. 3C

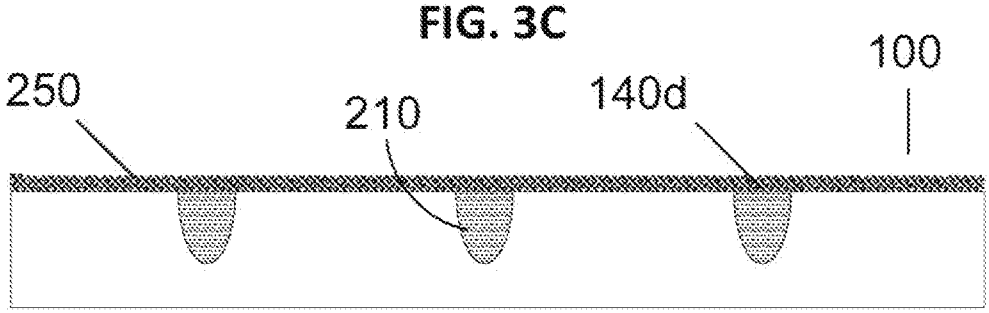


FIG. 3D

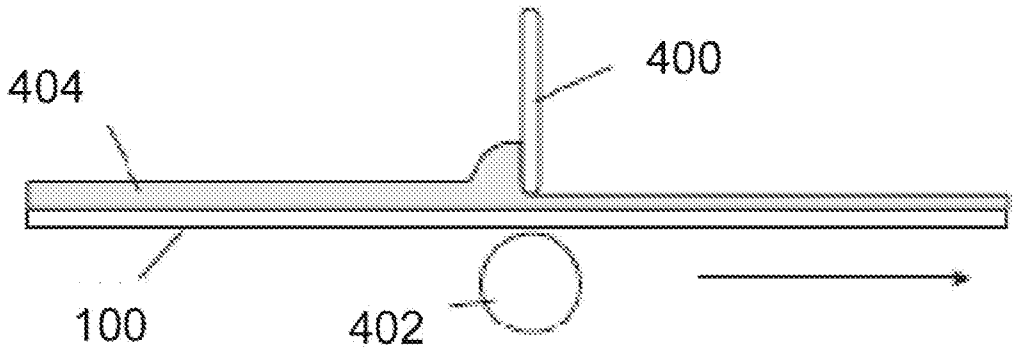


FIG. 4A

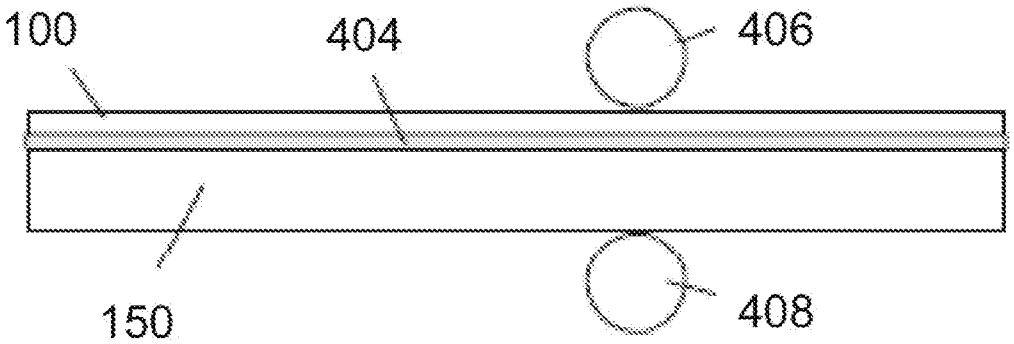


FIG. 4B

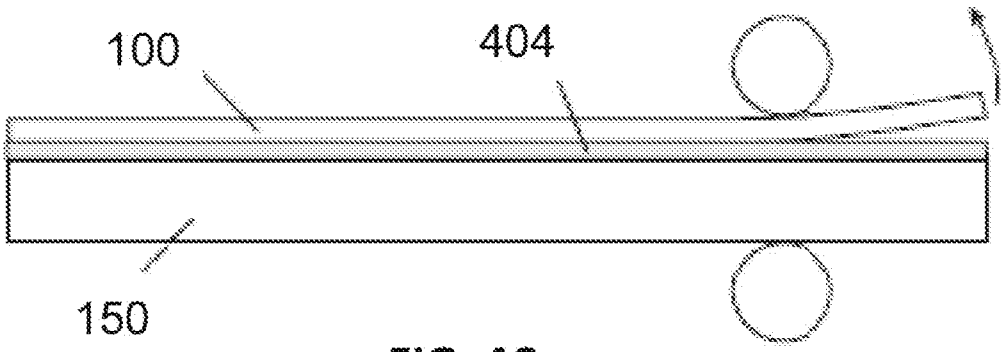


FIG. 4C

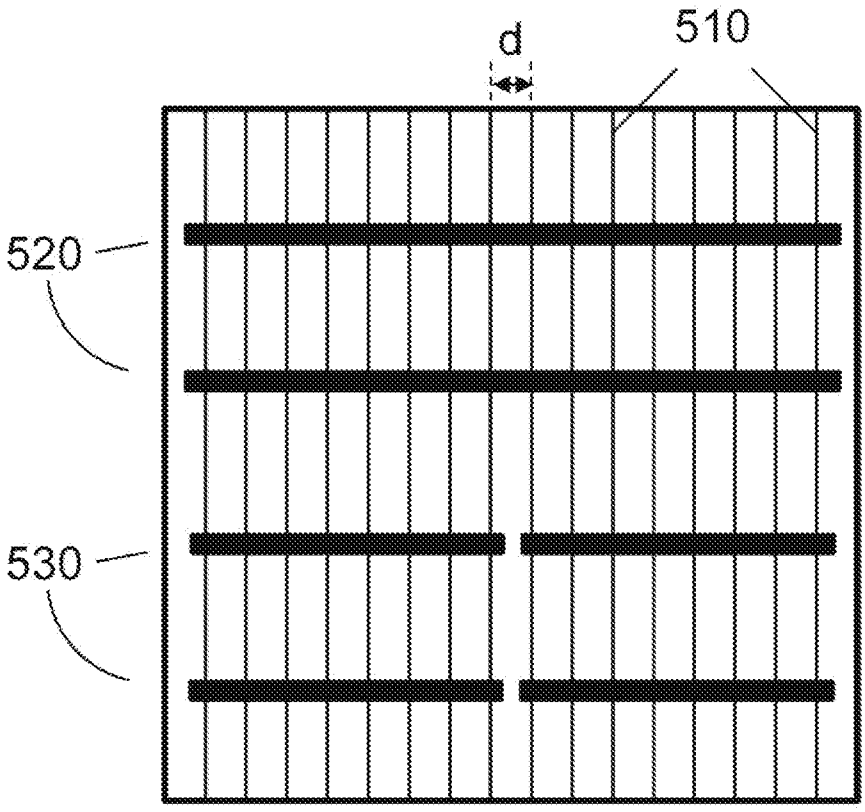


FIG. 5A

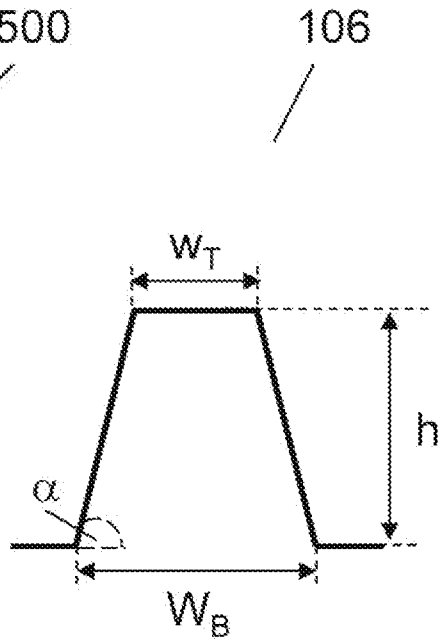


FIG. 5B

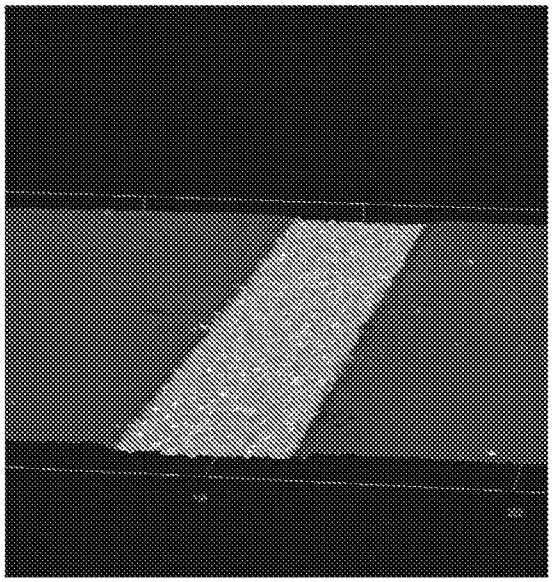


FIG. 5C

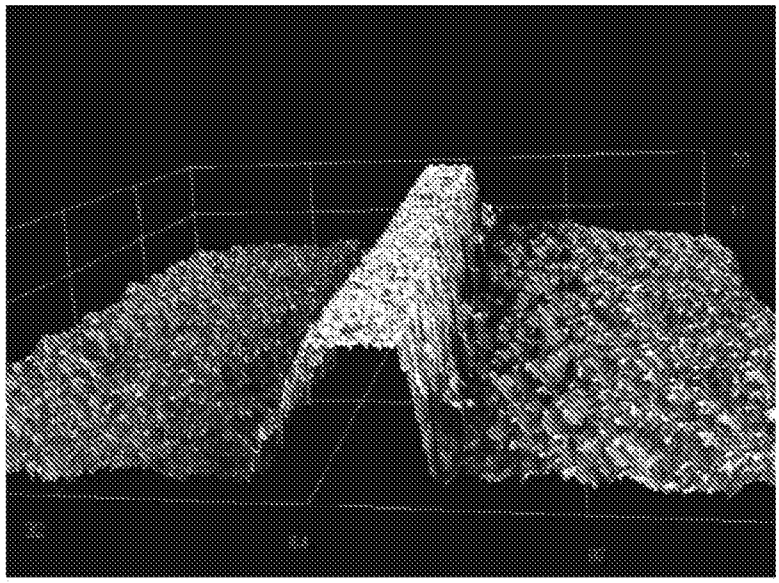


FIG. 5D

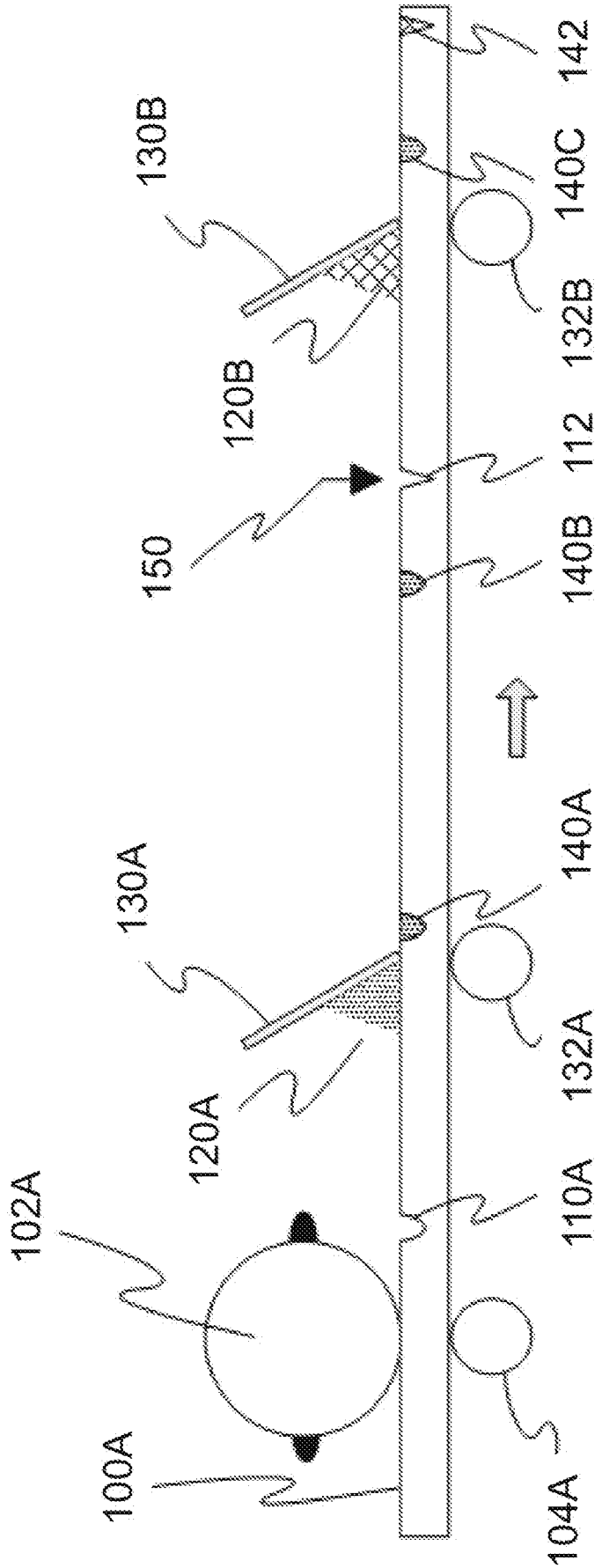

102A
100A
104A
120A
130A
110A
132A
140A
150
120B
130B
112
132B
140B
140C
142

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/054626

A. CLASSIFICATION OF SUBJECT MATTER
INV. H05K3/20 H01L31/0224
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H05K H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2013 0090590 A (KOREA ADVANCED INST SCI & TECH [KR]; HANA MICRO CO LTD [KR]) 14 August 2013 (2013-08-14) abstract; figures 1,5 paragraphs [0015], [0020], [0023], [0027], [0028], [0032], [0033]	1-29
X	US 5 609 704 A (HAYAMA MASAAKI [JP] ET AL) 11 March 1997 (1997-03-11)	1,27,28
A	abstract; figures 3-5 column 4, line 37 - column 11, line 11	29
X	US 2002/056509 A1 (MIURA KAZUHIRO [JP] ET AL) 16 May 2002 (2002-05-16)	1,27,28
A	abstract; figure 1 paragraph [0009] - paragraph [0020]	29

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 October 2017	12/10/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Favre, Pierre

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/054626

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	abstract; figures 6-12	29

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A	abstract; figures 1-15 column 2, line 11 - column 5, line 30 column 12, line 66 - column 13, line 3	29

X	JP 5 889439 B2 (-) 22 March 2016 (2016-03-22)	29
A	abstract; figures 1-10	1

X	US 2011/209749 A1 (YANG MIN YANG [KR] ET AL) 1 September 2011 (2011-09-01)	29
A	abstract; figures 7-12 paragraph [0003]	1

1

INTERNATIONAL SEARCH REPORT

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