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(54) **Titre : PROCEDES DE PRODUCTION DE COUCHES DE TRANSPORT A SELECTION DES CHARGES ET EN FILM MINCE**
(54) **Title: METHODS FOR PRODUCING THIN FILM CHARGE SELECTIVE TRANSPORT LAYERS**

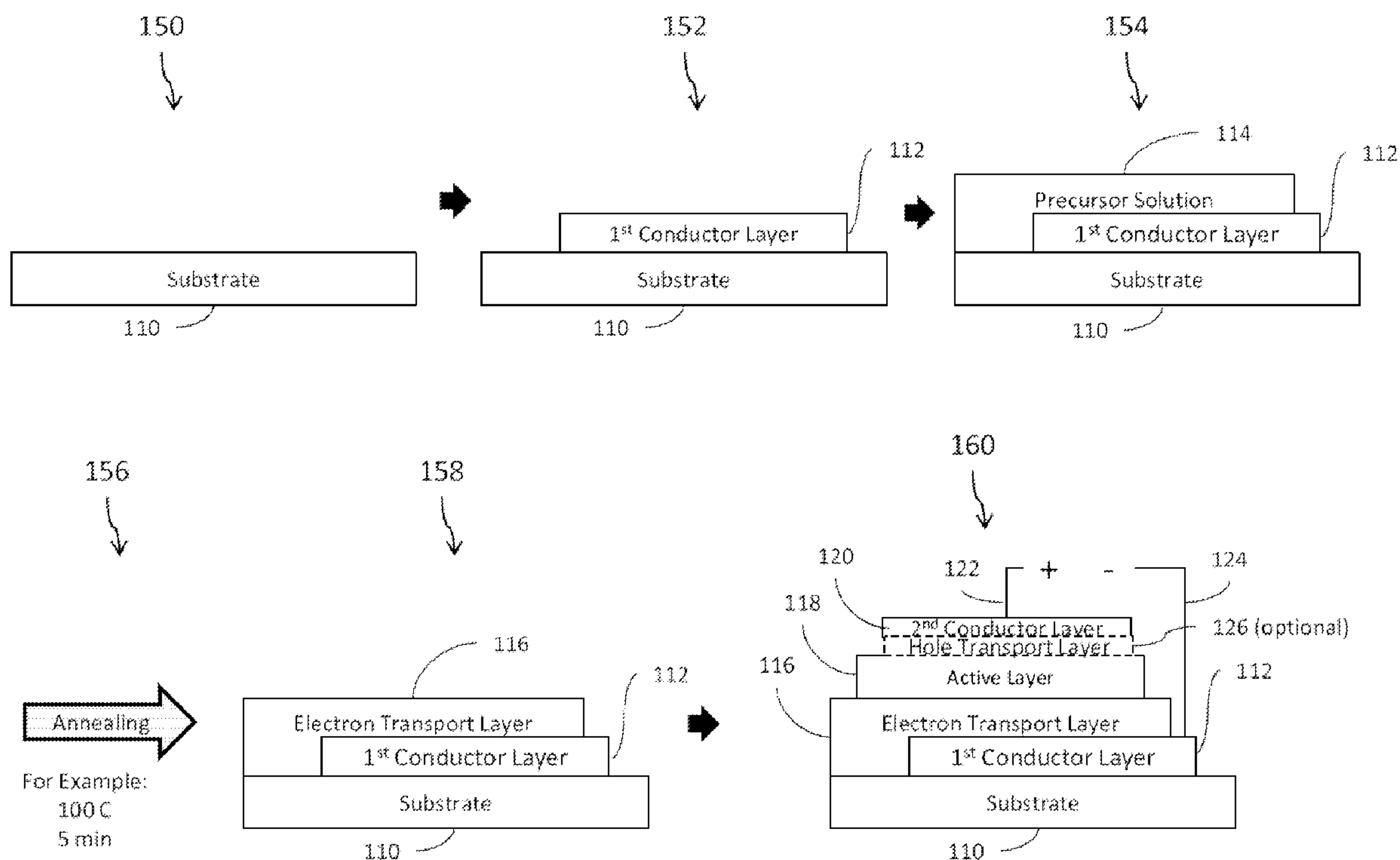

Figure 1

(57) **Abrégé/Abstract:**
Methods for producing thin film charge selective transport layers are provided. In one embodiment, a method for forming a thin film charge selective transport layer comprises: providing a precursor solution comprising a metal containing reactive precursor material

(57) **Abrégé(suite)/Abstract(continued):**
dissolved into a complexing solvent; depositing the precursor solution onto a surface of a substrate to form a film; and forming a charge selective transport layer on the substrate by annealing the film.

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(54) Title: METHODS FOR PRODUCING THIN FILM CHARGE SELECTIVE TRANSPORT LAYERS

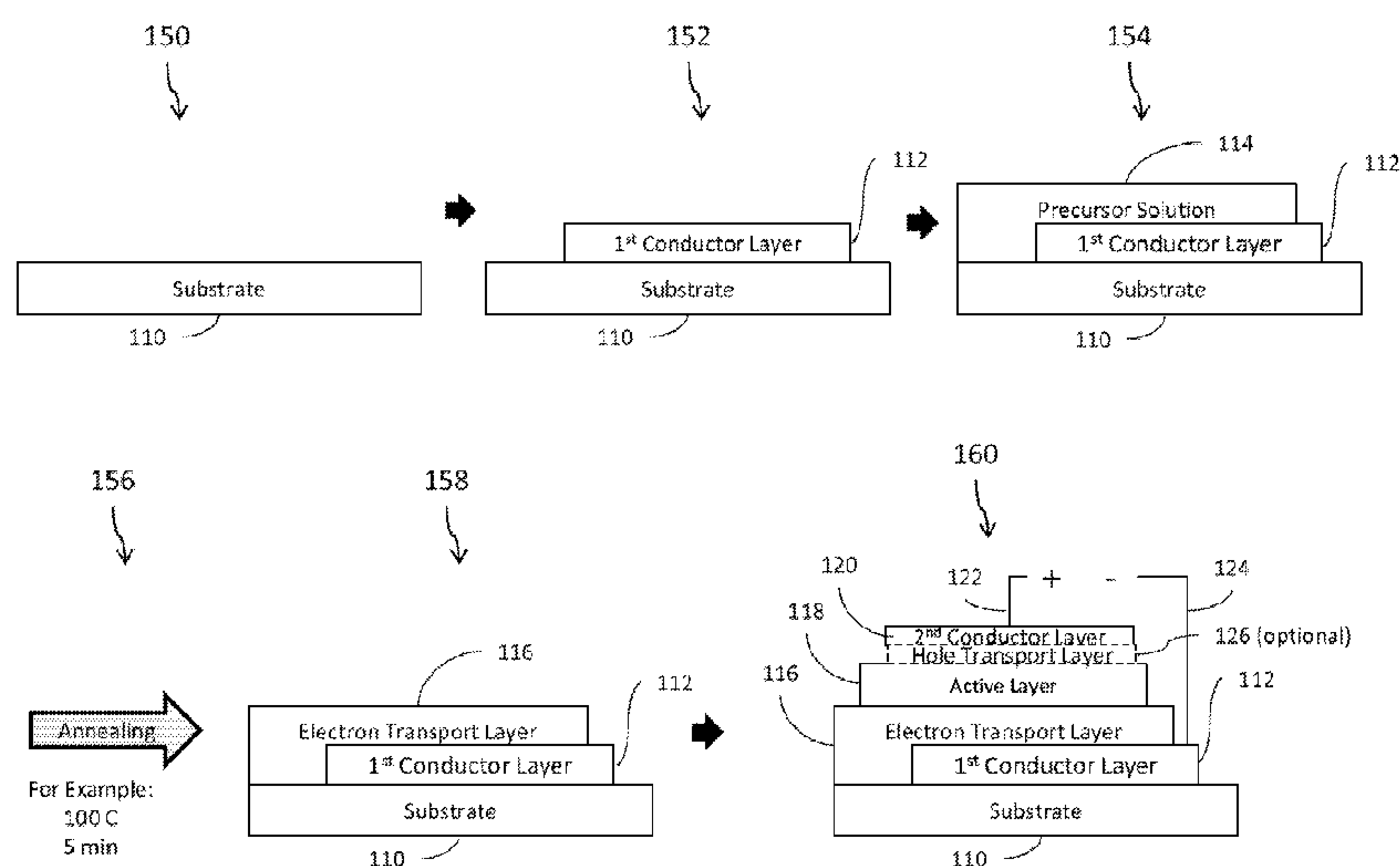

Figure 1

(57) Abstract: Methods for producing thin film charge selective transport layers are provided. In one embodiment, a method for forming a thin film charge selective transport layer comprises: providing a precursor solution comprising a metal containing reactive precursor material dissolved into a complexing solvent; depositing the precursor solution onto a surface of a substrate to form a film; and forming a charge selective transport layer on the substrate by annealing the film.

METHODS FOR PRODUCING THIN FILM CHARGE SELECTIVE TRANSPORT LAYERS

Cross-Reference to Related Applications

[0001] This Application claims priority to, and the benefit of, U.S. Provisional Application No. 61/774,200, entitled "A METHOD OF PRODUCING A THIN FILM FOR USE AS AN ELECTRON- OR HOLE-TRANSPORT LAYER IN OPTOELECTRONIC DEVICES" filed on March 7, 2013, which is incorporated herein by reference in its entirety.

Contractual Origin

[0002] The United States Government has rights in this invention under Contract No. DE-AC36-08GO28308 between United States Department of Energy and the Alliance for Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy Laboratory.

Background

[0003] Optoelectronic devices are an increasingly central part of everyday life. Smart phones, computers, televisions, handheld electronics, radio-frequency ID tags (RFIDs), 'smart' appliances, photovoltaic devices, and more, include such optoelectronic devices. Examples of such devices include: displays, such as liquid crystal displays (LCDs) and organic light emitting diode displays (OLEDs); photovoltaic (PV) devices, including crystalline silicon, inorganic thin-film, and organic photovoltaic (OPV); and field-effect transistors (FETs), which are a key element in many electronic devices. The trend is to reduce the size and/or cost of these optoelectronic devices in order to enable widespread commercial adoption. Once low enough thresholds are reached for size and/or cost, such devices are expected to become nearly ubiquitous in everyday life.

[0004] In order to make these devices more cost-effective, techniques that allow high-throughput large-area manufacturing are needed to reduce the cost per unit device to reasonable levels. While optoelectronic devices are diverse, and thus the materials and manufacturing techniques involved vary quite a bit, there are a number of common elements in a variety of optoelectronic devices. Many such devices require the controlled transport of electrons and/or holes (i.e., electron vacancies) into or out of the device, in order to precisely control the flow (e.g., in FETs),

separation (e.g., in PV), or recombination (e.g., in OLEDs) of such particles in the device, enabling the desired device properties. The materials used to enable such controlled flow of electrons or holes in a device are referred to as electron transport layers or hole transport layers (ETLs or HTLs), respectively. An ETL will allow the transport (flow, collection, or injection, depending on the device) of electrons, while blocking the transport of holes in a device, while a HTL will do the opposite.

[0005] While there are a variety of ETL and HTL materials used in the many various types and versions of optoelectronic devices in existence, many common transport layers are based upon metal oxide thin films. Metal oxide thin films have a number of advantages over alternative materials, such as thin polymer films and self-assembled monolayers (SAMs). Metal oxide thin films are relatively well-studied and understood materials and are generally physically, thermally, and chemically robust. The variety of metals that form useable oxides ensure a broad range of such device-important physical properties, such as n-type or p-type material, work function, conductivity, electron/hole mobility, optical transparency and reflectivity. In contrast to metal oxides, thin polymer film transport layers are generally much less well studied and understood materials, often have low mobilities, which require very thin films (~5 nm) to ensure adequate performance, and as such often have poor physical robustness. Additionally, thin polymer films are generally much less thermally stable than metal oxides. Similarly, SAM transport layers are poorly studied materials, and are not currently well understood. Their monolayer nature ensures very fragile films with high potential for pinholes/shorts and often exhibit poor thermal and chemical stability.

[0006] Metal oxide thin films can be produced via a variety of techniques, including: sputtering, chemical vapour deposition (CVD), pulsed-laser deposition (PLD), atomic layer deposition (ALD), thermal evaporation, and sol-gel chemistry methods. These techniques share a common disadvantage in that they either require a vacuum based process to enable the film deposition or they require subjecting materials to high temperatures for extended time periods. Vacuum-based process significantly increases the time and cost of depositing metal oxide thin films, as samples are pumped down to the desired vacuum levels, the deposition performed, and then the samples returned to atmospheric pressure levels. High temperature techniques, which often require temperatures in excess of 300 °C, add significant cost due to the high energy demands on obtaining and maintaining such temperatures. Furthermore, such high temperatures significantly

limit the range of substrates that can be used. For example, temperatures above 150 °C for extended periods prevent the use of many polymer foils, such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), often used in high-throughput roll-to-roll manufacturing lines. Additionally, elevated temperatures tend to cause damage to any other underlying layers exposed to the high temperatures. Meanwhile, nanoparticle techniques produce materials with diminished transport and hole blocking characteristics as compared metal oxide thin films produced using the sol-gel or vacuum deposition methods, and their use is complicated by wetting and aggregation issues that hinder large-scale production.

[0007] The foregoing examples of the related art and limitations related therewith are intended to be illustrative and not exclusive. Other limitations of the related art will become apparent to those of skill in the art upon a reading of the specification and a study of the drawings.

Brief Description of the Drawings

[0008] Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting. Those skilled in the art will understand that the drawings, described herein, are for illustration purposes only. The drawings are not intended to limit the scope of the present disclosure.

[0009] Figures 1, and 1A -1E illustrate fabrication of a photovoltaic device having a charge selective transport layer of one example embodiment of the present disclosure.

[0010] Figures 2 and 2A – 2E illustrate methods for producing a charge selective transport layer of one example embodiment of the present disclosure.

[0011] Figure 3 is a graph of current density vs. voltage comparing spin-cast vs. slot-die coated zinc oxide ETL according to exemplary embodiments disclosed in the present disclosure.

[0012] Figure 4 is a graph illustrating the performance of a photovoltaic module of one embodiment of the present disclosure.

Detailed Description

[0013] Embodiments of the present disclosure present low temperature solution based methods for fabrication charge selective transport layers for use, for example, in photovoltaic and other optoelectronic devices. More particularly, the present disclosure describes methods of generating thin films suitable for use as charge selective transport layers from precursor

solutions. These charge selective transport layers include both electron transport layers and hole transport layers. In the various embodiments described below, precursor solutions suitable for forming charge selective transport layers may be produced by dissolving a metal containing reactive precursor material into a complexing solvent. The resulting solution is then deposited and annealed to form either an electron transport layer or a hole transport layer. As explained below, whether the charge selective transport layer functions as a hole transport layer or an electron transport layer will depend at least in part on the composition of the metal containing reactive precursor material and the location of the resulting material layer within the device.

[0014] As further detailed below, an electron transport layer is a layer formed between an active layer (such as an active semiconductor hetero-junction layer) and a conductive layer designed to function as an electron emitting terminal (i.e., a cathode) for a device. The presence of an electron transport layer serves two functions: it will have a low enough work function to help provide the built-in field necessary to assist in charge collection, and it will have a proper energy level to efficiently transport electrons while blocking holes. For example, a charge selective transport layer having a work function in the range of 3-4.5 eV would be considered suitable for functioning as an electron transport layer in most applications. This range is however provided as a general guideline because how a work function is measured will cause the measured value to vary. At the same time, one of ordinary skill in the art after reading this disclosure would readily be able to determine, for their particular application, whether a resulting material layer has a work function sufficient for providing an electron transport layer.

[0015] A number of different materials can serve as an electron transport layer, including but not limited to such metal oxides as zinc oxide (ZnO) and titanium oxide (TiO_x) as well as caesium carbonate (Cs_2CO_3), thin polymer dielectrics such as poly[(9,9-bis(3′-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene) (PFN), or self-assembled monolayers (SAMs) based on molecules such as N-propyl trimethoxysilane or aminopropyl triethoxysilane.

[0016] Similarly, and as further detailed below, a hole transport layer is a layer formed between an active layer and a conductive layer that is designed to function as the hole emitting terminal (i.e., an anode) for a device. A hole transport layer should have a high enough work function to help provide the built-in field and have proper energy levels to efficiently transport holes while blocking electrons. For example, a charge selective transport layer having a work function in the range of 4.9-6 eV would be considered suitable for functioning as a hole transport layer in most

applications. This range is however provided as a general guideline because how a work function is measured will cause the measured value to vary. One of ordinary skill in the art after reading this disclosure would readily be able determine for their particular application whether the resulting material layer has a work function sufficient for providing a hole transport layer. As such, a number of different materials can act as a hole transport layer, including but not limited to such metal oxides as: molybdenum oxide (MoO_3), tungsten oxide (WO_3), vanadium oxide (V_2O_5), and nickel oxide (NiO). HTLs may also include doped organic polymeric materials such as polyethylenedioxythiophene:polystyrene sulfonate (PEDOT:PSS).

[0017] Figures 1 and 1A-1E, are diagrams illustrating fabrication of a device comprising charge selective transport layers for example embodiments of the present disclosure. As shown generally at **150**, an exemplary structure begins with a substrate **110**. The substrate material **110** can be any one or more of a number of substrates suitable for deposition of a conducting film. In some embodiments, the substrate comprises one or more of a glass, ceramic, plastic and other organic polymers, semiconductor material, a silicon wafer or other wafer material, or similar materials. In other embodiments, the substrate itself may comprise a photovoltaic cell. Examples of organic polymers, like plastics, include, but are not limited to polyesters such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN).

[0018] Referring next to **152**, a first conductor layer **112** is deposited onto the substrate **110**. The first conductor layer **112** can be any one or more of a number of conducting materials suitable for collecting charge. In some embodiments, first conductor layer **112** comprises a transparent conductor. For example, such a transparent conductor may be implemented using a transparent conducting oxide (TCO), which may include one or more doped metal oxides with considerable conductivity. In one exemplary embodiment, the first conductor layer **112** comprises a doped TCO such as indium tin oxide (ITO). In other embodiments, other materials suitable for fabricating a conductor layer may comprise metal oxides including one or more of many doped metal oxides, including but not limited to: gallium-doped zinc oxide (GZO), indium-doped zinc oxide (IZO), tin-doped indium-oxide (TIO), aluminium-doped zinc-oxide (AZO), indium-doped cadmium-oxide, fluorine-doped tin-oxide (FTO), and combinations thereof.

[0019] In certain embodiments, the first conductor layer **112** can include one or more non-oxide conducting materials, including but not limited to: silver nanowire or carbon nanotube meshes; continuous graphene sheets or small overlapping graphene sheets; highly doped organic

semiconducting polymers, including but not limited to poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS); and TCO nanoparticle films; or any combination thereof.

[0020] In some implementations, the first conductor layer **112** may be employed as a conducting material deposited on top of the substrate **110** (such as shown at **152**) or the first conductor layer **112** may be a layer of conductive material embedded within the substrate **110**. In still other implementations, the first conductor layer **112** may comprise a layer that is adjacent to the region where the precursor solution **114** is deposited.

[0021] Referring next to **154**, a precursor solution **114** is deposited onto one or both of substrate **110** and first conductor layer **112**. Precursor solution **114** is deposited in such a way as to facilitate the electrical coupling of what will become the electron transport layer to the first conductor layer **112**. Some embodiments may optionally include one or more intervening layers (such as a conducting buffer material layer) between the deposited precursor solution **114** and the first conductor layer **112**. In such embodiments, the resulting charge selective transport layer will be electrically coupled to the first conductor layer through the buffer material layer.

[0022] The precursor solution **114** is a solution that comprises a metal-containing reactive precursor material that has been mixed with a complexing solvent. As used herein, a metal containing reactive precursor material is a reactive precursor material which includes compounds having a metal atom, M, which is bonded to one or more species, X. The nature of the M-X bond is such that the molecule readily reacts with water and/or oxygen in an ambient environment in such a way as to convert the M-X bond to a M-O bond, where O represents an oxygen atom, and the H represents a hydrogen atom. This reaction may be represented by: $M\text{-}X_n + H_2O/O_2 \rightarrow M\text{-}O_n(H)$. The O atom may be, but does not necessarily need to be, bonded to a hydrogen atom, H. For example, the metal containing reactive precursor may comprise a pyrophoric precursor material, but it need not be pyrophoric. The complexing solvent serves to stabilize the reactive metal-containing precursor material, mitigating its reactive nature, enabling the handling of the precursor solution in ambient environments containing oxygen and water without compromising the integrity of the precursor material. The precursor material will not react with oxygen or water, and instead will remain complexed with the solvent, over an extended period of time (commonly referred to as the 'shelf-life' of the precursor material). For example, in one embodiment, the precursor solution **114** may contain a pyrophoric precursor material that is stabilized by dissolving it in a complexing solvent under mild conditions. That

is, for such embodiments the precursor solution **114** can be handled at room temperature under normal atmospheric conditions because the complexing solvent renders the solution non-pyrophoric. Utilizing such a precursor solution eliminates the need to provide rigorous oxygen and water-free environments, significantly reducing costs.

[0023] Precursor solution **114** in some embodiments may include an organometallic or a fully inorganic metal material, such as a metal organic (for example, organozinc), metal inorganic (for example, metal halide), metal hydroxide, metal oxide, or any combination thereof, containing for example zinc and/or titanium. In some embodiments, the reactive metal-containing precursor material is diethylzinc, while in other cases it is dimethylzinc.

[0024] A complexing solvent, as the term is used herein, is defined as a solvent wherein the constituent molecules are capable of donating electron density, generally in the form of an electron lone pair, to an electron deficient molecule, such as in a reactive metal-containing precursor material, thus stabilizing it. In such a case, the complexing solvent generally donates the electron density directly to the otherwise electron-deficient metal atom. Examples of complexing solvents include, but are not limited to, diethyl ether, tetrahydrofuran, and diglyme. Other complexing solvents such as, but not limited to, pyridine, acetonitrile, tetramethylethylenediamine, methylpyrrolidone, and dimethyl sulfoxide may also be used.

[0025] Several methods are available for applying a precursor solution onto the preceding layers of the device that avoids any need for high vacuum and high temperature deposition techniques. These methods include, but are not limited to: slot-die coating, spin-casting, drop-casting, dip-coating, knife coating, spray-coating, ink-jet printing, screen printing, Mayer rod coating, Gravure coating, Flexo printing, or curtain coating.

[0026] For example, in some embodiments precursor solution **114** is deposited onto the substrate **110** and first conductor layer **112** via spin-casting. The thickness of the resulting electron-transport layer **116** can be controlled by adjusting the concentration of the precursor in the complexing solvent, and by controlling the spin speed. In some embodiments, the precursor solution **114** is deposited onto the substrate **110** and first conductor layer **112** by using a technique that is compatible with high-throughput roll-to-roll manufacturing, such as slot-die coating. In that case, the thickness of the electron transport layer **116** can be controlled by adjusting the concentration of the precursor in the complexing solvent, by controlling the web

speed, and/or by controlling the flow rate at which the precursor solution **114** is provided into the process.

[0027] Referring next to **156**, the precursor solution **114** is annealed resulting in the formation of an electron transport layer **116**, as shown generally at **158**. Depending on the nature of the reactive metal-containing precursor material and the target metal, the annealing step can vary in both temperature and time, but due to the reactive nature of the precursor material, the conversion process is generally accomplished at low temperatures that are compatible with a wide variety of substrate and conductor materials. That is, at the temperatures applied, the annealing does not result in adverse degradation of the substrate, conductor or any other prior layer. Both the time and temperature of the annealing can be tailored to the materials utilized.

[0028] In some embodiments, annealing can occur for a period of time ranging from about 1 minute to about 15 minutes. In other embodiments, the annealing can occur at a temperature ranging from about 100 °C to about 120 °C, which is advantageous for use with sensitive substrate materials, such as polymer substrates in high-throughput roll-to-roll manufacturing conditions, or in the case of sensitive first conductor materials. In yet other embodiments, the annealing can occur at a temperature ranging from 100-300 °C. It should be considered within the skill of one of ordinary skill in the art who has studied the teachings of this disclosure to choose appropriate annealing times and temperatures for the particular precursor, substrate and conductor layer materials they have selected.

[0029] In Figure 1, the electron transport layer **116** is positioned between the first conductor layer **112** and an active layer **118**. Exemplary embodiments of the electron transport layer **116** may have a thickness between 25-200nm. In the laboratory, exemplary embodiments such as those described herein have shown uniformity of the films produced to be at least 90% over large areas. It should be noted that the resulting electron transport layer **116** in some embodiments will comprise the same base materials as a transparent conductor. For example, a ZnO electron transport layer may be formed onto a doped ZnO transparent conductor, such as aluminium-doped zinc oxide (AZO).

[0030] Figures 1A and 1B provide illustrations of alternate implementations of the process illustrated in Figure 1 where one or both of the precursor depositions shown at **154** and the annealing shown at **156** are performed through two are more interactive steps.

[0031] For example, referring to Figure 1A, an alternate embodiment is illustrated at **170** and **171** where the precursor solution **114** is deposited as a first precursor solution layer **114-1** followed by deposition of at least one subsequent precursor solution layer **114-2**. Although Figure 1A illustrates two precursor layers (**114-1** and **114-2**), any number of multiple depositions may be performed to form any number of precursor solution layers. The plurality of precursor solution layers are then annealed at **156** to form the electron transport layer **116**.

[0032] In Figure 1B another embodiment is illustrated where precursor deposition and annealing steps are alternated to form electron transport layer **116**. That is, a first precursor solution layer **114-1** is deposited as shown generally at **175**. This is followed by an annealing step (shown at **176**), which forms a first layer **116-1** of material for the electron transport layer **116** (shown at **177**). Then a second precursor solution layer **114-2** is deposited on top of the previously formed electron transport material **116-1** as shown generally at **178**. This is followed by another annealing step (shown at **179**), which forms a second layer **116-2** of material for the electron transport layer **116** (shown at **180**). Multiple iterations of these alternating deposition and annealing steps may be performed until an electron transport layer **116** of the desired thickness is achieved.

[0033] Forming the electron transport layer **116** through multiple depositions of precursor material, as shown by either Figures 1A or 1B, has the benefit of avoiding pinhole voids that otherwise may form and penetrate completely through the electron transport layer **116**. Conductive materials from later applied layers can enter these pinholes degrading the effectiveness of electron transport layer **116** in blocking hole transport. When such pinholes occur, they do so with a random distribution with respect to the upper surface of the layer **116**. Deposition of layer **116** in multiple passes (either as shown in Figure 1A or 1B) results in different sub-layers of the electron transport layer **116** with different randomly located pinholes, substantially reducing the probability of any pinhole completely penetrating through the entirety of electron transport layer **116**.

[0034] As shown in Figure 1 at **160**, once formation of the electron transport layer **116** is completed, subsequent layers may be deposited based on the desired function of the completed device. In some embodiments, the resulting device will further include an active layer **118** and a second conductor layer **120**. It may also include an optional second charge selective transport layer that functions as a hole transport layer **126**. To complete fabrication, in one embodiment a

first conductive lead **124** is coupled to the first conductor layer **112** and a second conductive lead **122** coupled to the second conductor layer **120**.

[0035] Depending on the type of device being implemented, the active layer **118** may comprise an appropriate semiconductor junction. For example, for an organic photovoltaic device (OPV) active layer 118 may comprise a heterojunction, such as a bulk or planar heterojunction, for example. For an OPV device, the materials used to fabricate active layer **118** may include, but are not limited to, poly(3-hexylthiophene):phenyl C_{61} butyric acid methyl ester (P3HT:PCBM) blends, PCPDTBT:PCBM blends, Si-PCPDTBT:PCBM blends, PCDTBT:PCBM blends, PTB7:PC_{71}BM blends, or any combinations thereof. The second conductor layer **120** can be any one or more of a number of conducting materials suitable for collecting charge such as those mentioned for 1st conducting layer **112**. Further, either of the conductor layers **112** and **120** may comprise one or more metals including, but not limited to magnesium, silver, gold, aluminium, copper, palladium, cadmium, nickel, or zinc. Other optoelectronic devices may be implemented such as, but not limited to: inorganic thin-film PV devices and modules, organic or inorganic light-emitting diodes (LEDs), and organic or inorganic field-effect transistors (FETs).

[0036] As mentioned above, the embodiment shown in Figure 1 at **160**, further comprises a hole-transport layer **126** positioned between the active layer **118** and the second conductor layer **120**. This second charge selective transport layer may be fabricated in the same way as described above for an electron transport layer, but using a second precursor solution having a different selection of metal containing reactive precursor material and a complexing solvent appropriate for that material. For example, a precursor solution for a hole transport layer may be prepared by dissolving a metal containing reactive precursor material, such as one containing nickel. This precursor solution may be deposited onto an active layer and annealed into a nickel oxide (NiO) hole transport layer. A number of other materials can also be used to provide a hole transport layer, including but not limited to such metal oxides as: molybdenum oxide (MoO_3), tungsten oxide (WO_3), and vanadium oxide (V_2O_5).

[0037] As illustrated in Figure 1C, after deposition of the active layer **118** (shown at **161**), the second precursor solution **121** is deposited onto the surface of the active layer **118** (shown at **162**). Any of the solution deposition methods described above for the first precursor material **114** may be utilized to deposit the second precursor material **121**, again avoiding the need for high vacuum or high temperature deposition techniques to create this layer. The second

precursor solution **121** is then annealed (shown at **163**) to form a hole transport layer **126** (shown at **164**). The second conductor layer **120** would then be deposited on the hole transport layer **164** and used to electrically couple an anode for the device to the active layer **118**.

[0038] Figures 1D and 1E provide illustrations of alternate implementations of the process illustrated in Figure 1C where one or both of the second precursor depositions shown at **162** and the annealing shown at **163** are performed through two or more interactive steps.

[0039] For example, referring to Figure 1D, an alternate embodiment is illustrated at **165** and **166** where the precursor solution **121** is deposited as a first precursor solution layer **121-1** followed by deposition of at least one subsequent precursor solution layer **121-2**. Although Figure 1D illustrates two precursor layers (**121-1** and **121-2**), any number of multiple depositions may be performed to form any number of precursor solution layers. The plurality of precursor solution layer are then annealed at **163** to form the hole transport layer **126**.

[0040] In Figure 1E another embodiment is illustrated where precursor deposition and annealing steps are alternated to form hole transport layer **126**. That is, a first layer of the second precursor solution **121-1** is deposited as shown generally at **194**. This is followed by an annealing step (shown at **195**), which forms a first layer **126-1** of material that will form the hole transport layer **126** (shown at **196**). Then a second layer of the second precursor solution **121-2** is deposited on top of the previously formed hole transport material **126-1** as shown generally at **197**. This is followed by another annealing step (shown at **198**), which forms a second layer **126-2** of material for the hole transport layer **126** (shown at **199**). Multiple iterations of these alternating deposition and annealing steps may be performed until a hole transport layer **116** of the desired thickness is achieved.

[0041] As discussed with respect to the electron transport layer **116**, forming the hole transport layer **126** through multiple depositions of precursor material, as shown by either Figures 1D or 1E, has the benefit of avoiding pinhole voids that otherwise may form and penetrate completely through the hole transport layer **126**. Deposition of layer **126** in multiple passes (either as shown in Figure 1D or 1E) results in different sub-layers of the hole transport layer **126** with different randomly located pinholes, substantially reducing the probability of any pinhole completely penetrating through the entirety of hole transport layer **126**.

[0042] In different embodiments, the ETL and HTL layers produced as described above can be used in other optoelectronic devices, including but not limited to: inorganic thin-film PV devices

and modules, organic or inorganic light-emitting diodes (LEDs), and organic or inorganic field-effect transistors (FETs).

[0043] Figure 2 is flow chart illustrating a method **200** for fabricating a charge selective transport layer via one embodiment of the present disclosure. In one embodiment, the method of Figure 2 is utilized in conjunction with fabrication of a photovoltaic device such as the one described above with respect to any of Figures 1 and 1A-1E.

[0044] Method **200** begins at **210** with providing a precursor solution that comprises a metal containing reactive precursor material dissolved into a complexing solvent. As explained above, the metal containing reactive precursor material is a reactive precursor material which includes compounds having a metal atom, M, which is bonded to one or more species, X. The nature of the M-X bond is such that the molecule readily reacts with water and/or oxygen in an ambient environment to convert the M-X bond to a M-O bond. The O atom may be, but does not necessarily need to be, bonded to a hydrogen atom, H. For example, the metal containing reactive precursor may comprise a pyrophoric precursor material, but it need not be pyrophoric. Also as described above, the complexing solvent is a solvent where constituent molecules are capable of donating electron density, generally in the form of an electron lone pair, to an electron deficient molecule. Examples of complexing solvents which may be used at **210** include, but are not limited to: diethyl ether, tetrahydrofuran (THF), and diglyme, pyridine, acetonitrile, tetramethylethylenediamine, methylpyrrolidone, and dimethyl sulfoxide. Such combinations of a metal containing reactive precursor material with a complexing solvent may be used to form the precursor solution **114** shown in Figure 1.

[0045] In one example embodiment, a ZnO electron transport layer is fabricated from a metal containing reactive precursor material such as diethylzinc dissolved into the complexing solvent THF. In one implementation of such an embodiment, a 10 mL of a 15 wt. % solution of diethylzinc in toluene is mixed with 50 mL of THF in the absence of water and oxygen to produce a precursor solution of 2.5 wt. % diethylzinc/THF/toluene solution. In one alternate implementation, the diethylzinc can be mixed directly with THF, without the use of a toluene solution, in the absence of water and oxygen, to produce a precursor solution of 2.5 wt. % diethylzinc/THF solution. Either of such precursor solutions may be used, for example, for formulating precursor solution **114**.

[0046] Method **200** proceeds to **220** with depositing the precursor solution onto a surface of a substrate to form a film. In one embodiment, the film at least in part contacts a first conductor. As discussed above, the first conductor's ultimate purpose is to conduct electrons received from the electron transport layer that will be created from the precursor solution. As such, the precursor solution is deposited in such a way as to facilitate the electrical coupling of the electron transport layer with the first conductor. In one embodiment, the first conductor comprises a conductor layer deposited on top of a substrate surface. Figure 1 illustrates one such embodiment at **154** where first conductor layer **112** is deposited on top of substrate **110**. In other implementations, the conductor layer may be a layer of conductive material embedded within the substrate. In still other implementations, the first conductor may comprise a layer that is adjacent to the region where the precursor solution is deposited. Further, in some embodiments, one or more intervening layers may exist between the deposited precursor solution **114** and the first conductor. However, in such embodiments, the one or more intervening layers either are, or will become, conductive layers that will establish electrical coupling between the electron transport layer and the first conductor. For example, the one or more intervening layers may comprise a buffer layer that indirectly couples the electron transport layer to the first conductor.

[0047] Examples of deposition methods which may be used at **220** include, but are not limited to, slot-die coating, spin-casting, drop-casting, dip-coating, knife coating (also known as doctor blading), spray-coating, ink-jet printing, screen printing, Mayer rod coating (also known as metering rod coating), Gravure coating, Flexo printing, and curtain coating. The particular method used may be selected based on its compatibility with other manufacturing processes being used. For example, in one implementation, the precursor solution is deposited using a technique that is compatible with high-throughput roll-to-roll manufacturing, such as slot-die coating. In that case, the thickness of the electron transport layer can be controlled, for example, by varying the concentration of the metal containing reactive precursor material mixed with the complexing solvent, by controlling the web speed and/or the flow rate at which the precursor solution is applied to the substrate.

[0048] **Method 200** proceeds to **230** with annealing the film to transform the precursor film into an electron transport layer. Such annealing is represented in **Figure 1** generally at **156** to form the electron transport layer **116** shown generally at **158** and **160**. Both the time and temperature of annealing at **230** may be controlled so as to not adversely affect the substrate material or other

previously deposited materials. Depending on the particular material used, typical annealing can be achieved within a period of time ranging from about 1 minute to about 15 minutes and temperatures ranging from about 100 °C to about 120 °C. Such duration and temperatures would, for example, be advantageous for use with substrates, such as polymer substrates used in high-throughput roll-to-roll manufacturing conditions. However, when the particular materials permit, annealing can be performed at a temperature ranging from 100-300 °C.

[0049] In the above-mentioned embodiment where method **200** is utilized to produce a ZnO electron transport layer, the depositing performed at **220** may comprise slot-die coating of the precursor solution. For example, in one implementation, the precursor solution produced from the diethylzinc and THF is slot-die coated onto the substrate at room temperature, in normal ambient atmosphere, to form a film. The resulting thin film, which will include zinc oxides and hydroxides, is annealed at **230**, at a temperature of 100 °C for 5 minutes to produce an electron transport layer comprising a ZnO thin film. Slot-die coating of such ZnO thin films from stabilized diethylzinc solutions on substrates as large as 6" x 6" have produced very high quality thin and uniform films, which demonstrates the potential for very large area roll-to-roll fabrication. Optical profilometry of such films show very smooth films with root-mean-squared surface roughness (R_q) values of ~ 1.65 nm. The thickness of the ZnO thin film electron transport layer can be varied depending on the precursor concentration (1-10 wt.%), solution flow rate (0.1-5 mL/min), and coating speed (0.5-5 m/min), with typical thickness values of 25-200 nm, as determined via stylus profilometry. The uniformity of the films produced has been estimated via UV-visible absorption mapping to be as high as 90% over large areas. The work function of the ZnO produced has been measured to be between 4.0 and 4.5 eV by Kelvin probe (referenced to a gold film).

[0050] Forming the electron transport layer **116** through multiple depositions of precursor material, as shown by either Figures 1A or 1B, has the benefit of avoiding pinhole voids that otherwise may form and penetrate completely through the electron transport layer **116**. Conductive materials from later applied layers can enter these pinholes degrading the effectiveness of electron transport layer **116** in blocking hole transport. When such pinholes occur, they do so with a random distribution with respect to the upper surface of the layer **116**. Deposition of layer **116** in multiple passes (either as shown in Figure 1A or 1B) results in different sub-layers of the electron transport layer **116** with different randomly located pinholes,

substantially reducing the probability of any pinhole completely penetrating through the entirety of electron transport layer **116**.

[0051] Figures 2A and 2B provide illustrations of alternate implementations of the process illustrated in Figure 2 where one or both of the precursor deposition shown at **220** and the annealing shown at **230** are performed through two are more interactive steps. Forming a charge selective transport layer through multiple depositions of precursor material, as shown by either Figures 2A or 2B or elsewhere in this description, has the benefit of avoiding pinhole voids that otherwise may form an penetrate completely through the electron transport layer for the reasons previously described above.

[0052] For example, referring to Figure 2A, an alternate embodiment is illustrated at **202** where the deposit of block **220** and annealing at block **230** are further defined. In this embodiment, **221** comprises depositing a precursor solution onto a surface of a substrate to form a first film layer, where the first film at least in part contracts a 1st conductor. The process then proceeds to **222** with depositing the precursor solution onto a surface of the first film to form a second film layer. The process then proceeds to **231** with annealing the first film layer and the second film layer to transform the first film layer and second film layer into an electron transport layer. It would be appreciated that depositing one or more additional layers of the precursor solution onto the previously deposited precursor solutions may be performed before proceeding to **231**. The plurality of precursor solution layers are then annealed at **231** to form the electron transport layer.

[0053] In Figure 2B another embodiment is illustrated where precursor deposition (block **220**) and annealing (block **230**) steps are alternated to form the electron transport layer. That is, a first deposition is shown generally at **235** with depositing a precursor solution onto a surface of a substrate to form a first film layer. This deposition may lay the first film so that it at least in part contracts a 1st conductor, or it may be deposited on an intervening layer that provides a conductive path to the 1st conductor. The method proceeds with annealing the first film layer to transform the first film layer into a first electron transport layer at **235**. Then another layer of precursor solution is applied and annealed. At **226**, the process proceeds with depositing a precursor solution onto a surface of the first electron transport layer to form a second film layer and then to **236** with annealing the second film layer to transform the second film layer and the first electron transport layer into single electron transport layer. Multiple iterations of these

alternating deposition and annealing steps may be performed until an electron transport layer of the desired thickness is achieved.

[0054] Also as shown in **Figure 2**, method **200** may further comprise one or more additional steps to achieve various optional or alternate embodiments for specific applications. For example, in one embodiment, method **200** proceeds to **240** with forming an active layer on the electron transport layer. The particular materials for forming the active layer are selected based on the desired function of the device as already described above for active layer **118** and apply to this method, and as such are not repeated here in detail.

[0055] Regardless of the particular application, the placement of the electron transport layer between the active layer and the **first** conductor will result in a device where electrons are permitted to flow from the active layer to the **first** conductor, but holes are not, so that an electrical lead coupled to the **first** conductor will function as the cathode lead for the device (such as mentioned at **250**). In one embodiment (illustrated at **247**), a second conductor is electrically coupled to the active layer such that an electrical lead coupled to the second conductor will function as the anode lead for the device (such as mentioned at **250**). Further, in one embodiment illustrated by **245**, a hole transport layer is formed on the active layer prior to the second conductor (such as hole transport layer **126** shown in **Figure 1**). Analogous in function to the electron transport layer, the placement of a hole transport layer between the active layer and the second conductor will result in a device where hole current is permitted to flow from the active layer to the second conductor, but electrons are not.

[0056] As shown in Figure 2C, the forming of the hole transport layer is consistent with the process described above with respect to Figures 1 and 1A-1E. In one embodiment, the step at **260** comprises depositing a second precursor solution onto a surface of an active layer to form a film. This is followed at **261** with annealing the film to transform the film into a hole transport layer. Also as shown in Figures 2D and 2E, the deposition and annealing can be subdivided into interactive steps.

[0057] In Figure 2D at **208**, the process may comprise depositing a second precursor solution onto a surface of an active layer to form a third film layer (at **262**), depositing the second precursor solution onto a surface of the third film layer to form a fourth film layer (at **263**) and annealing the third film layer and the fourth film layer to transform the third film layer and fourth film layer into a hole transport layer (at **264**, Figure 2E). It would be appreciated that

depositing one or more additional layers of the precursor solution onto the previously deposited precursor solutions may be performed before proceeding to **264**. The plurality of precursor solution layers is then annealed at **264** to form the electron transport layer.

[0058] In Figure 2E another embodiment is illustrated at **209** where precursor deposition and annealing steps are alternated to form the hole transport layer. That is, a first deposition is shown generally at **264** with depositing the second precursor solution onto a surface of a substrate to form a third film layer. This deposition may lay the third film layer so that it at least in part contracts the previously deposited active layer, or it may be deposited on an intervening layer that provides a conductive path to the active layer. The method proceeds with annealing the first film layer to transform the third film layer into a first hold transport layer at **265**. Then another layer of the second precursor solution is applied and annealed. At **266**, the process proceeds with depositing the second precursor solution onto a surface of the first hole transport layer to form a fourth film layer and then to **267** with annealing the fourth film layer to transform the fourth film layer and the first hole transport layer into a single hole transport layer. Multiple iterations of these alternating deposition and annealing steps may be performed until a hole transport layer of the desired thickness is achieved.

[0059] In alternate embodiments, one or both of the **first** conductor and the second conductor may be implemented as transparent conductor layers. For example, in one example embodiment where the ZnO electron transport layer is produced from **230**, a single-cell photovoltaic device may be produced by coating the electron transport layer with an active layer that provides a bulk heterojunction (BHJ) solution, followed by a hole-transport layer, and finally depositing a high work-function top electrode, such as silver, for the second conductor. In such devices, the electron transport layer serves to facilitate electron extraction and block hole extraction, which helps to maximize the open-circuit voltage (V_{OC}) from the photovoltaic device. Representative current density-voltage (J-V) traces for 0.11 cm^2 devices fabricated based upon such a slot-die coated ZnO electron transport layer with a P3HT:PCBM active layer and a PEDOT:PSS-based hole transport layer are shown in **Figure 3**, along with average device performance characteristics in **Table 1** (below), demonstrating comparable performance of a device with a spin-cast ZnO electron transport layer.

	Voc (mV)	Jsc (mA/cm^2)	Fill Factor	Efficiency (%)	R Shunt (Ohms)	R Rect. (Ohms)	R Series (Ohms)	Number of Suns
Spin-Cast ZnO	500	11.3	44.1	2.53	6.04E+04	75	15	0.984
Slot-Die ZnO	482	10.2	45.3	2.26	7.91E+04	108	20	0.983

Table 1

[0060] For the production of large-area modules based upon the slot-die coated ZnO electron transport layers, a ZnO electron transport layer and first conductor layer (which may be a transparent conducting oxide, like indium tin oxide (ITO)), can be patterned to permit formation of discrete cells that are then connected in either a serial or paralleled fashion to yield voltage or current addition, respectively. Examples using a convention P1, P2, P3 scribing process, a ZnO/ITO, BHJ, and PEDOT/Ag layers, respectively, can be patterned to produce a serial interconnection of cell stripes to produce modules with additive voltage.

[0061] Figure 4 illustrates a performance plot, certified by the National Renewable Energy Laboratory (NREL), of a large-area Organic Photovoltaic Module incorporating a Zinc Oxide electron transport layer fabricated via an embodiment of the method described herein. As demonstrated by this plot, this Zinc Oxide electron transport layer is quite suitable for use in large-area, high-performance Organic Photovoltaic Modules. The favourable V_{oc} demonstrates the effective nature of the ZnO electron transport layer produced from a precursor solution comprising the stabilized diethylzinc solution, and the potential this technology has to enable low-temperature, atmospheric production of inverted-architecture OPV modules in a high-throughput roll-to-roll compatible process.

[0062] While a number of exemplary aspects and embodiments have been discussed above, those of skill in the art will recognize certain modifications, permutations, additions and sub combinations thereof. It is therefore intended that the following appended claims and claims hereafter introduced are interpreted to include all such modifications, permutations, additions and sub-combinations as are within their true spirit and scope.

Claims

What is claimed is:

1. A method for forming a thin film charge selective transport layer, the method comprising:

   providing a precursor solution comprising a metal containing reactive precursor material dissolved into a complexing solvent;

   depositing the precursor solution onto a surface of a substrate to form a film;

   forming a charge selective transport layer on the substrate by annealing the film.

2. The method of claim 1, wherein depositing the precursor solution further comprises:

   depositing the precursor solution onto a surface of the substrate to form the film, wherein the film at least in part contacts a first conductor.

3. The method of claim 1, wherein depositing the precursor solution further comprises:

   depositing the precursor solution onto at least one intervening layer comprising a material that electrically couples the charge selective transport layer to the substrate after the annealing.

4. The method of claim 1, wherein the precursor solution comprises a metal containing reactive precursor material that forms an electron transport layer when annealed.

5. The method of claim 1, wherein the precursor solution comprises a metal containing reactive precursor material that forms a hole transport layer when annealed.

6. The method of claim 1, wherein the substrate comprises an active layer of a heterojunction semiconductor device.

7. The method of claim 1, further comprising:

   providing a second precursor solution comprising a second metal containing reactive precursor material dissolved into a second complexing solvent;

depositing the precursor solution onto a surface of a second substrate to form a second film,

forming a second charge selective transport layer on the second substrate by annealing the film;

forming a second conductor electrically coupled to the second charge selective transport layer.

8. The method of claim 7, wherein the first charge selective transport layer forms an electron transport layer, the second electron transport layer forms a hole transport layer.

9. The method of claim 7, wherein the second substrate comprises an active layer of a heterojunction semiconductor device.

10. The method of claim 1, wherein the metal containing reactive precursor material comprises either diethylzinc or dimethylzinc.

11. The method of claim 1, wherein the charge selective electron transport layer comprises either a ZnO film or a TiO_x film.

12. The method of claim 1, wherein the complexing solvent comprises one or more of tetrahydrofuran (THF), diethyl ether, diethylene glycol dimethyl ether (diglyme), pyridine, acetonitrile, and tetramethylethylenediamine.

13. The method of claim 1, wherein depositing the precursor solution further comprises at least one of: a slot-die coating process, spin-casting, drop-casting, dip-coating, knife coating, spray-coating, ink-jet printing, screen printing, Mayer rod coating, Gravure coating, Flexo printing, or curtain coating.

14. The method of claim 1, wherein the first conductor comprises a transparent conductor material.

15. The method of claim 1, wherein the charge selective transport layer comprises an electron transport layer, the method further comprising:

    forming an active layer on the electron transport layer; and

    forming a second conductor that is electrically coupled to the active layer.

16. The method of claim 15, further comprising:

    forming a hole transport layer on the active layer, wherein the hole transport layer separates the active layer from the second conductor layer.

17. A method of making an inverted architecture organic photovoltaic device containing a metal oxide electron transport layer, the method comprising:

    fabricating an organic photovoltaic cell having a substrate, a first conductor comprising a transparent conductor material, an electron transport layer comprising a metal oxide thin film, an active layer comprising a heterojunction, and a second conductor;

    wherein the metal oxide thin film is fabricated by:

        dissolving an organometallic precursor compound in a complexing solvent to form a precursor solution;

        coating the substrate and first conductor with the precursor solution to produce a film; and

        annealing the oxide thin film to produce a transparent metal oxide film which is electrically coupled to the first conductor.

18. The method of claim 17 wherein the organometallic precursor compound comprises either diethylzinc or dimethylzinc.

19. The method of claim 17, wherein the complexing solvent is tetrahydrofuran (THF), diethyl ether, diethylene glycol dimethyl ether (diglyme), pyridine, acetonitrile, tetramethylethylenediamine, or any combination thereof.

20. The method of claim 17, wherein the precursor solution is deposited on the substrate under atmospheric conditions using a solution coating method selected from a group consisting of: slot-die coating, spin-casting, drop-casting, dip-coating, knife coating, spray-coating, ink-jet printing, screen printing, Mayer rod coating, Gravure coating, Flexo printing, or curtain coating.

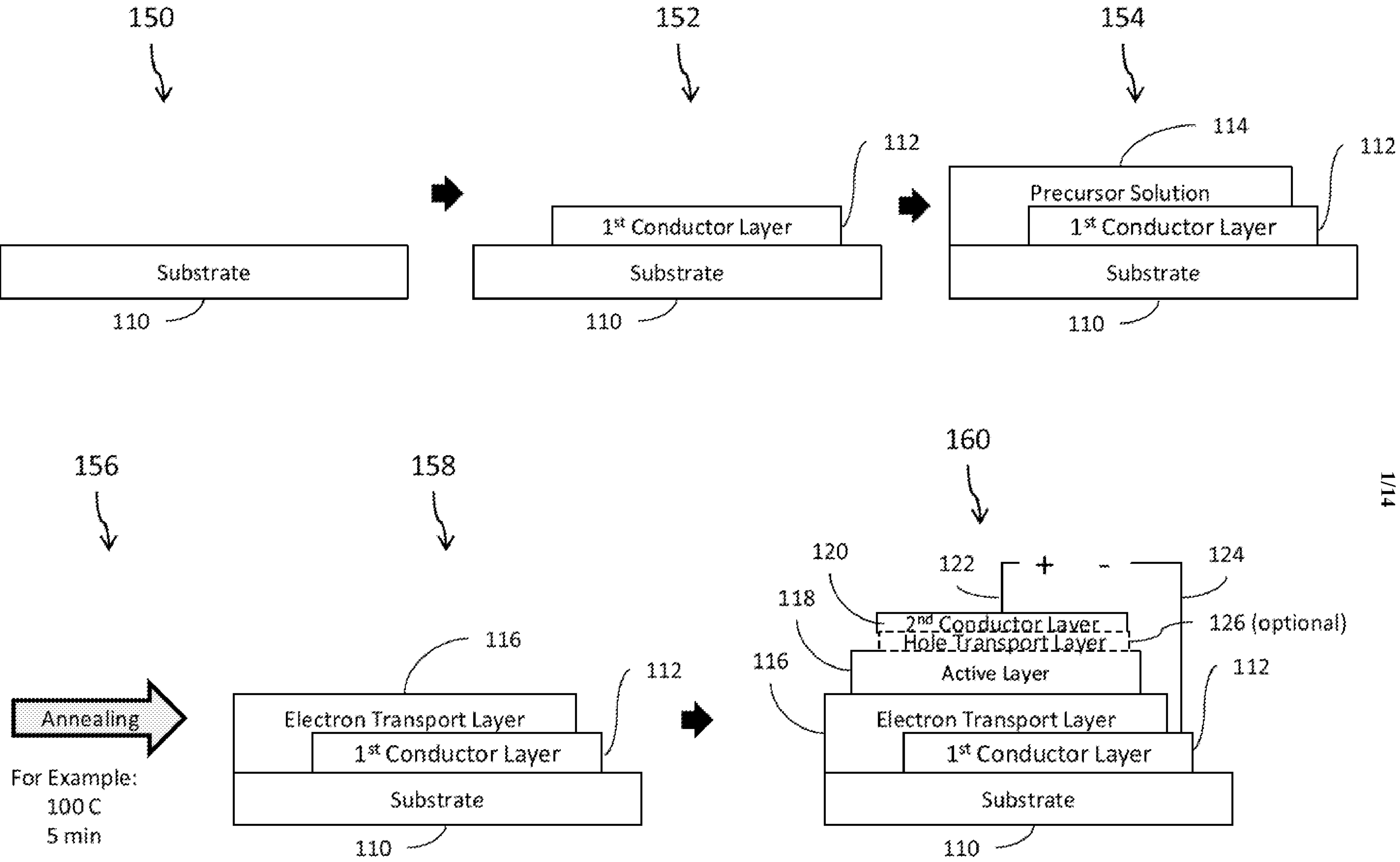

Figure 1

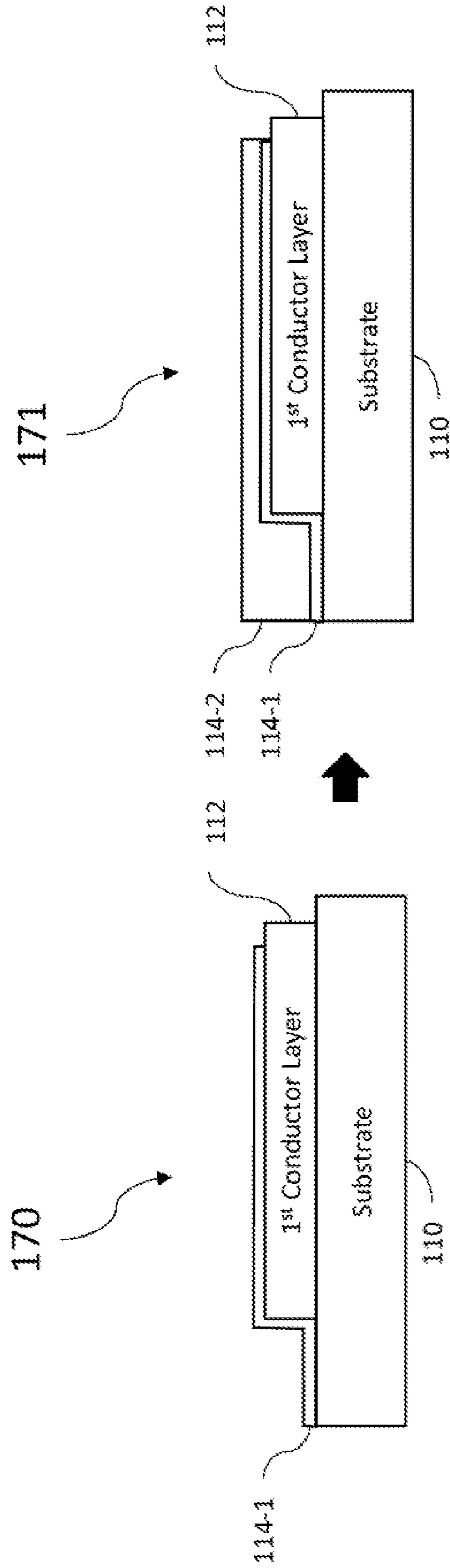

Figure 1A

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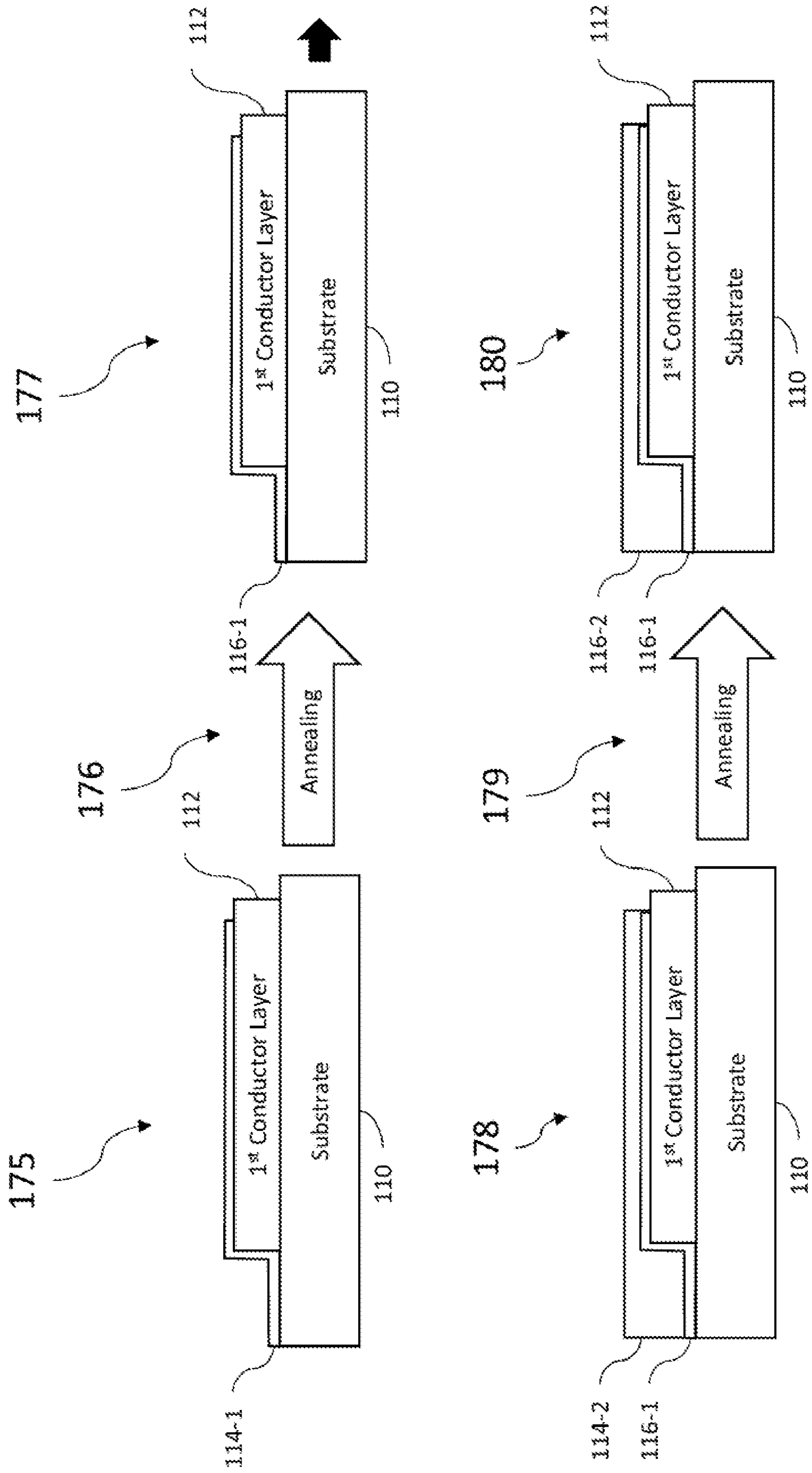

Figure 1B

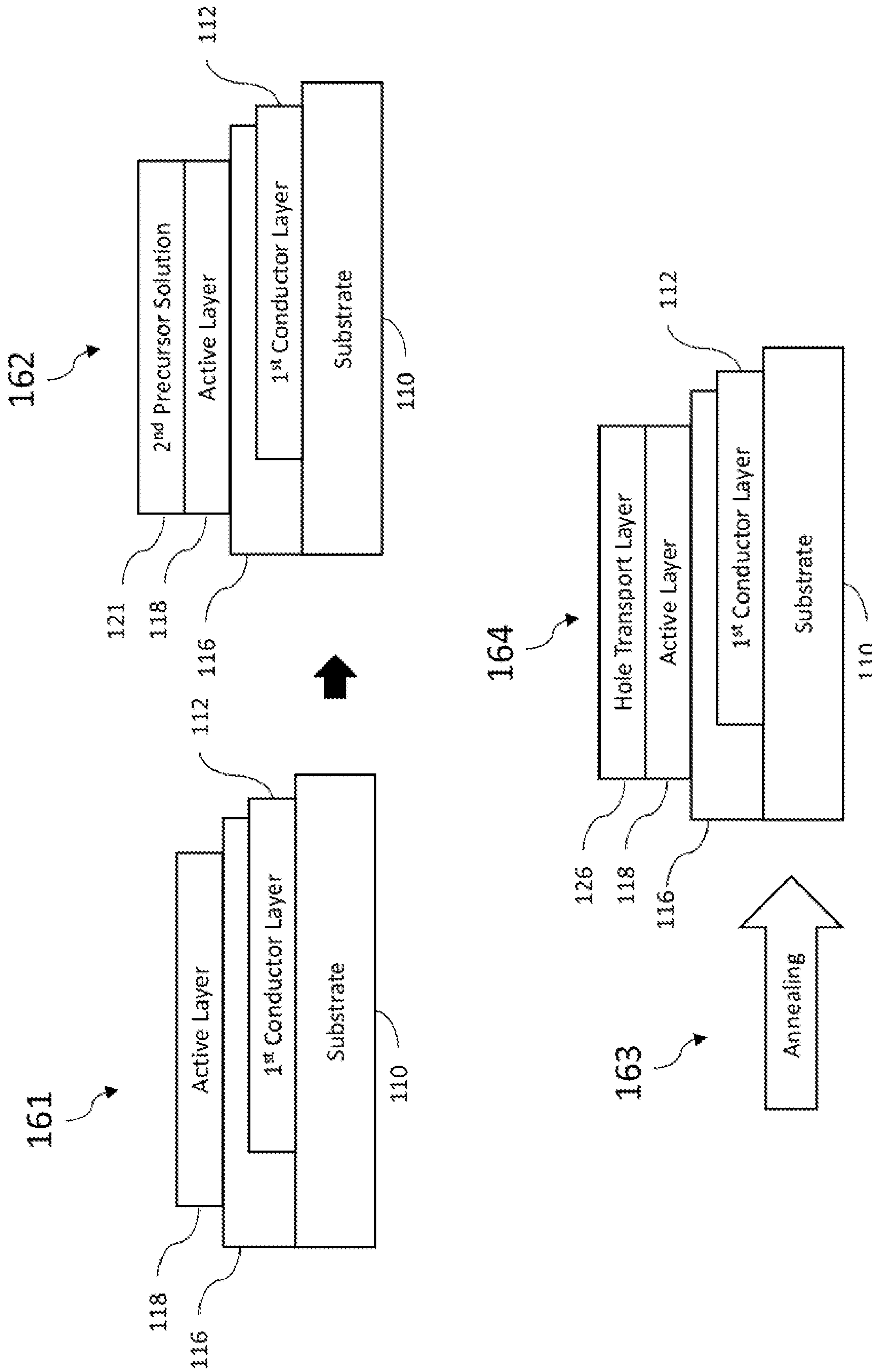

Figure 1C

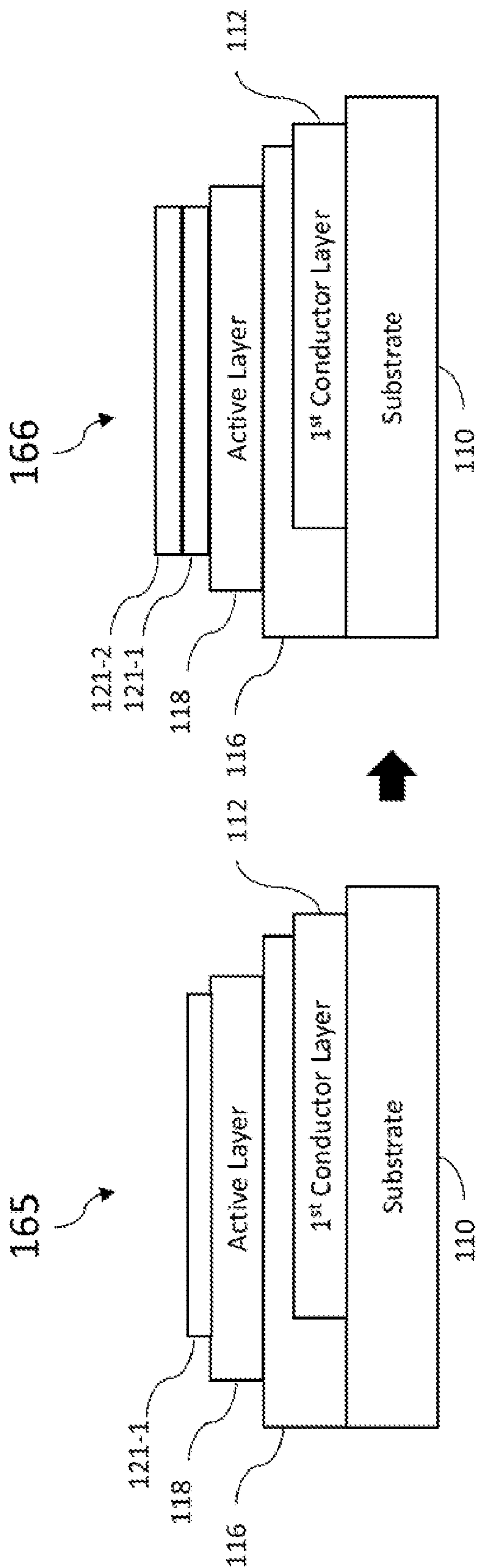

Figure 1D

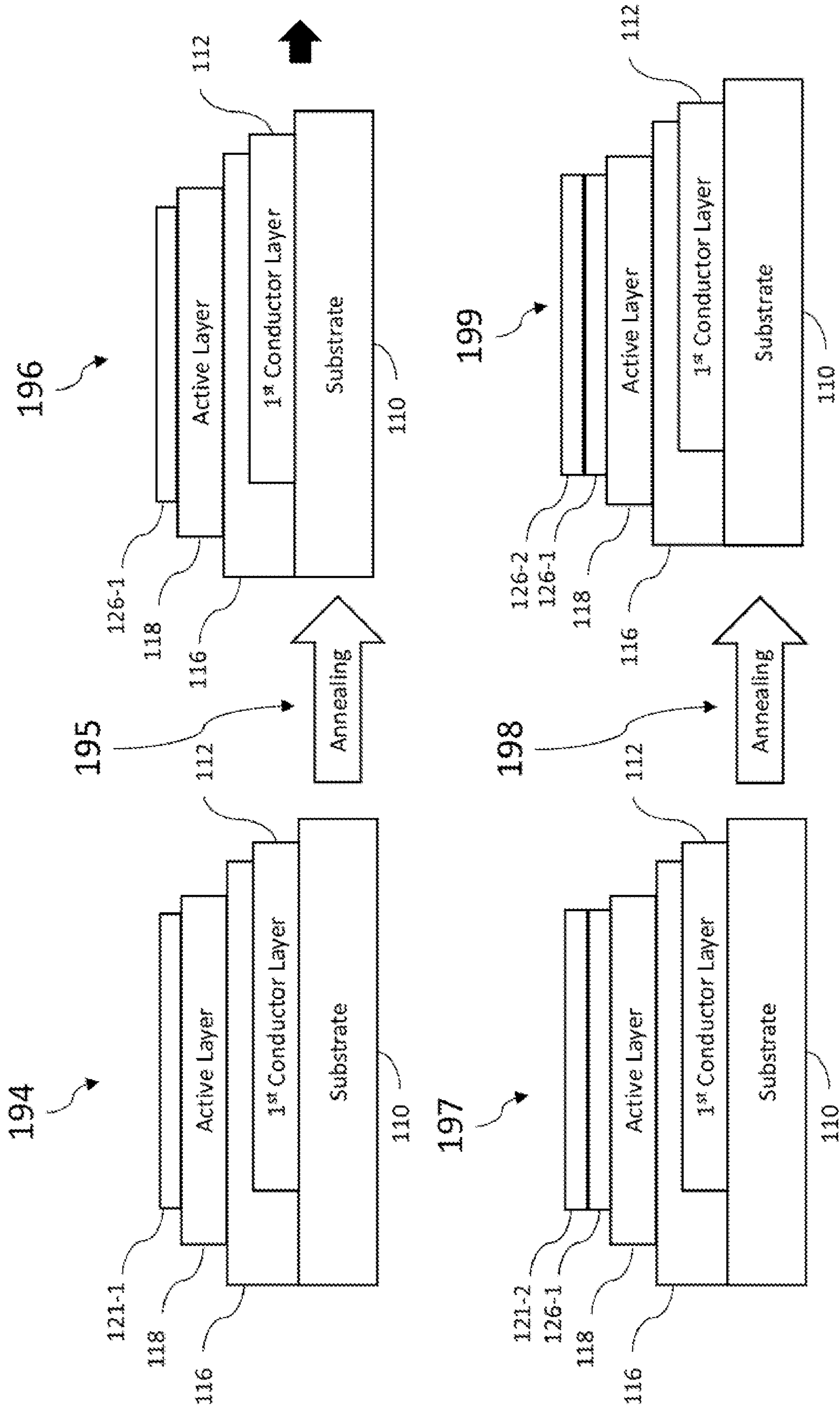

Figure 1E

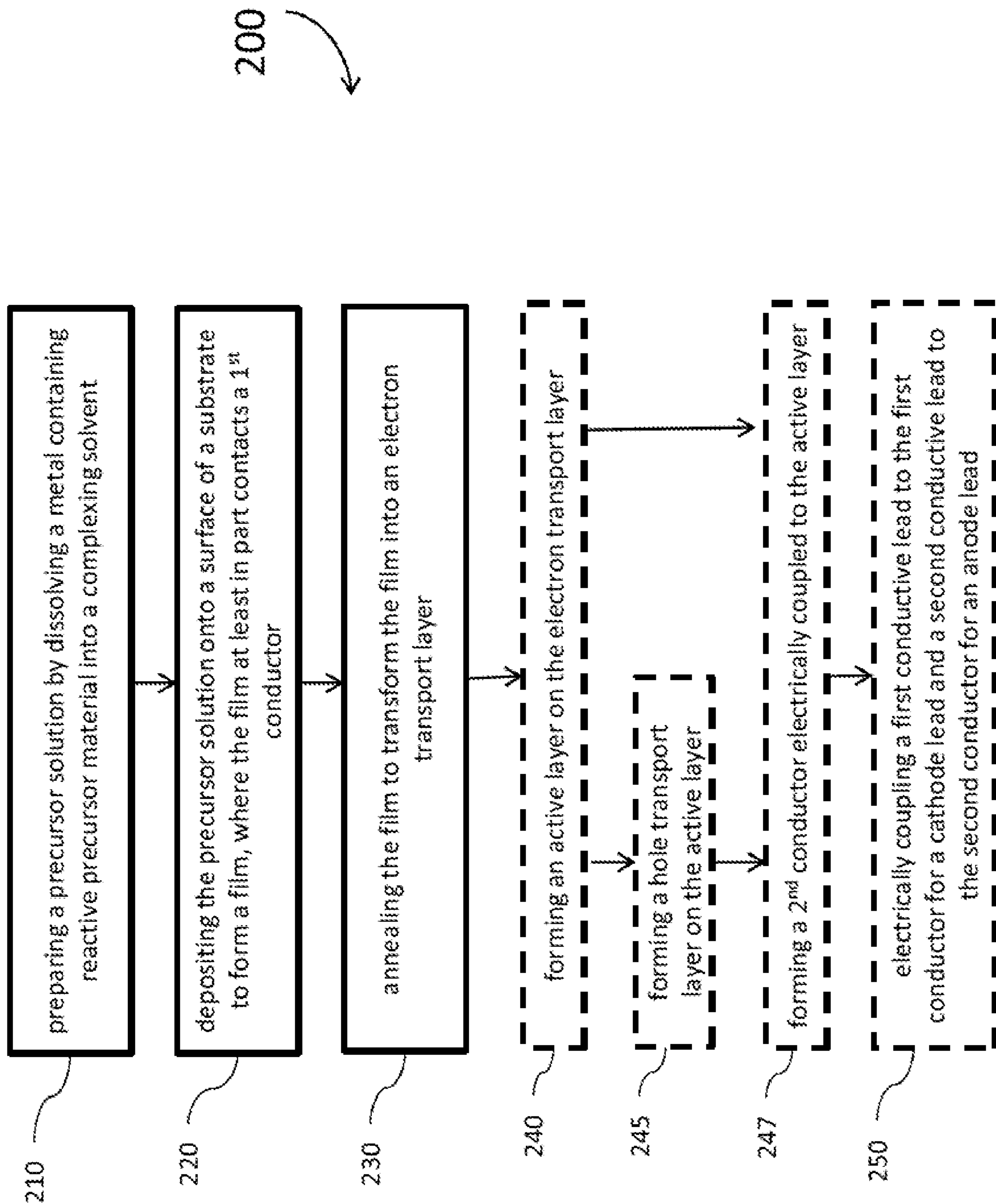

Figure 2

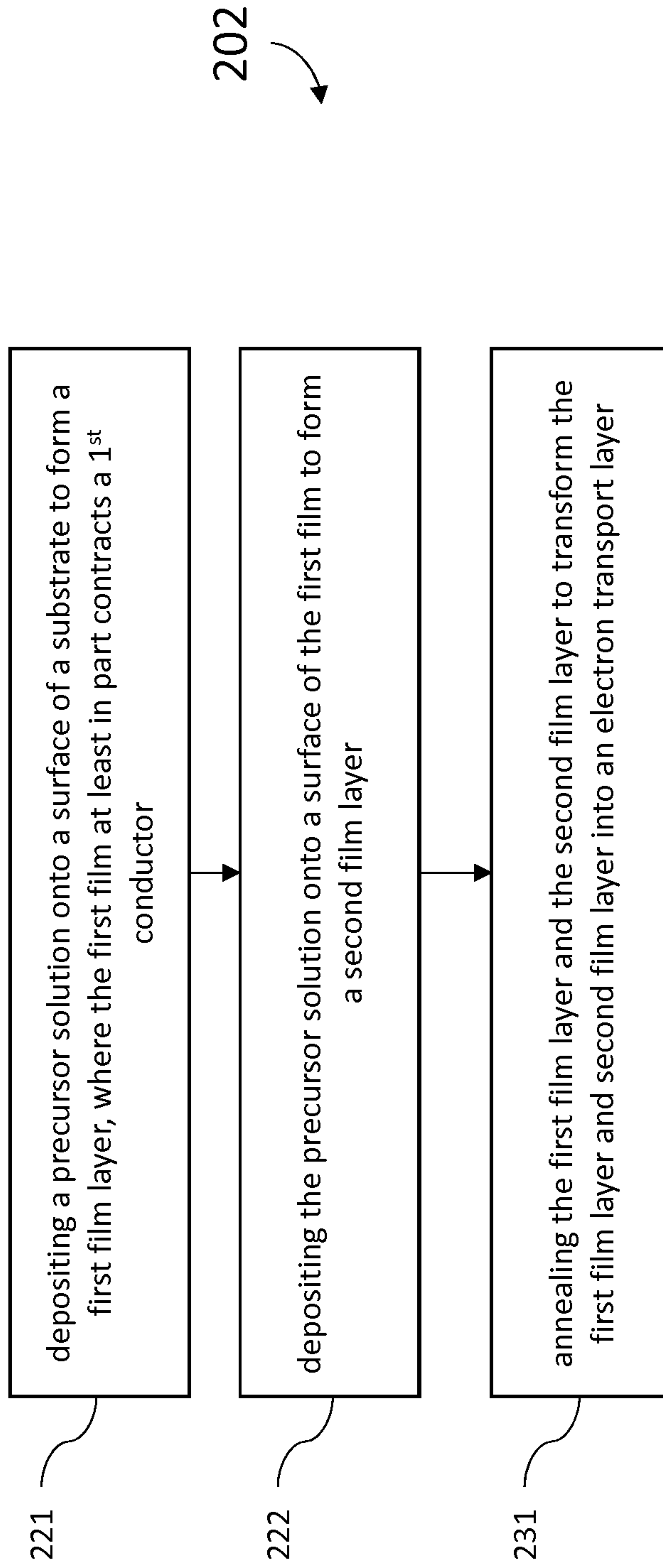

Figure 2A

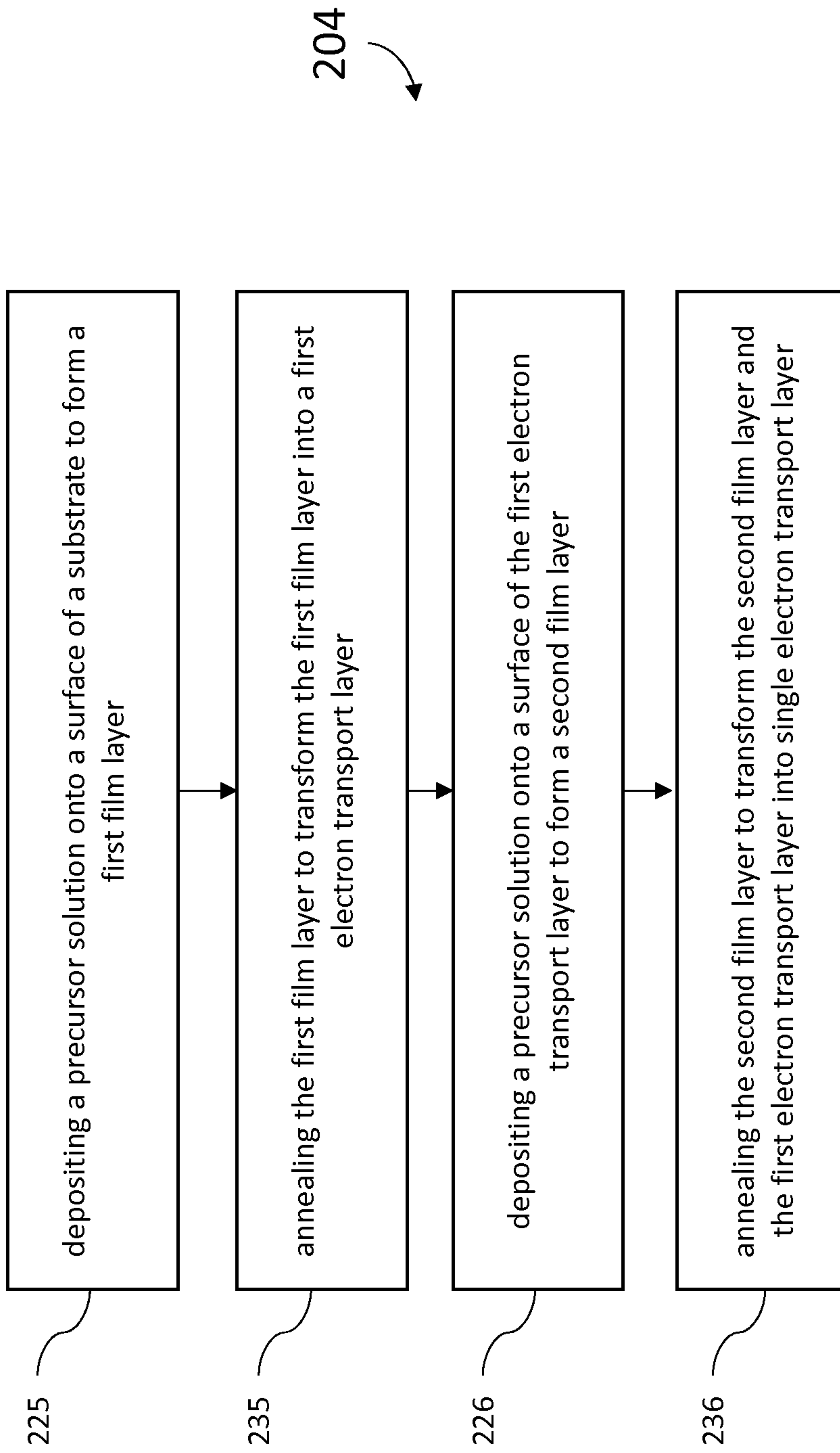

Figure 2B

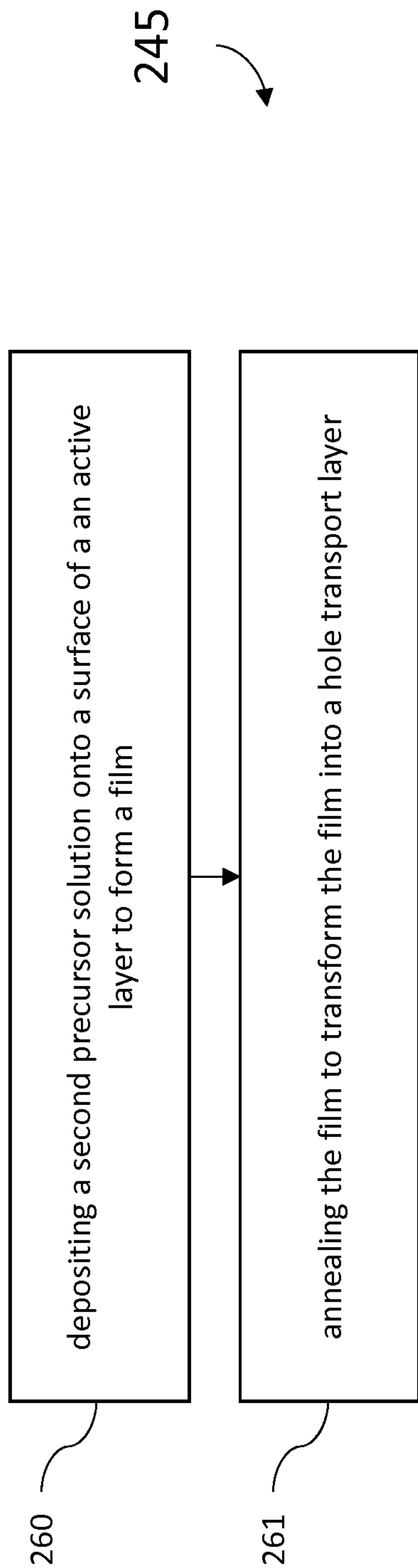

Figure 2C

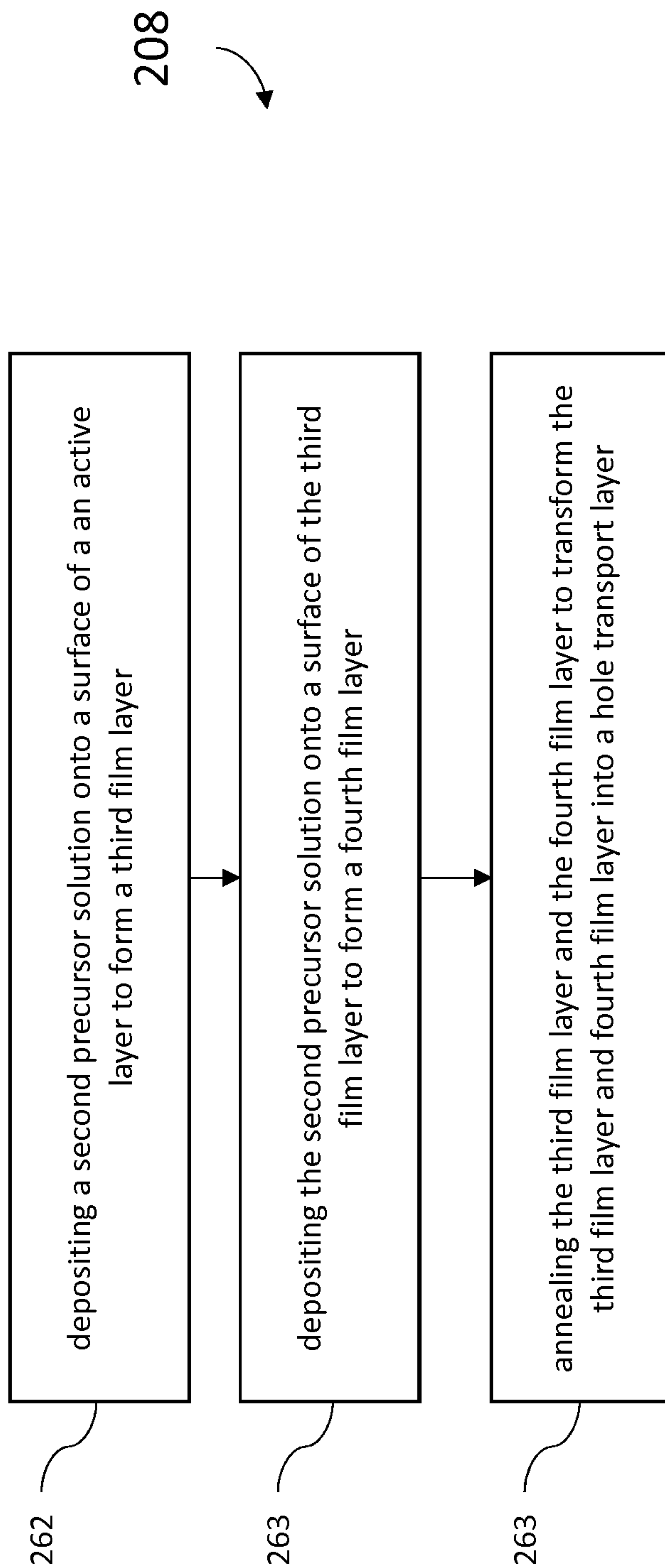

Figure 2D

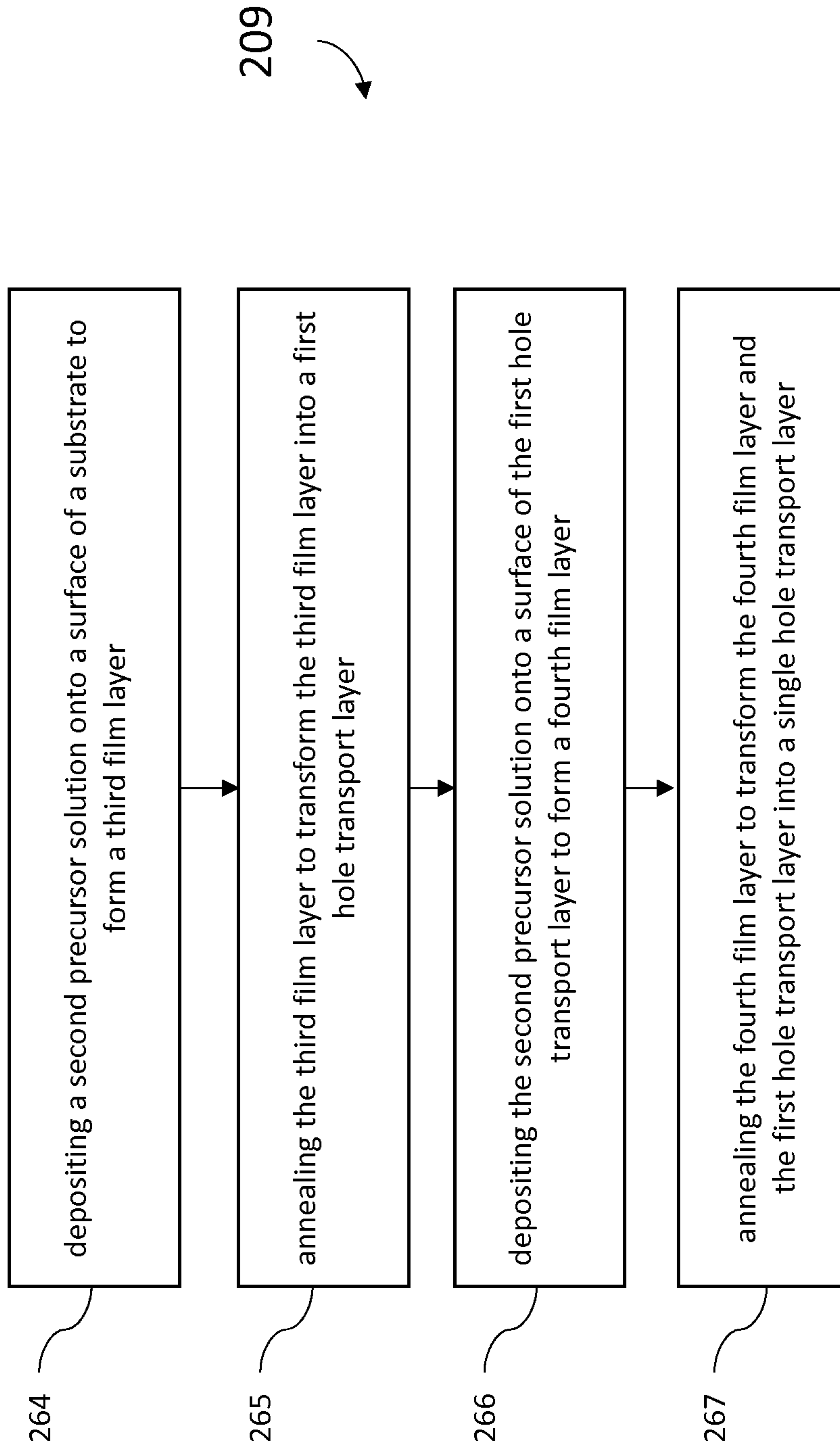

Figure 2E

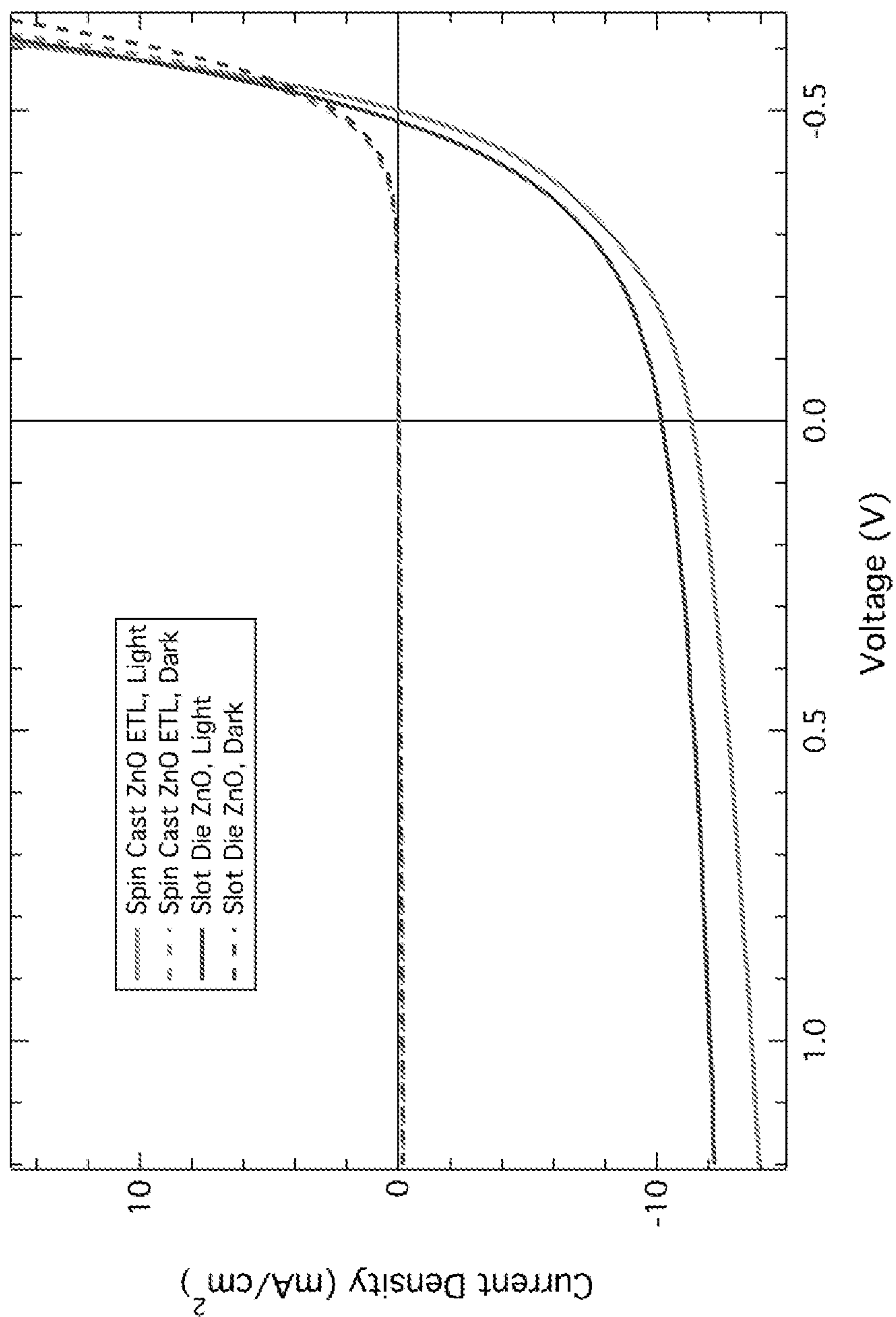

Figure 3

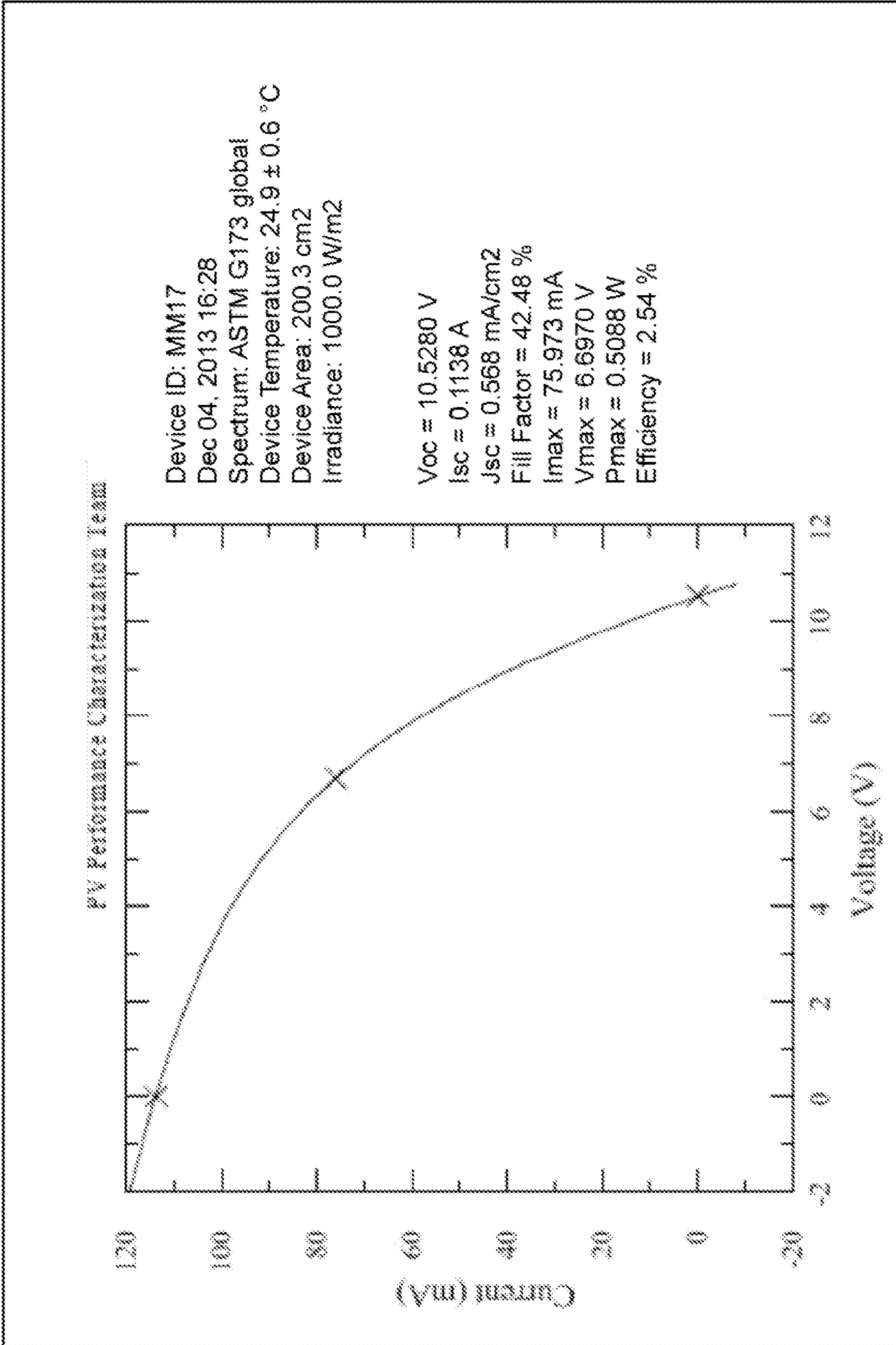

Figure 4

150

Substrate

110

152

112

1st Conductor Layer

Substrate

110

154

114

112

Precursor Solution

1st Conductor Layer

Substrate

110

156

Annealing

For Example:
100 C
5 min

158

116

112

Electron Transport Layer

1st Conductor Layer

Substrate

110

160

120

122

+ -

124

118

2nd Conductor Layer

Hole Transport Layer

126 (optional)

116

Active Layer

112

Electron Transport Layer

1st Conductor Layer

Substrate

110

Figure 1