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[Continued on next page]

(54) Title: SHEET ASSEMBLY WITH ALUMINUM BASED ELECTRODES

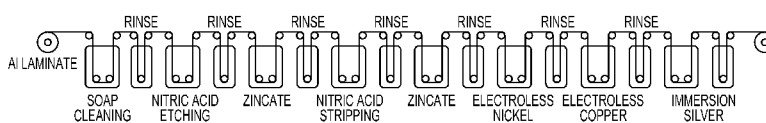


FIG. 1A

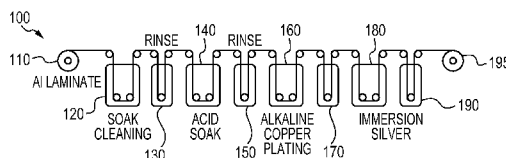


FIG. 1B

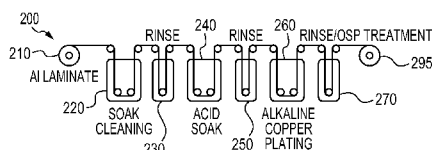


FIG. 1C

(57) Abstract: Various methods for preparing and/or processing electrically conductive aluminum members such as used in elec-
tronic circuits and components are described. Also described are various sheet assemblies using patterned aluminum conductive ele-
ments as components of electric circuitry. The sheet assemblies can be used as backsheets for back contact photovoltaic cells or as
antennas for RFID tags.



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- *with information concerning request for restoration of the right of priority in respect of one or more priority claims (Rules 26bis.3 and 48.2(b)(vii))*

SHEET ASSEMBLY WITH ALUMINUM BASED ELECTRODES**Cross Reference to Related Application**

[0001] The present application claims the benefit of U.S. Provisional Patent Application No. 61/594,597 filed February 3, 2012, which is incorporated herein by reference in its entirety.

Field

[0002] The present subject matter relates to sheet assemblies with aluminum based conductive patterns. More particularly, the present subject matter relates to backsheet assemblies for back contact photovoltaic modules and methods of making such assemblies. Furthermore, the present subject matter relates to sheet assemblies with aluminum based electrodes and methods for producing such sheet assemblies that may be used in manufacturing intricately formed circuits, antennas, and other specialized applications that utilize metal conductors to conduct electrical current.

Background

[0003] A new type of photovoltaic (PV) module includes various silicon wafers that are electrically connected to a conductive backsheet or member. Unlike traditional designs, this type of photovoltaic cell employs printed silver (Ag) ink disposed in one or more laser drilled vias connecting a front surface current collector junction to an electrode grid on the back surface. Therefore, back contact silicon cells use only coplanar contacts on the back surface (as described in US Patents 5,468,652 and 5,951,786, both to Gee) and avoid the difficulty in making the front to back lead attachment. This coplanar connection allows all the cells in a photovoltaic module to be electrically connected in a single step during a manufacturing process. Collections of these cells are typically referred to as a monolithic module assembly (MMA).

[0004] Copper (Cu) has been used as an electrode material for the backsheet assembly for back contact photovoltaic modules. Since copper is relatively expensive, it is desirable to use less expensive electrically conductive materials. Aluminum is desired as a material for forming electrodes for back contact photovoltaic applications due to its relatively low cost.

[0005] However, a naturally occurring oxide layer typically forms and/or exists on the surface of aluminum. The oxide layer exhibits relatively high electrical resistance. And so, if low resistance electrical connections are to be made to aluminum electrode(s) or conductor(s), the oxide layer must be removed.

[0006] Various methods are known for removing oxide layers from an aluminum surface to form an electrically conductive surface. However, the resulting fresh aluminum layer quickly re-oxidizes even under ambient conditions. Furthermore, aluminum rapidly re-oxidizes if subjected to high temperatures and/or high humidity. The typical industry approach for protecting a freshly exposed aluminum surface is to plate a second metal on top of the freshly exposed aluminum surface. Typically, such methods are expensive or time consuming and involve treating an entire sheet of aluminum foil or an entire face of the aluminum surface of interest. Accordingly, a need exists for methods by which aluminum based electrodes, and particularly those used in photovoltaic assemblies, can be economically prepared or processed to be resistant to oxidation yet be electrically conductive.

Summary

[0007] The difficulties and drawbacks associated with previously known approaches are addressed in the present methods, assemblies, and devices.

[0008] In one aspect, a method is provided for forming a protected sheet assembly having an aluminum conductor. The method comprises providing a laminate including a substrate and an aluminum layer disposed thereon, the aluminum layer having an oxidation layer constituting an outer surface of the aluminum layer. The method also comprises removing at least a portion of the oxidation layer to expose at least one region of fresh aluminum. The method also comprises depositing copper on at least a portion of the at least one region of fresh aluminum. And, the method additionally comprises protecting the deposited copper by applying at least one of (i) a silver layer on the deposited copper and (ii) an organic solderability preservative coating on the deposited copper to thereby form a protected sheet assembly having an aluminum conductor.

[0009] In another aspect, a method for forming a protected current collector is provided. The protected current collector includes a first electrode, a second electrode, a gap separating the first electrode and the second electrode, and a plurality of contact points. The method comprises providing a laminate including a substrate and an aluminum layer disposed thereon, the aluminum layer defining a first electrode, a second electrode, a gap separating the first electrode and the second electrode, and a plurality of contact points. The aluminum layer includes an oxidation layer constituting an outer surface

of the aluminum layer. The method also comprises depositing a first layer of an etching resist material on the oxidation layer such that the gap and the plurality of contact points are not covered with the etching resist material. The method further comprises removing the oxidation layer in the gap and the plurality of contact points to expose fresh aluminum in the gap and the plurality of contact points. The method additionally comprises depositing copper on at least a portion of the gap and the plurality of contact points. The method further comprises depositing a second layer of an etching resist material on the deposited copper in the plurality of contact points such that the gap is not covered with the second layer of the etching resist material. The method still further comprises removing copper and aluminum in the gap to thereby form a metal-free gap. The method also comprises removing etching resist material. And, the method also comprises protecting any exposed copper to thereby form a protected current collector.

[0010] In yet other aspects, a photovoltaic cell is provided. The cell comprises a c-Si cell and a backsheet. The backsheet comprises a substrate layer, and a patterned aluminum conductive layer on the substrate layer, wherein the patterned aluminum conductive layer is in electrical contact with the c-Si cell and the aluminum conductive layer includes at least one oxidation resistant region.

[0011] In still other aspects, various protected sheet assemblies such as a photovoltaic backsheet are provided.

[0012] In yet other aspects, oxidation resistant aluminum based electrodes on an aluminum foil laminate are provided.

[0013] And in still other aspects, various protected current collectors are provided.

[0014] As will be realized, the subject matter is capable of other and different embodiments and its several details are capable of modifications in various respects, all without departing from the subject matter. Accordingly, the drawings and description are to be regarded as illustrative and not restrictive.

Brief Description of the Drawings

[0015] Figure 1A is a schematic process diagram of a standard zincate process for plating copper on aluminum.

[0016] Figure 1B is a schematic process diagram of a preferred embodiment alkaline copper plating process for plating copper on aluminum.

[0017] Figure 1C is a schematic process diagram of another preferred embodiment process for plating copper on aluminum.

- [0018]** Figure 2A is a schematic process diagram of plating copper on aluminum in a standard patterning method.
- [0019]** Figure 2B is a schematic process diagram of printing etching resist on an aluminum laminate in the standard patterning method.
- [0020]** Figure 2C is a schematic process diagram of etching to remove exposed copper areas in the standard patterning method.
- [0021]** Figure 3A is a schematic process diagram of printing etching resist on an aluminum laminate in a preferred embodiment process.
- [0022]** Figure 3B is a schematic process diagram of plating copper on an aluminum laminate in the preferred embodiment process.
- [0023]** Figure 3C is a schematic process diagram of printing resist ink in the preferred embodiment process.
- [0024]** Figure 3D is a schematic process diagram of etching to remove exposed copper areas in the preferred embodiment process.
- [0025]** Figure 4 is a schematic illustration of a test sample used in evaluating various preferred embodiment structures.
- [0026]** Figure 5 is a schematic illustration of an aging test measurement configuration used in various evaluations.
- [0027]** Figure 6 is a schematic cross sectional illustration of a test assembly for assessing contact resistance in the evaluations described herein.
- [0028]** Figure 6A is a schematic cross sectional illustration of a test strip described in the evaluations herein.
- [0029]** Figure 6B is a schematic cross sectional illustration of a test piece described in the evaluations herein.
- [0030]** Figure 7 is a schematic flow chart illustrating a preferred embodiment process.
- [0031]** Figure 8 is a schematic flow chart illustrating another preferred embodiment process.
- [0032]** Figure 9 is a schematic illustration of a preferred embodiment photovoltaic module current collector.
- [0033]** Figures 10A-10H illustrate cross sectional schematic views of a preferred current collector at various stages of a preferred embodiment process for forming the current collector.

Detailed Description of the Embodiments

[0034] The present subject matter is based upon a discovery that aluminum foils or other thin layers of aluminum, and particularly those used in various photovoltaic applications, can be economically prepared and/or processed to remove oxide layers residing on the aluminum foil, and then subjected to operation(s) in which a thin layer of another electrically conductive material, such as nickel, copper, silver or the like, is deposited on the aluminum to thereby protect the underlying aluminum from oxidation, yet provide an electrically conductive surface. Additional and/or optional operations may be performed to deposit another layer of an electrically conductive or non-conductive material on the layer of material previously deposited on the aluminum.

[0035] In certain embodiments, methods of forming an oxidation resistant electrode on an aluminum foil laminate are provided. The methods comprise providing an aluminum or aluminum alloy foil having an outer surface that is naturally oxidized. The aluminum or aluminum alloy foil is laminated to a polymeric film. The methods also comprise removing at least a portion of the oxidation from the outer surface of the aluminum foil to form a region of freshly exposed aluminum. The methods additionally comprise depositing at least one layer of an electrically conductive material on the region of freshly exposed aluminum to thereby form the oxidation resistant electrode.

[0036] In additional certain embodiments, methods are provided for reducing the use of etching and plating chemicals otherwise used in a converting process while also preserving the majority of aluminum oxide surface area. The remaining oxide surface area can be used as an electrical insulation layer in a photovoltaic module structure. Furthermore, this aluminum oxide layer exhibits superior adhesion properties with typical encapsulation films used in photovoltaic modules. A strong adhesion interface between a conductive backsheet and an encapsulation film will provide a longer service life for photovoltaic modules using such a backsheet, since the interface between the conductor material and the encapsulation film is less likely to fail.

[0037] In still further embodiments, alternative contact interfaces are provided for isotropic conductive pastes (ICP) or isotropic conductive adhesives (ICA), to bond to and provide the electrical connection between solar cells and an aluminum conductor backsheet, for example. Forming such interfaces preferably comprises a dip coating chemical treatment utilizing dilute organic additives in an aqueous solution instead of a costly precious metal acid solution. These methods are more environmentally friendly and lower cost as compared to currently known methods.

[0038] In yet other embodiments, a photovoltaic cell is provided comprising a c-Si cell, and a conductive backsheet. The backsheet comprises a substrate layer, and an aluminum foil on the

substrate layer. The aluminum foil is in electrical contact with the c-Si cell and the aluminum foil includes at least one oxidation resistant electrode or region.

[0039] A traditional chemical process for aluminum surface treatment, i.e. the zincate process, is illustrated in Figure 1A. In this process, an aluminum surface is cleaned, etched with nitric acids, zincate treated, stripped of the zincate with acid, then zincate treated a second time, electrolessly or electrolytically nickel plated, then electrolessly or electrolytically copper plated and then immersion silver plated. A rinsing step is included between each of the steps. This process is very costly. The resulting complexity and cost associated with this process outweigh any advantages of using aluminum as a lower cost conductor.

[0040] As illustrated in 1B, a preferred embodiment and less complex process 100 is described that provides the same stable interface for photovoltaic applications as assemblies created using the zincate process depicted in Figure 1A. Beginning at an initial operation in Figure 1B, the preferred embodiment process preferably begins with providing an aluminum foil laminate, which can be a thin aluminum foil laminated over a polymeric substrate, using adhesive or other laminating methods. The aluminum typically includes a thin oxide layer. This operation is designated as 110 in Figure 1B. The aluminum or oxide surface is preferably soaked with soap and/or alkaline solutions to mildly etch the surface. This operation is depicted as 120. Next, a rinse operation is performed which is shown as 130. The smuts and oxide surface are then removed in operation 140 with an acid solution (for example an aqueous solution of nitric or sulfuric acids). After treatment in operation 140, a rinse operation may be performed such as shown by operation 150. Next, the assembly is subjected to an electrolytic plating process to deposit a layer of copper, as shown by 160. Due to the nature of aluminum metal properties, an alkaline type of copper plating solution is more suitable for this operation since such solution does not severely etch the aluminum during the plating process. After plating copper to a desired thickness in operation 160, the assembly may be subjected to rinsing at 170.

[0041] In an alternative embodiment (not shown in Figure 1B), a second layer of copper is plated on top of the first layer of previously plated copper. Standard acid plating chemistry can be used in this operation since the aluminum is protected by the first layer of copper previously deposited and will not be attacked by the acid plating solution. Typical acid plating chemistries allow plating at higher current densities. Therefore, such techniques can build up the copper thickness quickly to reduce the overall plating process time.

[0042] Referring again to Figure 1B, the plated copper layer or layers can be protected by an immersion silver plating process. This is shown as operation 180 in Figure 1B. The resulting silver layer

is quickly oxidized to silver oxide. Silver oxide is a good electrical conductor and compatible with typical downstream photovoltaic module assembly processes. After depositing silver in operation 180, the assembly may be rinsed in rinse operation 190. A plated product is then collected at 195.

[0043] In accordance with another preferred embodiment process, the plated copper surface such as resulting from operation 160 in Figure 1B can be protected by an organic solderability preservative (OSP) coating. This process can utilize a dip coating treatment after the copper plating operation 160 depicted in Figure 1B since the plated copper surface is free of oxidation or other contamination. If the copper surface was not immediately treated after plating, the OSP treatment can be applied after a minor etching operation to remove any oxidation which may have occurred on the copper surface, then followed by the dip coating treatment at a later time.

[0044] Specifically, referring to Figure 1C, another preferred embodiment process 200 is provided which provides a stable interface for photovoltaic applications, such as those formed by the process 100 of Figure 1B. The preferred process 200 includes the same or substantially similar operations as operations 110, 120, 130, 140, 150, and 160 as previously described. The corresponding operations in process 200 are designated as operations 210, 220, 230, 240, 250, and 260, respectively. The process 200 additionally comprises an OSP treatment operation 270 which as noted is preferably in the form of a dip coating treatment. The OSP treatment operation 270 may optionally include one or more rinsing operations. Optionally, the process also includes pretreatment steps to enhance the adhesion between the fresh copper surface and the OSP layer. Details as to the OSP treatment formulations are provided in greater detail herein. After depositing the OSP layer in operation 270, a plated product is then collected at 295.

[0045] A preferred method for forming a protected sheet assembly generally corresponding to the process schematic diagrams of Figures 1B and 1C is illustrated in Figure 7 as method 500. This method 500 comprises an operation 510 of providing an aluminum face or surface having an oxidation layer. An operation 520 of removing at least one or more portions or regions of the oxidation layer is designated as 520. Upon removal of oxidation, one or more fresh region(s) of aluminum are thus exposed. In operation 530, copper is deposited on the one or more region(s) of fresh aluminum. The copper layer is then protected in operation 540. Protection may be performed by either applying a layer of silver on the copper as operation 550 or by an OSP treatment as operation 560. Optionally, prior to protection in operation 540, a second or subsequent layers of copper can be deposited on the previously formed copper layer in operation 570. The second or subsequent layers of copper are preferably protected in operation 540, such as by operations 550 or 560.

[0046] Figures 2A, 2B, and to 2C illustrate a standard patterning method for forming patterns or components of electrically conductive copper on aluminum. The aluminum surface of a laminated structure (for example aluminum foil, adhesive and plastic carrier) is fully converted or covered with copper to prevent the regeneration of an aluminum oxide layer using the method described previously and schematically depicted in Figure 1A. Figure 2A illustrates application of the noted method to a laminated structure. Then an etching resist material is printed and cured on the copper plated aluminum foil based on the photovoltaic current collector design. This is shown in Figure 2B. Then, the full substrate goes through a chemical etching process. During this etching operation, exposed copper is removed. The etching resist material is then stripped with an appropriate chemical solution to reveal a fresh copper surface corresponding to the photovoltaic module current collector design. This is shown in Figure 2C. The copper surface needs to be protected in order to prevent an oxidation layer forming on the fresh copper surface.

[0047] Figure 9 schematically illustrates a photovoltaic module current collector having contacts and electrodes. A foil laminate 900 includes regions 901 and 902 that serve as a positive electrode and a negative electrode respectively, a gap 903 that is free of metal materials to separate the two electrodes, and multiple contact points 904. According to the process described in Figures 2A to 2C, the electrodes 901 and 902 and the contact points 904 are comprised of copper plated aluminum. The copper surface is further protected with immersion silver or OSP.

[0048] The removal of the naturally occurring oxide layer on aluminum foil can be achieved through wet chemical etching, or dry laser ablation. In the case of wet chemical etching, in many applications it is desirable to minimize the surface area that is to be treated to thereby reduce chemical consumption, process variation and waste. In accordance with another preferred embodiment process 300, a collection of process operations are schematically illustrated in Figures 3A to 3D. It is preferred to deposit an etching resist layer to cover at least a portion and preferably a majority proportion of the oxide layer on the aluminum surface except for regions of the photovoltaic conductive backsheet pattern, e.g., gaps between the positive and negative current collectors, and associated contact points. This operation is depicted as operation 310 in Figure 3A. Specifically, an aluminum laminate 312 is provided as described herein, one or more etching resist materials are then deposited in operation 314, and if the etching resist materials are curable, they are then cured such as by exposure to UV light in operation 316. An intermediate assembly 318 is then produced.

[0049] Then, referring to Figure 3B, the exposed aluminum oxide of the intermediate assembly 318 is removed and the aluminum surface is activated by an acid solution. This operation is depicted in

Figure 3B as operation 340. Prior to operation 340, the assembly 318 can be subjected to a cleaning or soaking operation 320 and a rinsing operation 330 as shown in Figure 3B. After removing smuts and oxide in operation 340, rinsing may be performed in operation 350. Then, the freshly exposed aluminum surface, e.g., gaps between the two types of current collectors and contact points, is subjected to an electrolytic copper plating process, to cover the exposed aluminum. This operation is shown as 360 in Figure 3B. After copper deposition in operation 360, the assembly may be subjected to one or more rinsing operations and/or OSP treatment operations as previously described. The resulting assembly is shown as assembly 375.

[0050] Next, referring to Figure 3C, a resist ink or other material is printed to cover the ICP or ICA contact points. As a result of this process, the contact points will be covered by etching resist, which can be applied by screen printing, ink jetting printing, or any other suitable way to dispense the etching resist. These operations are depicted as operation(s) 380 in Figure 3C. Specifically, the assembly 375 receives etching resist in regions or locations that correspond to contact points in the photovoltaic backsheet. An etching resist ink can be deposited and preferably by printing in operation 384. If the etching resist material is curable, a curing operation 386 is performed to cure the deposited etching resist material. Details as to preferred etching resist materials are provided herein. An intermediate product 388 is then produced.

[0051] Then, referring to Figure 3D, the patterned Cu/Al area, e.g., gap between the anode and cathode electrodes, is etched away by standard Cu/Al etching chemistry. During this etching operation, the contact points are protected by the etching resist. Specifically, referring to Figure 3D, the previously described product 388 is subjected to an etching operation 390. After etching, rinsing may be performed at 400. The etching resist is removed by a stripping solution shown as operation 410. The finished and exposed copper surface, i.e., including the contact points, can be protected by immersion in silver or by an OSP treatment as previously described. These operations are depicted as 420 in Figure 3D. A finished product 425 is produced. The final product according to this embodiment of the subject matter includes electrodes 901 and 902 (see Figure 9) comprised of aluminum with naturally occurring oxide, and contact points 904 comprised of copper plated aluminum protected by OSP.

[0052] An additional benefit of the preferred method 300 is that most of the conductor surface area is covered by an aluminum oxide layer. Aluminum oxide can serve as a dielectric layer to reduce the occurrence of electrical shorting between the backside of PV cells and current collectors. Furthermore, the adhesion strength between a typical encapsulate film and the aluminum oxide layer is

much better than the encapsulate film with OSP treated copper or even dielectric ink coated copper surfaces.

[0053] A preferred method generally corresponding to the process schematic diagrams of Figures 3A-3D is illustrated in Figure 8 as method 600. The method 600 comprises an operation 610 of providing an aluminum face or surface having an oxidation layer. Then, in operation 620, one or more etching resist materials are deposited in a desired pattern on the aluminum face having the oxidation layer leaving only the areas corresponding to the gap and the areas corresponding to the contact points exposed. In operation 630, remaining exposed regions of the oxidation layer are removed. The exposed regions are those regions of the oxidation layer that are not covered by the etching material deposited in operation 620, i.e. the gap and the contact points. Upon removal of the regions of oxidation in operation 630, fresh aluminum is exposed. In operation 640, copper is deposited on one or more regions of the freshly exposed aluminum from operation 640. In operation 645, an etching resist is printed on the copper surface at the contact points. The printing does not need to have very high resolution. Then the exposed copper plated aluminum areas, mostly in the gap area, is etched away, creating a metal free gap area. This is shown as operation 648 in Figure 8. Then in operation 650, the etching resist material is removed. The previously deposited copper is then protected in operation 660. The copper can be protected by any of the techniques described herein.

[0054] Figures 10A-10H schematically illustrate cross sectional views of a preferred current collector formed using a preferred embodiment process. Figure 10A illustrates a substrate 1002 such as a polymeric material having an aluminum layer 1004 disposed on the substrate 1002. An oxide layer 1006 is typically disposed on the aluminum layer 1004. A plurality of contact points 1008 and a gap 1010 are defined on the laminate. It will be appreciated that the gap 1010 or region corresponding to the gap 1010 separates the laminate into regions 1012 and 1014 corresponding to a first electrode and a second electrode, respectively.

[0055] Figure 10B illustrates the cross sectional view of the laminate of Figure 10A after depositing a first layer 1016 of an etching resist material on the oxide layer 1006 such that the gap 1010 and the contact points 1008 are not covered with the layer 1016 of etching resist material.

[0056] Figure 10C illustrates a cross sectional view of the laminate of Figure 10B after removing the oxidation layer 1006 in the gap 1010 and in the contact points 1008 to expose fresh aluminum 1004 in the gap 1010 and the contact points 1008.

[0057] Figure 10D illustrates a cross sectional view of the laminate of Figure 10C after depositing copper 1018 in at least a portion of the gap 1010 and the contact points 1008. Preferably,

copper 1018 is deposited in all of the regions corresponding to the gap 1010 and the contact points 1008.

[0058] Figure 10E illustrates a cross sectional view of the laminate of Figure 10D after depositing a second layer 1016a of an etching resist material in or on the plurality of contact points 1008 such that the gap 1010 is not covered with the etching resist material.

[0059] Figure 10F illustrates a cross sectional view of the laminate of Figure 10E after removal of copper 1018 and aluminum 1004 within the region of the gap 1010, such as by etching of exposed copper 1018 and aluminum 1004 in the gap 1010 to thereby form a metal-free region in the gap. As will be appreciated, the metal-free gap 1010 electrically separates the first and second electrodes 1012, 1014 from one another.

[0060] Figure 10G illustrates removal of etching material 1016 and 1016a to thereby reveal exposed regions of oxide layer 1006, and copper 1018 in the regions of contact points 1008.

[0061] Figure 10H illustrates a cross sectional view of the laminate of Figure 10G after protecting any exposed copper with a protection layer 1020 to thereby form a protected current collector 1022. The protection layer 1020 can be silver such as applied by an immersion silver technique, or an OSP layer.

[0062] In other embodiments, photovoltaic cells are provided. These photovoltaic cells preferably include a c-Si cell in electrical connection with a backsheet. The backsheet includes a substrate and a patterned aluminum conductive layer as described herein.

[0063] Throughout this disclosure, the term "layer" refers to either a continuous material layer, a discontinuous material layer, or a discrete material layer.

[0064] Other features and advantages of the present subject matter will become apparent to those skilled in the art from the following detailed description. It is to be understood, however, that the detailed description of the various embodiments and specific examples, while indicating preferred and other embodiments of the present subject matter, are given by way of illustration and not limitation. Many changes and modifications within the scope of the present subject matter may be made without departing from the spirit thereof, and the subject matter includes all such modifications.

Removal of Oxide Layer(s) by Chemical Treatments

[0065] In many of the embodiments described herein, a sheet assembly is provided and includes a substrate and an aluminum foil layer disposed on the sheet. The aluminum layer is preferably in the form of a pattern and/or defines a pattern which is most preferably an electrical circuit including

one or more electrical contacts to be formed on the aluminum layer. Although the sheet assembly is preferably in the form of a conductive backsheet for a photovoltaic assembly or module, the present subject matter is not limited to such. Instead, the sheet assemblies as described herein can be configured for use in a wide range of applications.

[0066] The exposed regions or face surfaces of the aluminum are cleaned, and then etched with one or more chemical etching solution(s). As will be appreciated, these exposed surfaces typically contain a layer of oxide. A wide array of etchants and/or liquid etching solutions can be used to remove the oxide layer from the aluminum surface or from region(s) of the aluminum surface. Typically, such etching solutions include one or more acids such as nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, and combinations of these acids and potentially with other agents. A preferred commercially available liquid acidic etchant is Helios Al Acid Etch 901 available from MacDermid of Waterbury, Connecticut. Instead of using a liquid acidic etchant as noted, it is also contemplated to utilize one or more alkaline etchants. Nonlimiting examples of alkaline etchants include potassium hydroxide and sodium hydroxide. In many applications, a wet chemical etching process such as previously noted, is preferred.

[0067] In addition to, or instead of, chemical etching operations to remove oxide layer(s), it is also contemplated to use laser ablation strategies to remove any oxides from the aluminum. Representative description of such operations is provided in US Patents 6,727,970 and 6,856,086 assigned to the present assignee.

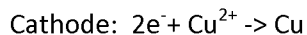
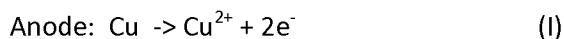
Etching Resist Materials

[0068] For the acid-based etching operations described herein, one or more etching resistant or "etching resist" materials are preferably used, such as by applying to the surface of interest which is to be protected from a subsequent etching operation. Typically, etching resist materials comprise one or more components that can be selectively polymerized and/or crosslinked, such as by exposure to UV radiation. A wide array of such etching resist materials are commercially available such as for example Helios Inkjet Resist from MacDermid.

Plating of Copper on Aluminum Conductor

[0069] After etching and removal of any oxides, residues, or other unwanted material from the aluminum surface, a coating or layer of an electrically conductive material is then applied or otherwise formed on the freshly cleaned aluminum surface. Preferably, the electrically conductive material is

copper, however other materials could be used. In a preferred embodiment, a Cu layer is formed by the following reaction (I):



[0070] Preferably, the copper layer is formed on the freshly exposed aluminum by contacting with, and preferably by immersing the aluminum, in an aqueous copper plating solution. This process is an electrolytic reaction, i.e. electroplating, and involves establishing an electrical connection between a source of electrical current and the aluminum foil as a cathode in the plating circuit. A preferred solution or bath for depositing copper on aluminum is commercially available under the designation CL-NC Alkaline Copper from Uyemura International Corporation, of Ontario, California. The preferred bath comprises various components also commercially available from Uyemura Corporation as follows: CL-NC Metal Salt, CL-NC Conductivity Salt, CL-NC Stabilizer Solution, and CL-NC Brightener. Representative operating conditions for such bath are set forth below in Table 1.

Table 1 - Operating Conditions for Copper Bath

Parameter	Optimum	Range
CL-NC Metal Salt	80 g/l	40-100 g/l
Copper as metal (in make-up salt)	40 g/l	20 – 50 g/l
CL-NC Conductivity Salt	270 g/l	240 – 300 g/l
CL-NC Stabilizer Solution	50 ml/l	40 - 60 ml/l
CL-NC Brightener	10 ml/l	8 – 15 ml/l
Temperature	149°F (65°C)	140 - 158 °F (60 – 70 °C)
pH	7.5	7.0 – 8.5
Current density rack	As needed	1.0 – 4.0 amp/dm ² (10-40 asf)
Current density barrel	As needed	0.5 – 1.0 amp/dm ² (5-10 asf)
Anode – cathode ratio	2:1 and 1:1	2:1 and 1:1

Protecting the Plated Copper Surface

[0071] More specifically, after acid etching and activation of the aluminum surface, the aluminum is plated or otherwise covered with one or more copper layers. It is preferred to protect the fresh copper surface. Several processes have been identified for treating the copper to prevent its oxidation. One operation involves a plating operation in which the copper surface is covered by a silver layer using an immersion silver process. This was previously described as operation 180 in Figure 1B. An example of such a bath is an immersion silver bath commercially available from MacDermid of Waterbury, Connecticut under the designation Helios Silver IM 560.

[0072] Another operation involves printing a thin silver layer comprising a silver nanoparticle ink and followed by drying/sintering of the ink. Preferably, the thin layer of silver nanoparticle ink is deposited by ink jet printing. A preferred nanoparticle ink is commercially available from Cabot of Albuquerque, NM 87113 under the designation CCI-300. It will be understood that deposition of silver can also be performed by providing a composition including particles of silver dispersed in a carrier and then printing the composition on the copper surface or other electrically conductive material surface.

[0073] Protecting copper with an OSP treatment was previously described as operation 270 in Figure 1C. Several commercially available materials such as Entek Plus Cu-106A, and Entek Cu-56 from Enthone, Inc, West Haven, Connecticut; Metex M-667 from MacDermid of Waterbury, Connecticut; and Schercoat Plus, Schercoat Plus Lead Free from Atotech of Rockhill, South Carolina utilize copper protect technology. These commercially available materials can be used to protect a fresh copper surface.

Additional Aspects

[0074] Preferred aspects and various details associated with preferred aluminum alloys or foil, deposition of copper on freshly exposed regions of aluminum, and an optional silver deposition operation are as follows.

[0075] The aluminum laminates described herein comprise a thin layer of aluminum or aluminum alloy on a polymeric substrate or film. The aluminum or aluminum alloy foil or thin layer can be laminated or otherwise provided on a polyethylene terephthalate (PET) or biaxially oriented polypropylene (BOPP) substrate or film. The substrate or film has a thickness of 10 micrometers to 500 micrometers. The aluminum laminate should withstand conditions resulting from electrical short circuits, e.g. arcing and temperature increases; withstand thermal expansion and contraction under high temperature conditions; and exhibit relatively high electrical conductivity. Preferred aluminum alloys

that exhibit these properties comprise at least 99.0% aluminum. Throughout this disclosure, the term “aluminum” includes both aluminum and aluminum alloys.

[0076] Table 2 below lists some of the aluminum alloys that have shown good compatibility with direct plating with CL-NC Alkaline Copper.

**Table 2 - Exemplary Aluminum Alloys that can be
Direct Plated with Alkaline Copper**

Aluminum Alloys
1008
1060
2024
4130
5052
6061
6064
1235

Assemblies

[0077] A wide array of assemblies are also provided. Representative versions of preferred embodiment assemblies are described in the following examples.

Examples

[0078] In Examples 1-4 described herein, copper contacts formed on patterned aluminum laminates by the methods described herein were prepared. Electrical resistance was measured over a time period of 2000 hours (84 days). Details as to the various samples prepared and results of resistance measurements are as follows.

[0079] Substrate: Al 1060 grade 50 micrometer foil laminated to a 2 mil or 5 mil PET film.

[0080] Plating set-up: CL-NC alkaline copper plating solution from, Uyemura, Ontario, California.

[0081] Bath components: CL-NC Metal Salt, CL-NC Conductivity Salt, CL-NC Stabilizer Solution, and CL-NC Brightener.

[0082] For a 5 liter bath, the bath was prepared as follows. A cleaned plating tank was filled with 3 liters of deionized water. The aqueous bath was heated to 50°C. 1.35 kg of CL-NC Conductivity Salt was added in small portions while stirring well until the salt was completely dissolved. 400 g of the CL-NC Metals Salts were added in small portions with stirring, until complete dissolution. 250 ml of the CL-NC Stabilizer Solution and 50 ml of the CL-NC Brightener was then added. The tanks were filled to 5 liters volume with deionized water. The pH was adjusted to 7.0 to 8.5 using analytical grade acetic acid or potassium hydroxide and the temperature was brought to 60 to 70°C.

[0083] A preferred plating parameter is that the typical plating density ranges from 10 to 40 asf. A typical plating procedure is as follows. The part to be plated is placed in a soak clean solution (Asahi-C4000), at 50 to 60°C for 5 minutes and rinsed with deionized water for 1 minute. Then the part is acid soaked (50% nitric acid) RT for 3 to 5 minutes, followed by rinsing with deionized water. The part is then ready to plate. The part is then placed in the previously noted CL-NC plating solution, connected to a cathode electrode, and the system set to a voltage at 1.5 to 3.5 V for 1 to 10 minutes or for a time period for desired thickness.

[0084] Contact resistance, sample preparation, resistance measurements and accelerated aging test details are as follows. Figure 4 is a schematic illustration of a test sample utilized in evaluating various preferred embodiment structures. Figure 5 is a schematic illustration of an aging test measurement assembly. Figure 6 is a schematic cross sectional illustration of a test assembly for assessing contact resistance. A series of small dots (eight) of isotropic conductive paste (ICP) 701 were placed on the center of a series of parallel immersion Ag plated Cu strips (3 mm x 40 mm). These are shown in Figures 4-6 as test strips 702. Specifically, a schematic cross sectional illustration of the test strip 702 is shown in Figure 6A. The test strip 702 comprises a polyethylene terephthalate (PET) substrate 702c, a copper layer 702b disposed on the substrate 702c, and a silver layer 702a disposed on the copper layer 702b. A test piece 703 was also used as shown in Figures 5 and 6. Figure 6B is a schematic cross sectional illustration of the test piece 703 which comprises a polyethylene terephthalate (PET) substrate 703a, a copper plated aluminum layer collectively designated as 703b disposed on the substrate 703a, and an OSP layer 703c disposed on the copper plated aluminum layer 703b. The test piece 703 was cut into an appropriate length and width (2 mm) to ensure that the test piece 703 adequately covers the first and last ICP dots on the Ag plated Cu test strips 702. The test piece 703 was then carefully placed on top of the test strip 702 as shown in Figure 6. The finished test structure was then placed between two pre-heated plates 704 with laterally positioned shims 705 between these two plates and 500 g of weight, illustrated as 706, placed on top of the upper shim 704, then heated by a hot

plate 707 to a desired ICP curing temperature and time. A schematic diagram of this testing configuration is shown in Figure 6.

[0085] The initial contact resistance was measured by a four point probe testing arrangement with sharp contact pins 710 positioned across two ICP dots as shown in Figure 5.

[0086] The accelerated aging test was performed by placing the test samples in an 85°C and 85% relative humidity (RH) environmental chamber. The contact resistance was measured after certain hours of storage as detailed in the following examples.

Example 1

[0087] Following the previously noted procedures, samples for evaluation were prepared as follows. A section of 1060 Al laminate was cleaned with Asahi C4000 solution, rinsed, soaked in 50% nitric solution, rinsed, plated at 25 asf for 5 minutes, and then rinsed again.

[0088] After the rinse cycle which was performed after plating, the 1060 Al laminate was placed in Enthone Entek Plus Cu-106 solution (40°C) for 1 minute.

[0089] The ICP (ECM DB, 1541, Delaware, Ohio) dots were dispensed on the immersion Ag plated copper test strips. Then, the copper plated aluminum sample was cut into a size of 2 mm x 50 mm and placed on top of the test strips.

[0090] The completed structure was placed between two pre-heated plates (150°C). The plates were placed on a hot plate for 15 minutes at 150°C. The assembly arrangement as illustrated in Figure 6 was utilized.

[0091] The contact resistance of each sample was measured before and after an aging test with a four point probe set-up as depicted in Figure 5. The results are presented in Table 3. These results indicate the bonding interface (Al/Cu/OSP/ICP/Ag/Cu) is very stable, and exhibits very little resistance increase in such harsh environments for long periods of time.

Table 3 – Results of Contact Resistance Testing

Sample ID	Initial (mohm)	170 hrs (mohm)	500 hrs (mohm)	1000 hrs (mohm)	1500 hrs (mohm)	2000 hrs (mohm)
1	7.9	8.2	8.0	8.4	8.3	8.2
2	8.0	8.7	8.6	9.0	8.9	9.0
3	7.7	8.0	7.7	8.3	8.1	8.2
4	7.3	7.6	7.4	7.9	7.7	7.7
Average Resistance	7.7	8.1	7.9	8.4	8.2	8.3
% Change		5%	3%	9%	6%	8%

Example 2:

[0092] In this example, the same plating and bonding set-up was followed as in Example 1. The plating parameters were adjusted to 2.5 minutes with CL-NC solution, and then another 2.5 minutes with a standard acid plating solution.

[0093] The contact resistance of the samples was measured before and after an aging test with a four point probe set-up as previously described.

[0094] The results of this testing are presented below in Table 4.

Table 4 – Results of Contact Resistance Testing

Sample ID	Initial (mohm)	170 hrs (mohm)	500 hrs (mohm)	1000 hrs (mohm)	1500 hrs (mohm)	2000 hrs (mohm)
1	8.1	7.9	7.6	8.3	8.0	8.0
2	7.7	7.8	7.5	8.0	7.8	7.8
3	8.0	7.9	7.6	8.0	7.8	8.0
4	8.2	8.1	7.9	8.2	8.0	8.1
Average Resistance	8.0	7.9	7.6	8.1	7.9	8.0
% Change		-1%	-5%	1%	-1%	0%

Example 3

[0095] The same plating and bonding set-up as used in Example 1 was followed. The plating parameters were adjusted to 5 minutes with CL-NC solution, and then another 5 minutes with a standard acid plating solution.

[0096] The contact resistance of the samples was measured before and after an aging test with a four point probe set-up as previously described. The results of this testing are presented below in Table 5.

Table 5 – Results of Contact Resistance Testing

Sample ID	Initial (mohm)	170 hrs (mohm)	500 hrs (mohm)	1000 hrs (mohm)	1500 hrs (mohm)	2000 hrs (mohm)
1	5.7	5.5	5.2	5.5	5.4	5.5
2	5.7	5.5	5.0	5.5	5.4	5.5
3	5.4	5.3	5.1	5.4	5.2	5.3
4	5.8	5.5	5.2	5.5	5.4	5.5
Average Resistance	5.6	5.5	5.1	5.5	5.4	5.4
% Change		-3.2%	-9.3%	-3.4%	-5.3%	-4.0%

Example 4

[0097] The same plating and bonding set-up as used in Example 1 was followed. The plating parameters were adjusted to 10 minutes with CL-NC solution.

[0098] The contact resistance of the sample was measured before and after an aging test with a four point probe set-up as previously described. The results of this testing are presented below in Table 6.

Table 6 – Results of Contact Resistance Testing

Sample ID	Initial (mohm)	170 hrs (mohm)	500 hrs (mohm)	1000 hrs (mohm)	1500 hrs (mohm)	2000 hrs (mohm)
1	8.0	8.3	8.1	8.4	8.4	8.4
2	7.2	7.5	7.1	7.5	7.5	7.4
3	7.5	7.8	7.5	8.1	7.9	7.8
4	7.0	7.2	6.9	7.3	7.2	7.2
Average Resistance	7.4	7.7	7.4	7.8	7.8	7.7
% Change		3.4%	-0.6%	5.3%	4.4%	3.7%

[0099] Each of the samples were further subject to a cross-hatch test according to ASTM D 3350. Table 7 is a summary of the test results. No copper was removed from the aluminum surface in any of the samples, indicating good adhesion between the two metal layers.

Table 7 – Results of Cross-Hatch Testing

Sample ID	Percent of Area Removed (%)
Example 1	0
Example 2	0
Example 3	0
Example 4	0

[00100] Many other benefits will not doubt become apparent from future application and development of this technology.

[00101] All patents, applications, and articles noted herein are hereby incorporated by reference in their entirety.

[00102] As described hereinabove, the present subject matter overcomes many problems associated with previous strategies, systems, and/or devices. However, it will be appreciated that various changes in the details, materials, and arrangements of components, which have been herein described and illustrated in order to explain the nature of the present subject matter, may be made by those skilled in the art without departing from the principle and scope of the claimed subject matter, as expressed in the appended claims.

WHAT IS CLAIMED IS:

1. A method for forming a protected sheet assembly having an aluminum conductor, the method comprising:

providing a laminate including a substrate and an aluminum layer disposed thereon, the aluminum layer having an oxidation layer constituting an outer surface of the aluminum layer;

removing at least a portion of the oxidation layer to expose at least one region of fresh aluminum;

depositing copper on at least a portion of the at least one region of fresh aluminum;

protecting the deposited copper by applying at least one of (i) a silver layer on the deposited copper and (ii) an organic solderability preservative coating on the deposited copper to thereby form a protected sheet assembly having an aluminum conductor.

2. The method of claim 1 wherein the deposited copper is a first copper layer, the method further comprising:

prior to protecting the deposited copper, depositing a second copper layer on the first copper layer.

3. The method of any one of claims 1-2 wherein the protecting is performed by applying a silver layer.

4. The method of any one of claims 1-2 wherein the protecting is performed by applying an organic solderability preservative coating.

5. A protected sheet assembly formed by any one of claims 1-4.

6. The protected sheet assembly of claim 5 wherein the sheet assembly is a photovoltaic backsheet.

7. A method for forming a protected current collector, the current collector including a first electrode, a second electrode, a gap separating the first electrode and the second electrode, and a plurality of contact points, the method comprising:

providing a laminate including a substrate and an aluminum layer disposed thereon, the aluminum layer defining a first electrode, a second electrode, a gap separating the first electrode and the second electrode, and a plurality of contact points, the aluminum layer having an oxidation layer constituting an outer surface of the aluminum layer;

depositing a first layer of an etching resist material on the oxidation layer such that the gap and the plurality of contact points are not covered with the etching resist material;

removing the oxidation layer in the gap and the plurality of contact points to expose fresh aluminum in the gap and the plurality of contact points;

depositing copper on at least a portion of the gap and the plurality of contact points;

depositing a second layer of an etching resist material on the deposited copper in the plurality of contact points such that the gap is not covered with the second layer of the etching resist material;

removing copper and aluminum in the gap to thereby form a metal-free gap;

removing etching resist material;

protecting any exposed copper to thereby form a protected current collector.

8. The method of claim 7 wherein the protecting exposed copper is performed by applying a silver layer.

9. The method of claim 7 wherein the protecting exposed copper is performed by applying an organic solderability preservative coating.

10. A protected current collector formed by any one of claims 7-9.

11. A photovoltaic cell, comprising;

a c-Si cell; and

a backsheet, wherein the backsheet comprises a substrate layer, and a patterned aluminum conductive layer on the substrate layer, wherein the patterned aluminum conductive layer is in electrical contact with the c-Si cell and the aluminum conductive layer includes at least one oxidation resistant region.

12. The photovoltaic cell of claim 11 wherein the at least one oxidation resistant region includes a copper layer disposed on the aluminum layer.

13. The photovoltaic cell of claim 12 wherein the at least one oxidation resistant region further includes a layer of silver on the copper layer.

14. The photovoltaic cell of claim 12 wherein the at least one oxidation resistant region further includes a layer of OSP on the copper layer.

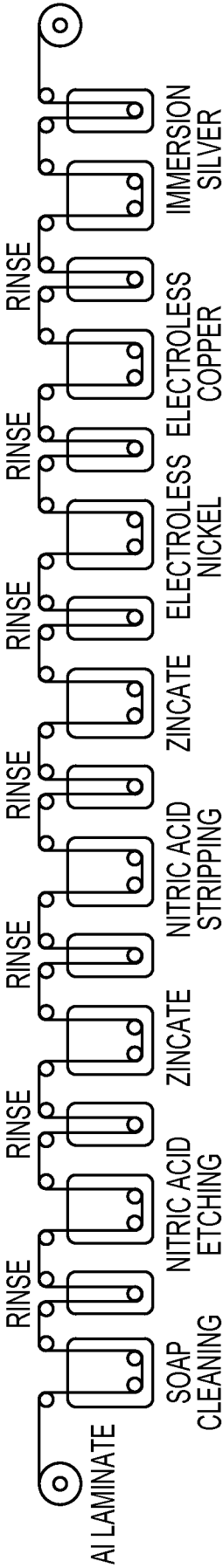


FIG. 1A

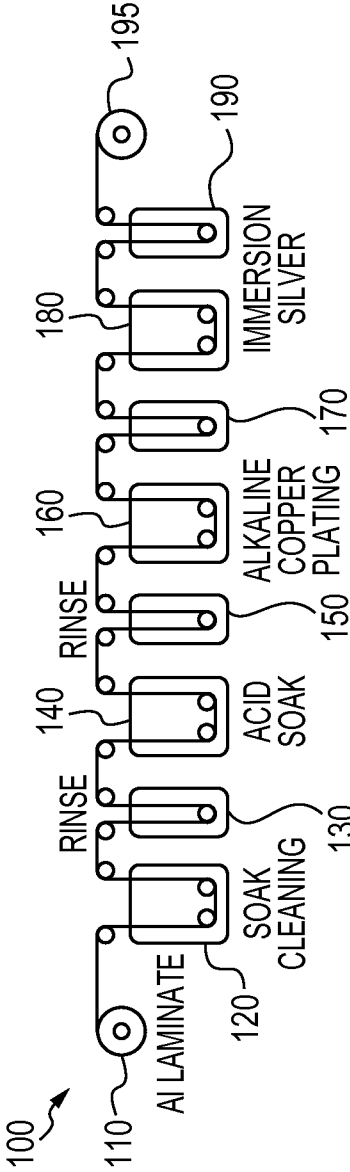


FIG. 1B

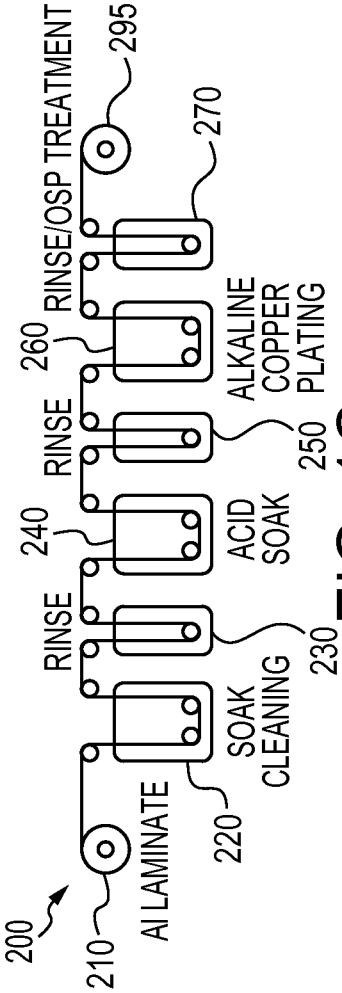
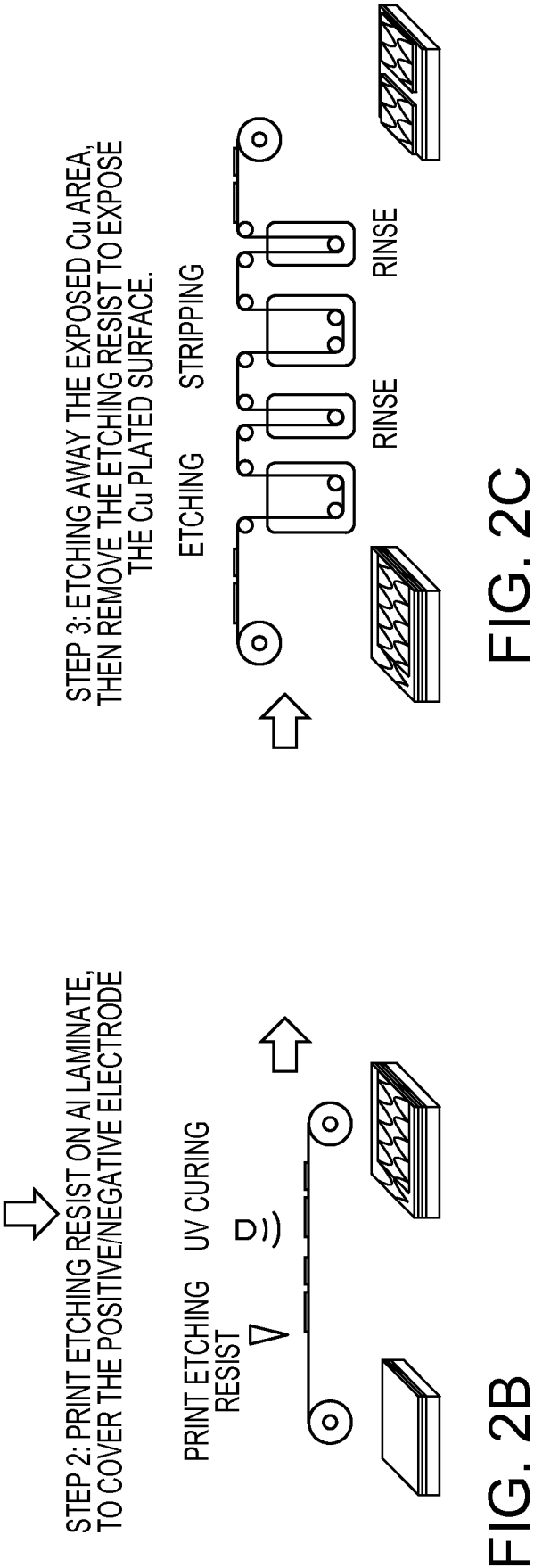
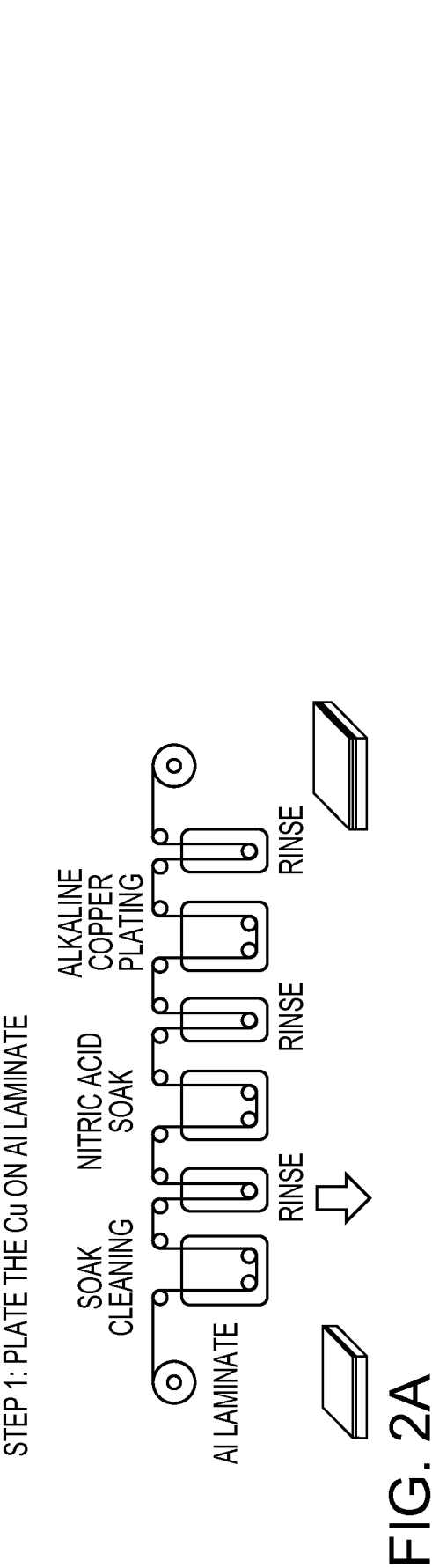
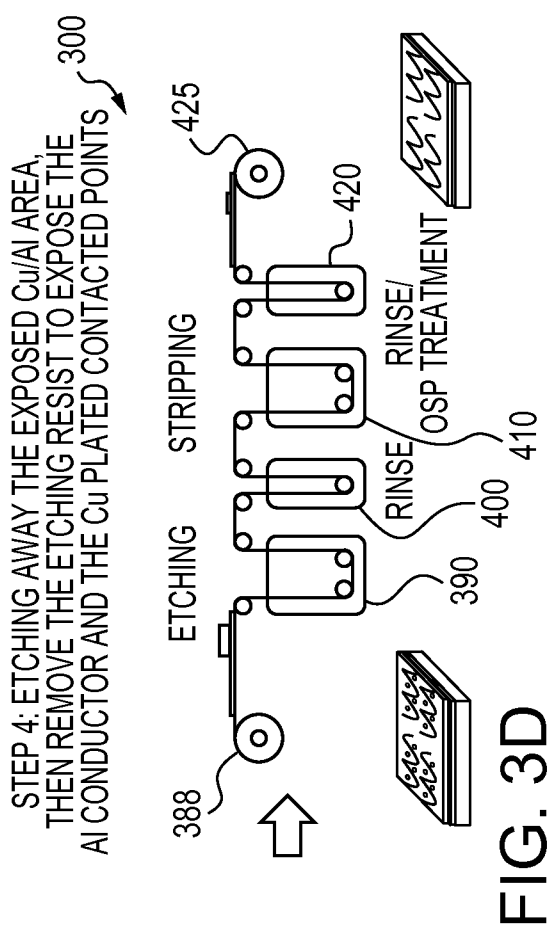
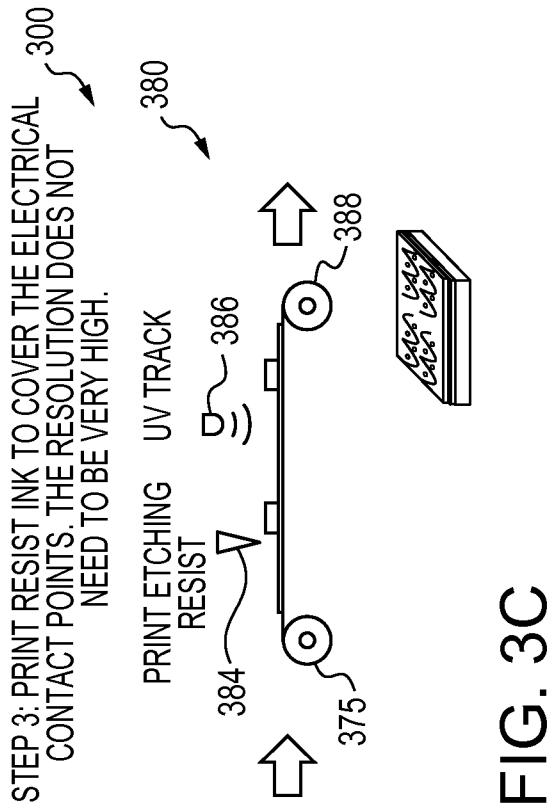
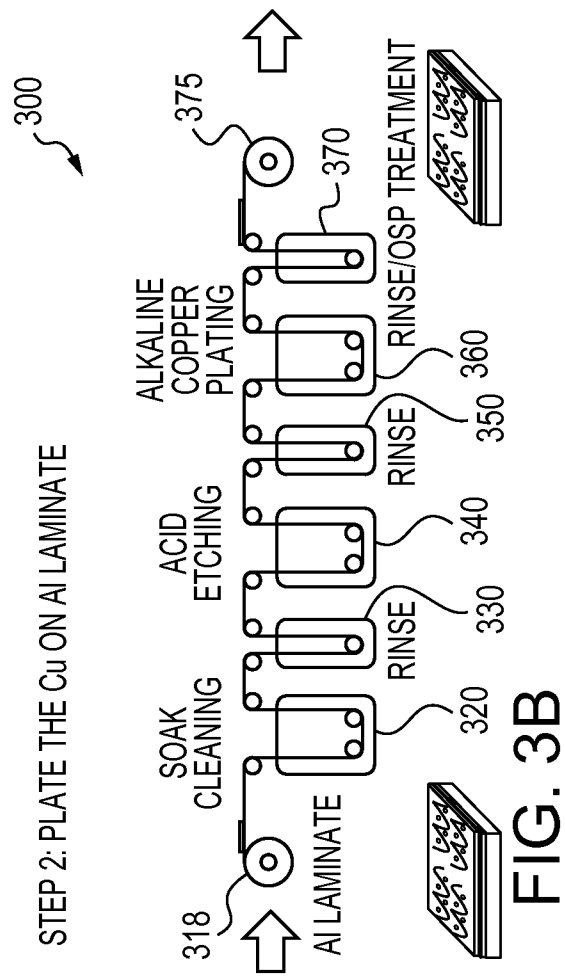
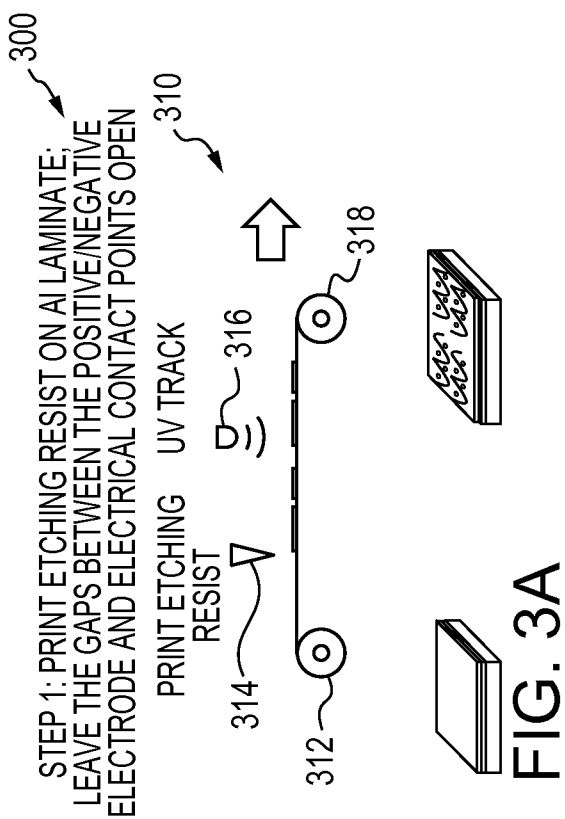


FIG. 1C





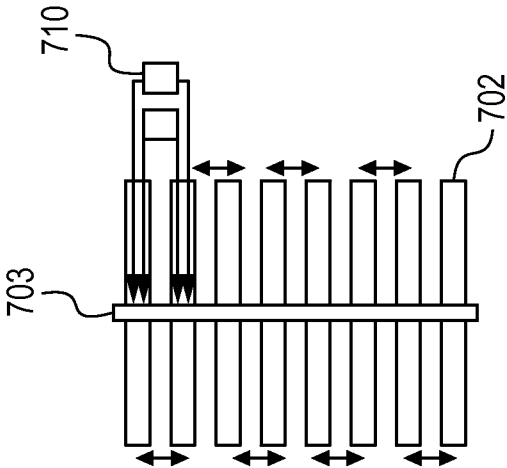


FIG. 5

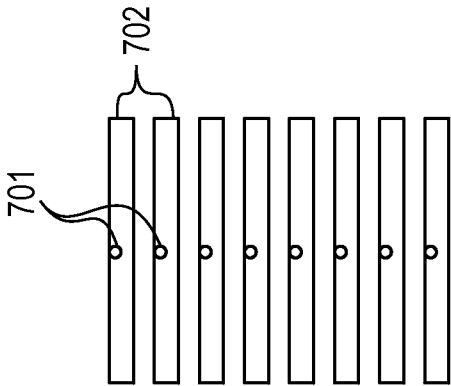


FIG. 4

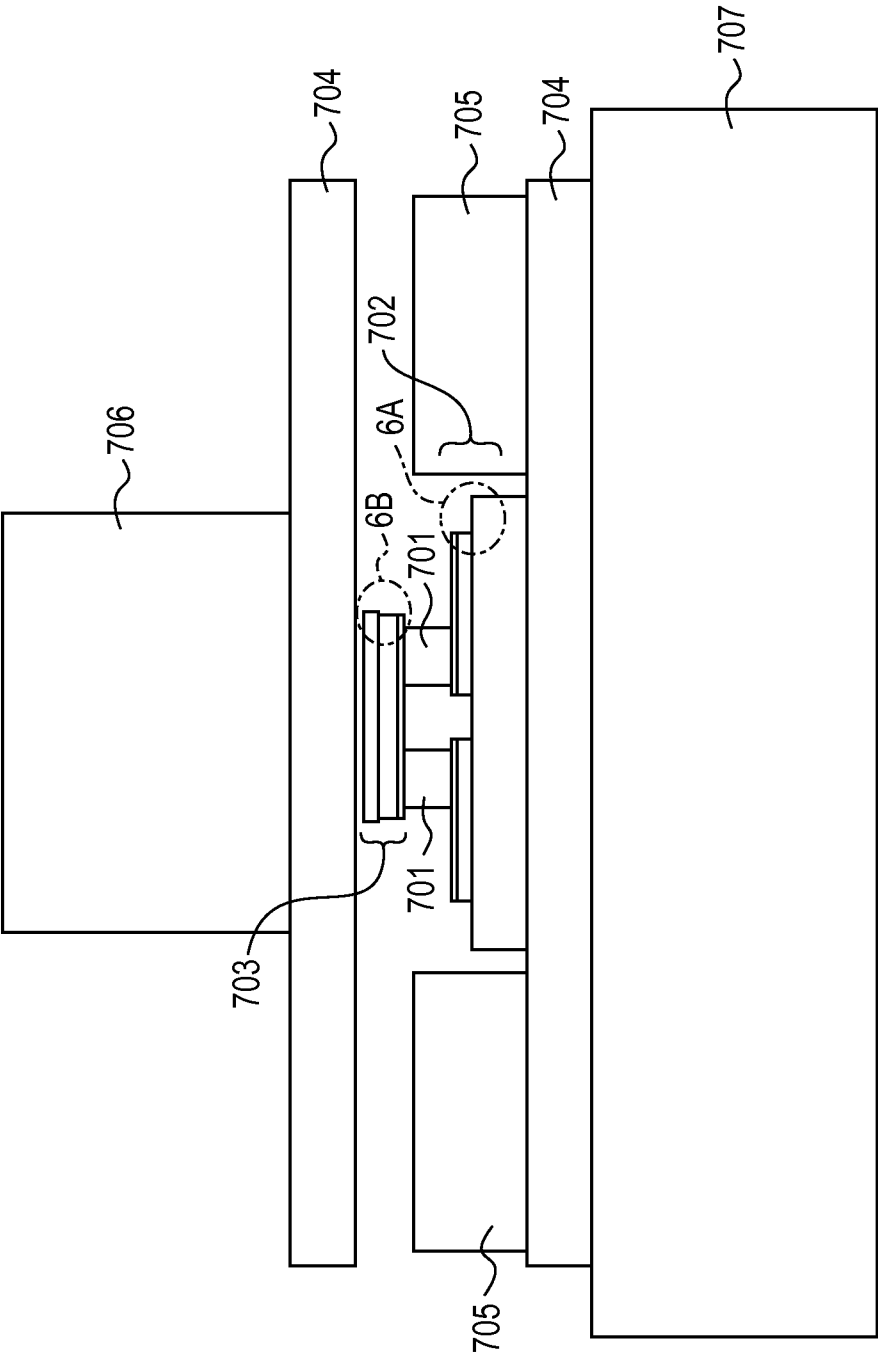


FIG. 6

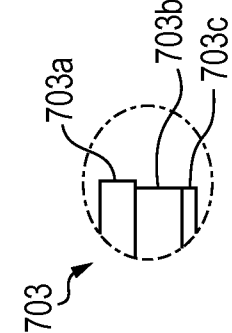


FIG. 6B

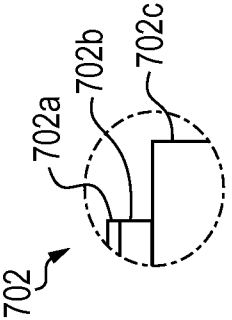


FIG. 6A

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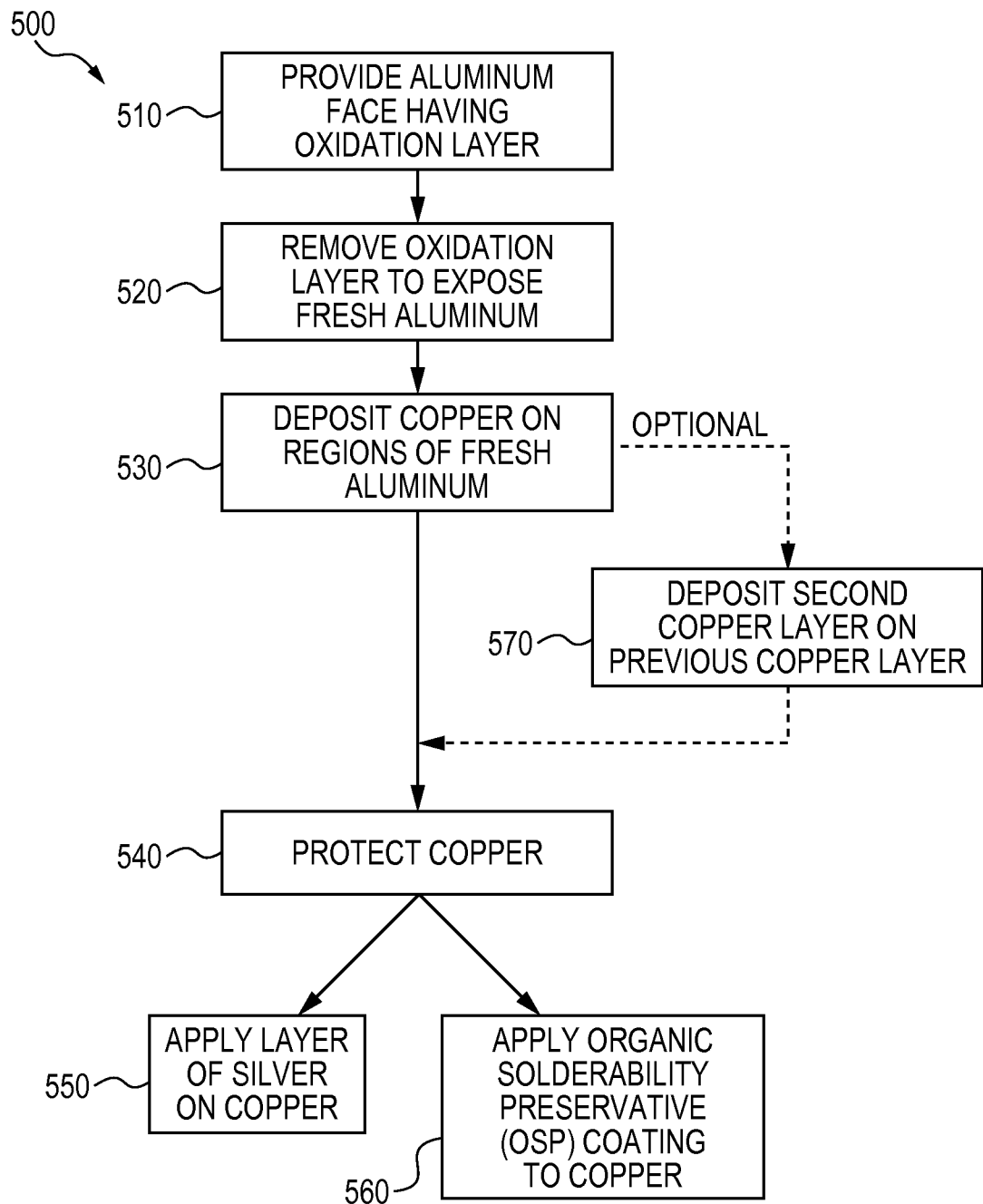


FIG. 7

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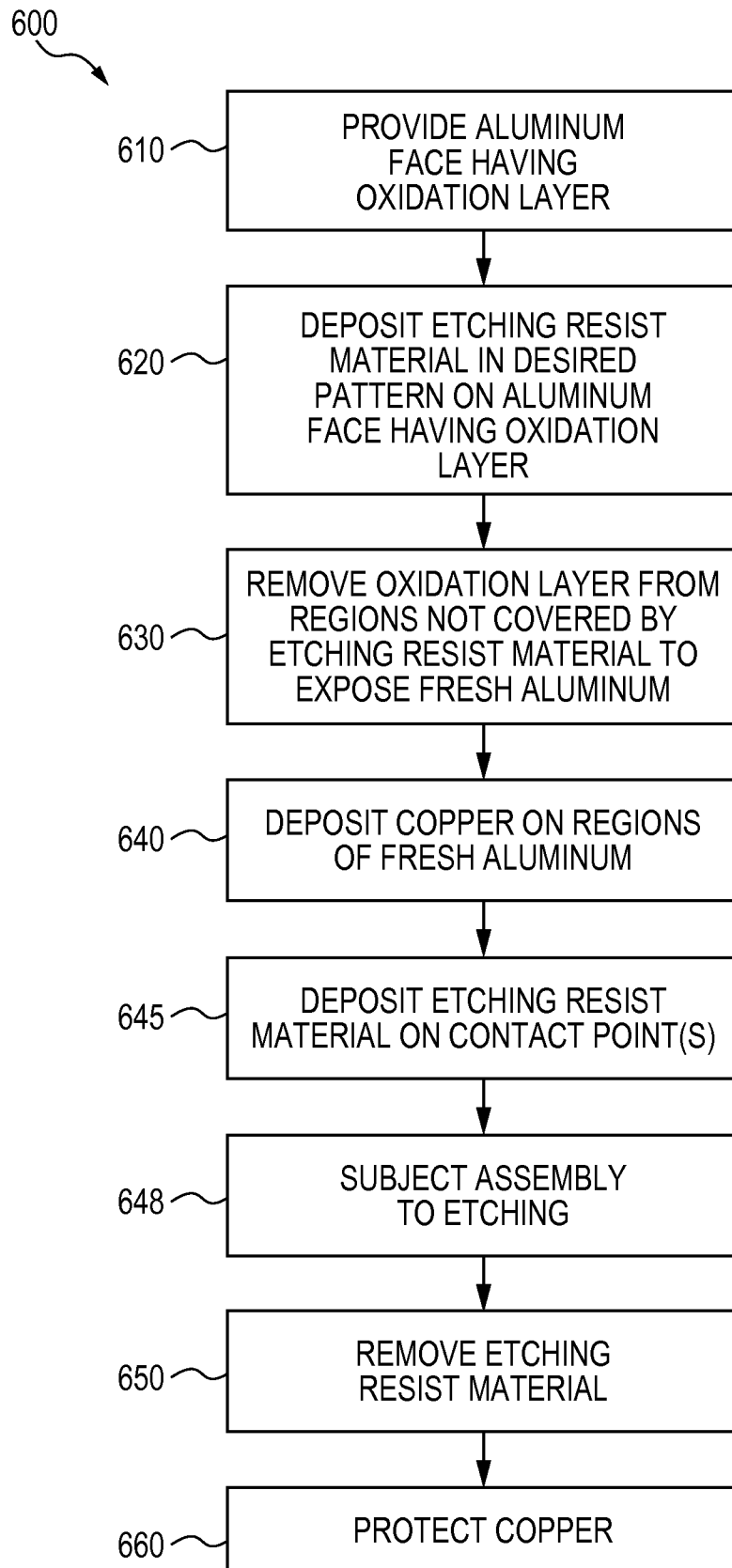


FIG. 8

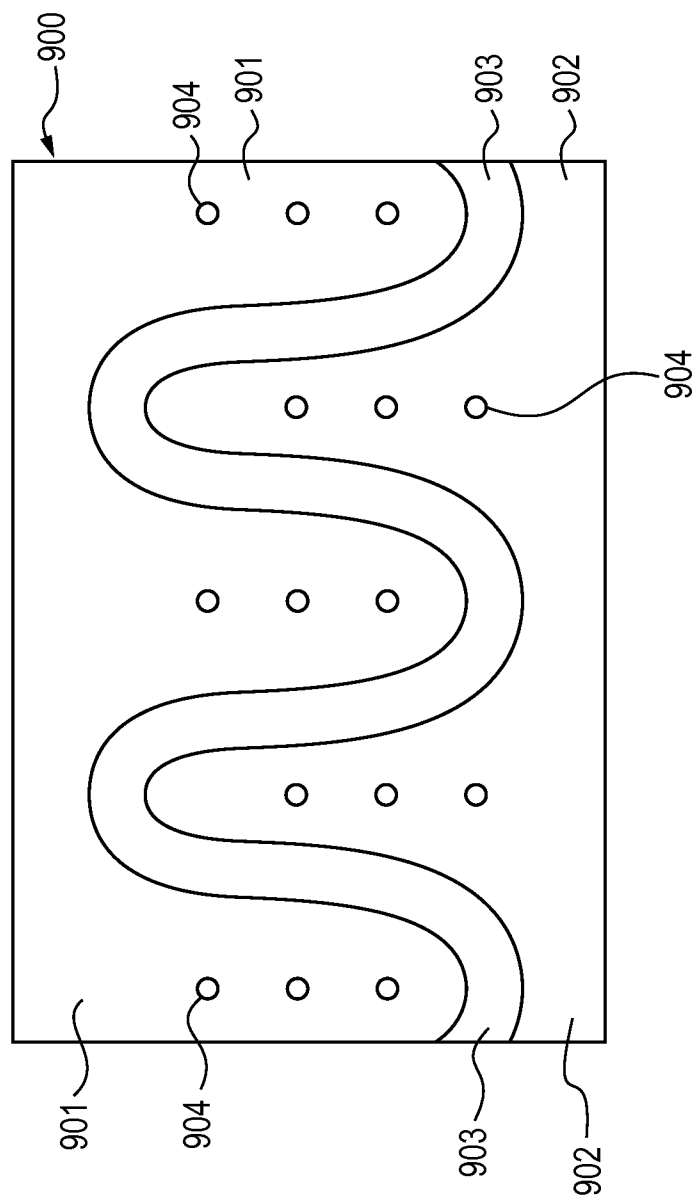


FIG. 9

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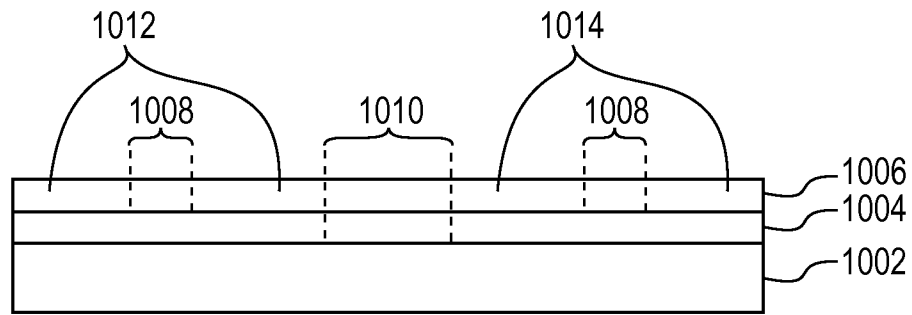


FIG. 10A

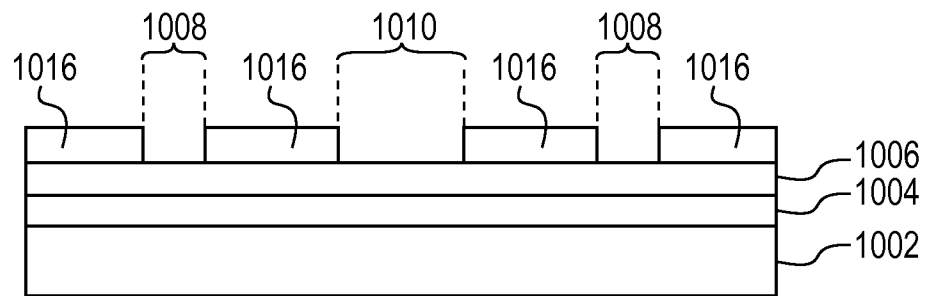


FIG. 10B

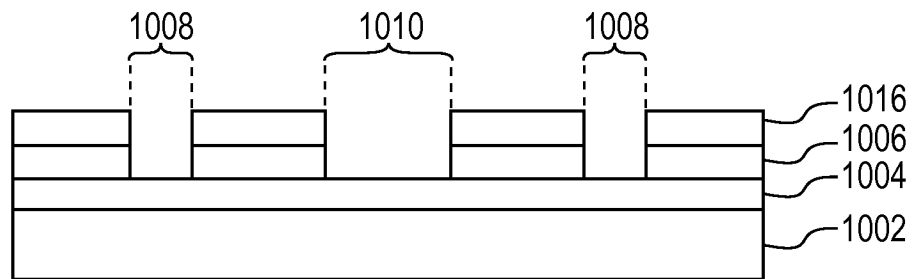


FIG. 10C

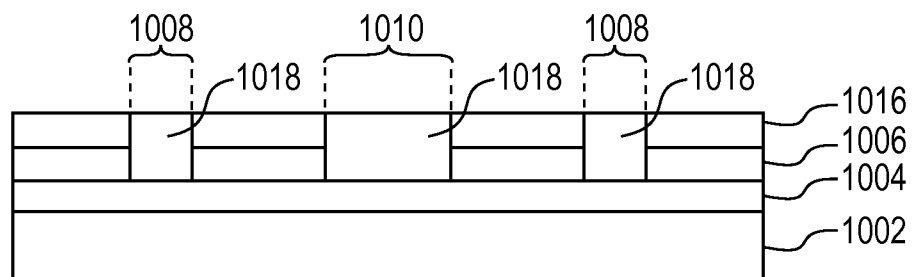


FIG. 10D

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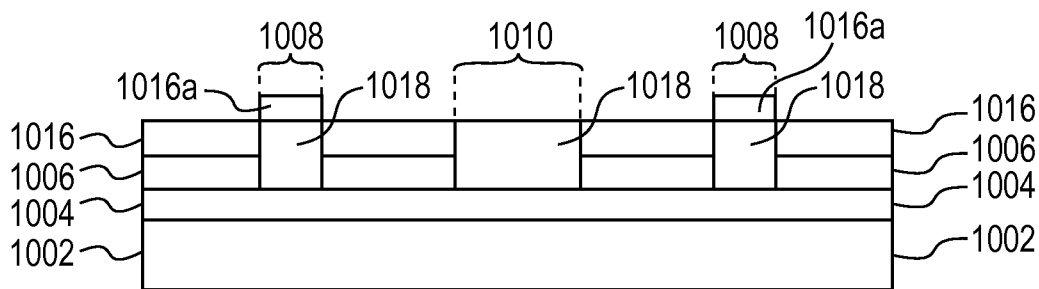


FIG. 10E

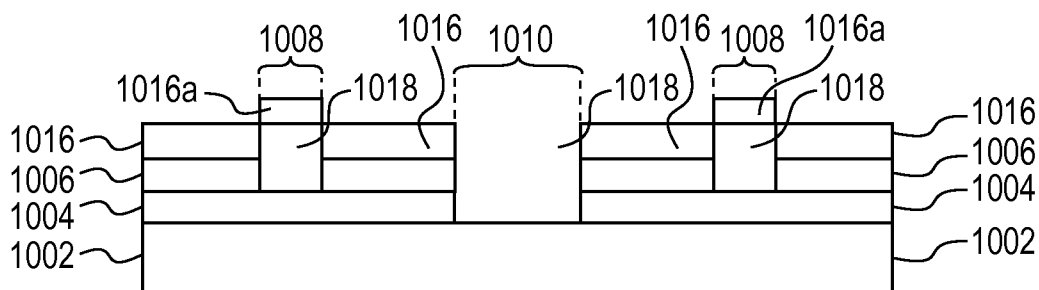


FIG. 10F

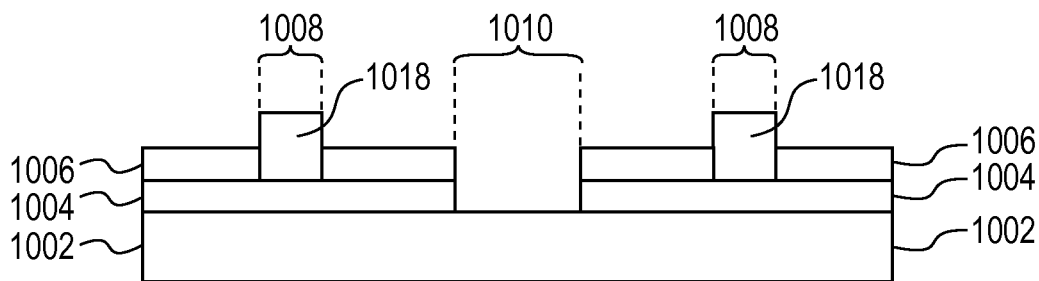


FIG. 10G

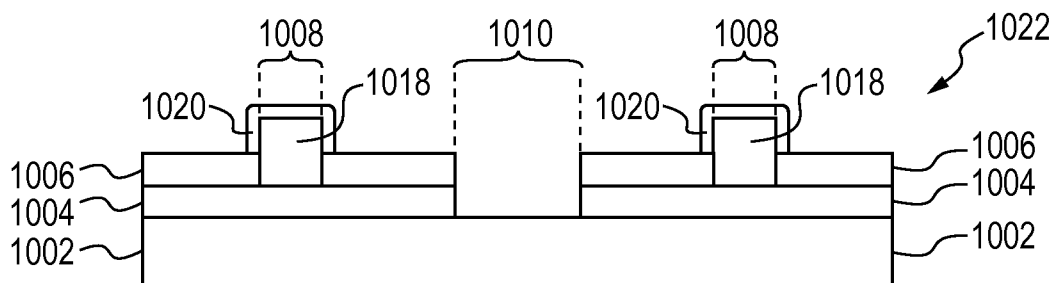


FIG. 10H