(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 September 2017 (14.09.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/155469 A1

(51) International Patent Classification:
H01L 21/00 (2006.01) *C25D 3/12* (2006.01)
H05K 3/00 (2006.01) *C25D 3/40* (2006.01)
C23F 1/00 (2006.01) *C25D 3/46* (2006.01)

(21) International Application Number: PCT/SG2017/050115

(22) International Filing Date: 9 March 2017 (09.03.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10201601865X 10 March 2016 (10.03.2016) SG

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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(54) Title: SEMICONDUCTOR DEVICE AND METHOD OF MANUFACTURE

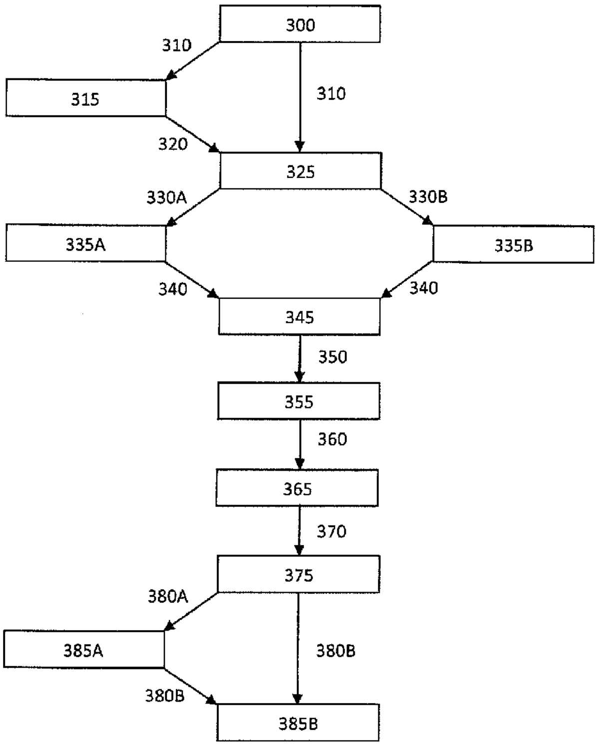


Fig. 2

(57) Abstract: The present invention relate to a leadframe or flexible printed circuit (FPC) and a method of manufacturing a leadframe or FPC having a GAM value of greater than 2.0. The method comprises subjecting an electrolytically cleaned leadframe or FPC to a microetching step to provide a microetched leadframe or FPC or subjecting an electrolytically cleaned leadframe or FPC to a copper plating process to provide a double copper plated leadframe or FPC. The microetched leadframe or double copper plated leadframe or FPC is then subjected to a bright-deposition nickel plating process, a silver strike electoplating process, a bright silver plating process, and then a silver stripping process to provide a mirror bright silver leadframe or FPC.

WO 2017/155469 A1

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

Semiconductor device and method of manufacture

Field of Invention

The invention relates to the manufacture of leadframes or flexible printed circuits (FPCs) for electronic devices. Specifically, the method relates to the process leading to plating a leadframe or FPC to produce a high brightness Light Emitting Diode (LED).

Background

A Light emitting diode (LED) is a semiconductor light source that is of interest for various illumination applications. Among other things, LEDs are commonly used in the electronics world to provide lighting within all manner of devices, such as, watches, traffic lights, televisions and the like. LEDs offer several advantages/benefits over conventional incandescent light bulbs and fluorescent illumination devices. LEDs are more reliable, they provide illumination immediately when supplied with power, and they can be switched on and off frequently without adversely affecting the lifetime or light emitting capabilities of the LEDs. Most notably, LEDs are extremely energy efficient and have an outstanding long operational life compared to conventional light sources.

LED technology is slowly revolutionizing the advertising industry as it allows for the creation of vibrant and dynamic display screens. It has long been known that passers-by are generally not attracted to low brightness static images. Hence there is desire to generate LED screens that are powerful and bright, even from a long distance. Brightness is usually measured in candelas per sq. m (also known as NITS). A small LCD screen may have a brightness level of 250 cd/m^2, while a 42 inch LCD can have a brightness level of 800 cd/m^2. An indoor LED screen normally has a brightness of 1500 cd/m^2, whereas a large outdoor screen can have a brightness of 10,000 cd/m^2. As such, there is a desire to achieve a higher degree of brightness from LEDs.

An LED generally comprises: an LED leadframe or FPC that includes a body having a mounting surface for directly or indirectly mounting an LED element and a reflective metal layer for reflecting light emitted from the LED deposited over the mounting surface of the LED leadframe/FPC. In addition, a weather-proofing resin can be applied over the assembly, forming a barrier against the elements.

The leadframe is typically a molded plastic member that is provided with a base layer of copper, copper alloy or stainless steel, upon which a layer of silver is plated. It is characterized by being low cost and of ease to assemble. The leadframe provides a support to protect the device and a platform upon which the device can be isolated from the various weather elements. A FPC is a pattern of conductive traces bonded on a flexible substrate. A FPC contains a metallic (commonly copper, though other metals may be used) layer of traces bonded onto a dielectric layer (e.g. made from a polyimide or polyester, though other polymers can be used too) on the substrate. An adhesive may be used to bond the metal to the substrate to form the FPC.

Conventionally, LED leadframes or FPCs are coated in a layer of metal prior to encapsulation. The coating produces a finish that is readily bondable, solderable, corrosion resistant and cosmetically acceptable. It is also desirable that the coasting be highly reflective.

Currently the base metallic coating on the LED leadframes or FPCs are silver plated using a strip-to-strip silver plating machine, whereby the leadframe/FPC is immersed in the floodcell of said machine. The floodcell contains a solution that comprises the required silver plating components, as well as a brightener to help achieve the desired brightness for the resulting LED formed using the leadframe or FPC. In the current generation of LEDs, the brightness conventionally achieved as measured using a transmission densitometer as a GAM value is from 1.0 to 1.3 GAM.

It is desired that the next generation of LEDs have a GAM value that are brighter and more vibrant, and so have a desired GAM value of greater than or equal to 2.0 GAM. However, this increased GAM value must also be maintained at the same time as maintaining a reflectivity of more than 90% for the silver-plated area (as measured by specular component included, SCI) and a reflectivity for the specular component excluded (SCE) of less than 30%.

Summary of Invention

We have surprisingly discovered a new method that enables one to provide a leadframe or FPC with the desired GAM value of 2.0 or greater.

Thus in a first aspect of the invention, there is provided a method of manufacturing a leadframe or FPC having a GAM value of greater than 2.0, the method comprising the steps of:

(a) providing a copper plated leadframe or FPC, where the copper plating is etched and is coated with an anti-tarnish layer;

(b) subjecting the copper plated leadframe or FPC to a first electrolytic cleaning step to provide an electrolytically cleaned leadframe or FPC;

(c) subjecting the electrolytically cleaned leadframe or FPC to a microetching step to provide a microetched leadframe or FPC or subjecting the electrolytically cleaned leadframe or FPC to a copper plating process to provide a double copper plated leadframe or FPC;

(d) subjecting the microetched leadframe or FPC or double copper plated leadframe or FPC to a bright-deposition nickel plating process to provide a nickel plated leadframe or FPC;

(e) subjecting the nickel plated leadframe or FPC to a silver strike electoplating process to provide a silver strike plated leadframe or FPC;

(f) subjecting the silver strike plated leadframe or FPC to a bright silver plating process to provide a bright silver leadframe or FPC;

(g) subjecting the bright silver plated leadframe or FPC to a silver stripping process to provide a mirror bright silver leadframe or FPC; and

(h) applying an anti-tarnish coating to the mirror bright silver plated leadframe or FPC.

In an embodiment of the invention, there is provided a method of manufacturing a leadframe or FPC having a GAM value of greater than 2.0 wherein before step (b) is performed, the copper plated leadframe or FPC of step (a) may be subjected to a soaking step in an acid bath to provide an acid-cleaned copper plated leadframe or FPC, optionally wherein the acid may be selected from one or more of the group selected from sulfuric acid, polysulfuric acids, dithionic acids, and peroxysulfuric acids.

In further embodiments of the invention, the microetching process of step (c) the process may comprise spraying a microetchant solution onto the electrolytically cleaned leadframe or FPC in an amount and for a sufficient period of time to remove from 0.5 to 1.3 µm of copper from the copper plating layer. For example, the microetchant solution may comprise an organic peroxide (e.g. ammonium persulfate) at a concentration of from 60 to 90 g/L and sulfuric acid at a concentration of from 1 to 2 vol%, optionally wherein the contact time of the microetchant solution with the electrolytically cleaned leadframe or FPC may be from 30 to 60 seconds. In alternative embodiments of the invention, step (c), may involve a copper plating step, which uses copper cyanide bath and may be conducted using a current density of from about 3.0 to about 4.0 A/dm^2, at a temperature of from about 50 to about 55°C.

In yet further embodiments of the invention, the nickel plating process of step (d) may use a nickel electrolyte solution that comprises:

nickel sulfate (e.g. nickel sulfate hexahydrate) in an amount of from about 300 to about 350g/L;

nickel chloride in an amount of from about 40 to about 60 g/L;

boric acid in an amount of from about 40 to about 50 g/L;

a wetting agent in an amount of around 0.3%v/v;

additive A in an amount of from 1.0 to 2.0%vv;

additive B in an amount of from 0.2 to 0.3%vv; and

additive C in an amount of from 0.5 to 0.75%vv; where:

additive A is selected from one or more of the group consisting of a substituted or unsubstituted aryl sulfonamide, a substituted or unsubstituted unsaturated alkyl sulfonamide, a substituted or unsubstituted aryl sulfonate, a substituted or unsubstituted unsaturated alkyl sulfonate, an aryl sulfonic acid and salts and solvates thereof;

additive B is selected from one or more of the group consisting of trifluoromethane sulfonic acid, halides of trifluoromethane sulfonic acid and aromatic substitted sufonic acids and salts and solvates thereof;

additive C is selected from one or more of the group consisting of 1,2-methyl-4-isothiazoline, carbendaxin, 1,2-benzisothiazole-3(2*H*)-one, 2-phenoxyethanol, benzoic acid, and methyl paraben; and the nickel solution has a pH of from 4.0 to 4.5. For example, the nickel plating process may be conducted using a current density of from about 5.0 to about 6.5 A/dm^2, at a temperature of from 50 to 65°C, and with soluble nickel anodes operated with cathode movement or air agitation.

In yet further embodiments of the invention, during the nickel plating process of step (d) depleted additives A and B are replenished by the further addition of:

additive D in an amount of from 0.05 to 0.1%vv;

additive D, is a mixture of at least one compound mentioned in the list provided for additive A and at least one compound mentioned in the list provided for additive B.

In yet further embodiments of the invention, the silver strike electroplating process of step (e) may use a silver strike electrolyte solution that comprises:

ionic silver in an amount of from 1.0 to 2.0 g/L; and

KCN in an amount of from 100 to 300 g/L. For example, the silver strike electroplating process may be conducted using a current density of around 2.0 A/dm^2 and a deposition time of from about 20 to about 60 seconds.

In still further embodiments of the invention, the bright silver plating process of step (f) may use a bright silver plating electrolyte solution that comprises:

potassium silver cyanide salt at a concentration of from 50 to 100 g/L;

potassium cyanide at a concentration of from 100 to 150 g/L;

potassium hydoxide at a concentration of from about 6 to 20 g/L;

brightener A at a concentration of from 3 to 15 mL/L;

brightener B at a concentration of from 2 to 7mL/L; and

brightener C at a concentration of from 2 to 7mL/L, where

brightener A is a mixture of organic brightener compounds that contain a ketone group and/or organometallic compounds;

brightener B is a mixture of organic brighterner compounds that contain a ketone group, such as ketones that provide an aroma and/or organometallic compounds;

brightener C is one or more alkyl acrylates; and

the pH of the solution is over 11.5. For example, the bright silver plating process is conducted using a current density from about 5.0 to about 6.5 A/dm^2 and at a temperature of from about 20 to about 40°C.

In certain embodiments of the invention, after step (f) has been completed and before step (g) is initiated, a second electrolytic cleaning process may be conducted. For example, the electrolytic cleaning process may use an electrolytic cleaning solution that comprises:

an alkaline material (e.g. sodium silicate) selected from one or more of the group consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal silicates and alkali metal phosphates; and

a sequestering agent selected from one or more of the group consisting of sodium tripolyphosphate, tetrapotassium pyrophosphate, and tetrasodium pyrophosphate, optionally wherein

the alkaline material is present in an amount of from 12 to 25 g/L. Suitable conditions for the electrolytic cleaning may involve using the leadframe or FPC as the cathode and a direct current of from 1 to 5 A/dm^2 at a temperature of from about 50 to about 60°C.

For the avoidance of doubt, any technically sensible combination of the embodiments of the first aspect of the invention are specifically contemplated

A second aspect of the invention relates to an LED leadframe or FPC that is obtained or obtainable from the method of the first aspect of the invention and any technically sensible combination of its embodiments, wherein the leadframe or FPC has a GAM value of greater than 2.0.

As used herein, the term 'comprising' and its antonyms does not preclude the presence of additional steps or substances in the methods and compositions, respectively, of the invention. The terms 'consisting of' and 'consisting essentially of' and their antonyms are used here to limit the presence of additional steps or substances in the methods and compositions, but for the presence of minor impurities. It will be understood that the term 'comprising' and its antonyms includes within its scope the terms 'consisting of' and 'consisting essentially of'. For the avoidance of doubt it is specifically intended that the term "comprising" and its antonyms may be replaced at each occurrence herein by "consisting of" or "consisting essentially of" or their antonyms, and *vice versa.*

Figures

The features of the invention will be more readily understood and appreciated from the following detailed description when read in conjunction with the accompanying drawings of embodiments of the present invention, in which:

FIG. 1 is a process flow chart that depicts the conventional process of preparing and plating a leadframe or FPC.

FIG. 2 is a process flow chat according to an embodiment of the present invention.

Detailed Description

An initial LED leadframe or FPC is provided. This initial leadframe or FPC may be made of a moulded plastic material that is subsequently coated in a layer of a metal, such as copper. Alternatively, the leadframe or FPC may be made entirely of a metal such as copper. As described hereinbelow with reference to Figures 1 and 2, the initial leadframe or FPC is subjected to two distinct operational stages - an etching phase, followed by a plating phase.

Starting with the conventional process as illustrated by Figure 1, the initial leadframe or FPC 100, is subjected to a pre-cleaning process 110 with an acid spray cleaner to remove any contaminants that may be present on the surface of the metal (i.e. copper), such as organic contaminants, chromate and any anti-tarnish coatings. Any suitable acid may be used, such as, but not limited to, sulfuric acid or citric acid.

The pre-cleaned leadframe or FPC 115 is then subjected to dry film lamination 120 using a suitable photoresist (e.g. a positive or negative photoresist) to provide a dry film laminate on the cleaned metal surface of the leadframe or FPC 125. The cleanliness of the metal surface is important in ensuring a good conformation of the resist on to the metal surface and this is critical for fine line applications.

After lamination, the dry film laminated leadframe or FPC 125 is transferred to an exposure machine where the area of the leadframe or FPC 125 to be plated is exposed 130 using collimated light and a film/glass artwork to provide an exposed leadframe or FPC 135. If a positive photoresist was used, then the portion of the photoresist that is exposed to light becomes soluble to the photoresist developer, while the portion of the photoresist that is unexposed remains insoluble to the photoresist developer. If negative photoresist was used, then the portion of the photoresist that is exposed to light becomes insoluble to the photoresist developer, while the portion of the photoresist that is unexposed can be dissolved by the photoresist developer. This process is typically conducted in a clean room environment, as this reduces particle contamination, which can block the light and prevent exposure of the photoresist, leading to problems during the subsequent etching and plating steps due to the imperfect exposure.

The exposed leadframe or FPC 135 is then subjected to a developing step 140. Assuming that a negative photoresist was used previously, then in the development process 140, the areas of the laminated dry film on the leadframe or FPC 135 that were not exposed to light are removed by the developing solution to expose the surface of the metal leadframe or FPC that is to be etched, thereby presenting an exposed metal leadframe or FPC 145.

During the etching process 150, the exposed metal surface of the exposed metal leadframe or FPC 145 is removed to a desired degree by the metal etchant that is used. The etching process is generally accomplished by spraying a metal etchant onto leadframe or FPC 145 and recycling the etchant. However, larger chips of etched metal may not dissolve fully which can lead to problems in the etching process as they may partially or fully block the spray nozzles used to supply the etchant, thereby limiting the spray pressure. To overcome this, a chip separator filtration system is used, wherein a pump sucks the etchant into the chip separator filtration system and separates the acid-base etchant from the metal chips and recycles the etchant to the spray nozzles for reuse. The chip separator is built from an etchant resistant material (e.g. titanium) and may comprise an inlet from the pump for the metal-containing etchant, an outlet for filtered etchant, a mesh with pores of a suitable size (e.g. a pore size that is smaller than the nozzle openings used to spray the etchant, such as around 20 microns), a basket for collecting the metal chips and a basket, such that when the chip-containing etchant is pumped into the chip separator, the metal chips that are larger than the opening size in the mesh are channeled off into the basket and the etchant (now free of chips that will block the etchant nozzles) is allowed to flow back to the etchant tank thought the outlet.

Once the etching process is complete, the etched leadframe or FPC 155 is subjected to a stripping process 160 that removes the remaining photoresist dryfilm laminate from the leadframe or FPC to provide a fully exposed and etched metal surface 165 on the leadframe or FPC. The etching and stripping processes generally result in the formation of an oxide layer on the surface of the fully exposed and etched metal surface 165 of the leadframe or FPC. To remove this oxidation layer, the fully exposed and etched metal surface 165 of the leadframe or FPC is subjected to an acid wash treatment 170 to provide an oxide-free leadframe or FPC 175. Finally, the leadframe or FPC 175 is coated with an anti-tarnish composition in an anti-tarnish step 180 to prevent oxidation of the surface before use in the plating phase. The anti-tarnish coated leadframes or FPCs 185 are then singulated using a singluation machine and are separated from reel to strip form, so that they can be used in a strip -to-strip plating machine. Following a final rinse 190 with deionised water, the lead frame 195 is now ready for the plating phase, which is discussed below.

The conventional plating phase comprises the steps of electro-cleaning 210, activation 220, a number of metal plating steps (230, 240, 250) and the application of a final anti-tarnish coating 260.

The electrocleaning process 210 is conducted to remove any unwanted contaminants or dirt from the surface to be plated with metal, thereby providing an electrocleaned leadframe or FPC 215. Contemporary cleaning systems must remove oil, grease, scale, rust and inert particles from the surface of the leadframe/FPC. Electrocleaning (or electrolytic cleaning) is an electrolytic process conducted in an alkaline electrolyte, through which a direct current is passed, where the part to be cleaned is connected as either the anode or the cathode (or both), which process may also involve agitation. Electrocleaning combines the effects of a soak alkaline cleaning and mechanical cleaning provided by gas bubbles, which form on the part's surface as a result of the electrochemical reaction. In embodiments of the invention mentioned herein, the electrocleaning process may involve cathodic electro cleaning where the part of the leadframe or FPC to be cleaned is connected to the cathode using a low current and with a residence time of around, which is generally sufficient to clean the leadframe or FPC. This process may lead to the liberation of hydrogen gas.

Alkaline cleaning blends used as the electrolyte for electrocleaning, typically contain a mixture of alkaline materials, to provide high conductivity at an established pH and to have enough reserve alkalinity. Alkali metal hydroxides (NaOH or KOH), carbonates, silicates and phosphates (e.g. trisodium phosphate) are used as the principal source of alkalinity. In addition, the cleaning blend may also contain a sequestering agent, such as sodium tripolyphosphate, tetrapotassium pyrophosphate, and tetrasodium pyrophosphate.

Due to its lower cost, sodium salts are more frequently used in the electrolyte for electrocleaning, although potassium based electrocleaners have better solubility, lower electrical resistance and better throwing power. Potassium salts are generally used when necessary to achieve the desired effect, such as when electrocleaning very large parts, where otherwise very large voltages would be needed to obtain the high current densities required.

A particular electrolytic cleaning composition that may be mentioned herein is one that contains alkaline silicates (e.g. sodium silicate). Alkaline silicates can also function as a soak cleaner, as well as an anodic and cathodic electrolytic cleaner. Alkaline silicate compounds are not designed to continuously remove heavy accumulations of oil, grease and buffing compounds and they are chiefly used to clean copper and copper alloys, because of the possibility of them causing caustic burns (tarnishing) on other metals. Alkaline metal silicate cleaning solutions are phosphate free, and are medium duty, high frequency alkaline cleaners for rapid and efficient cleaning. This rapid cleaning may be because they rapidly peptize and disperse oils and they also advantageously have emulsifying, corrosion inhibition properties. They are also very stable and have a long life-span which makes them useful in the electro-cleaning of LED leadframes or FPCs.

Following a rinse with deionised water, the electrocleaned leadframe or FPC 215 is subjected to an activation step 220. The activation step leads to mild etching of the metal on the leadframe or FPC surface and helps to remove any remaining organic substances or oxidation from the surface. The activation step may be accomplished by placing the leadframe or FPC in a floodcell and adding (or immersing) the leadframe or FPC in a solution containing an acidic substance (e.g. citric acid and ammonium persulfate). The activated leadframe or FPC 225 is then ready for plating.

In the conventional process, the activated leadframe or FPC 225 is plated in a nickel plating process 230 to provide a nickel plated leadframe or FPC 235. The intention of the nickel plating layer is to produce a semi-bright, ductile and smooth deposit of nickel on the leadframe or FPC. This deposition can be achieved under a wide variety of electrolysing conditions. For example, an aqueous acid solution of a nickel electrolyte consisting of nickel sulfate and nickel chloride that also contains three types of brighteners, a leveller and a wetting agent may be used. A particular nickel plating process that may be mentioned herein involves use of an electroplating solution consisting of about 185g/L of nickel sulphamate, from about 30 to about 40 g/L of Nickel Chloride ($NiCl_2.6H_2O$) and from about 40 to about 60 g/L of boric acid (H_3BO_3) having a pH range of from about 4.0 to about 4.5, and under the following conditions, a current density of from about 3.0 to 6.5 A/dm^2, a temperature of about 50-65°C, and soluble nickel anodes, with cathode movement or air agitation.

The resulting nickel plated leadframe or FPC 235 then undergoes a silver electroplating process 240 to provide a semi-bright silver plated leadframe/FPC 245. The silver deposition generally involves the use of aqueous electrolytes in which silver is present mainly as a complex cyanide and the semi-bright silver plated leadframe/FPC 245 may have a GAM value of 1.0 to 1.3 GAM. The intent of this process is to provide a semi-bright silver plated leadframe or FPC with a GAM value of from 1.0 to 1.3 GAM, using a silver cyanide as a silver source and using two kinds of brighteners with high current density.

For example, the silver electrolytic solution may contain potassium silver cyanide salt in an amount of from 50 to 70 g/L, potassium cyanide in an amount of from 10 to 15 g/L, a brightener B in an amount of from 0.2 to 0.7 % Vol and a brightener C in an amount of 0.2 to 0.5% Vol. Brightener B may be selected from one or more of the group consisting of trifluoromethane sulfonic acid, halides of trifluoromethane sulfonic acid and aromatic substitted sufonic acids and salts and solvates thereof. Particular compounds that may be mentioned herein as brightener B is the ammonium salt of trifluoromethane sulfonic acid and *p*-toluenesulfonic acid. Brightener C may be selected from one or more of the group consisting of 1,2-methyl-4-isothiazoline, carbendaxin, 1,2-benzisothiazole-3(2*H*)-one, 2-phenoxyethanol, benzoic acid, and methyl paraben. The conditions used may involve a current density of from about 3.0 to about 6.5 A/dm^2

and a temperature range of from about 20 to about 40°C. This plating solution and conditions will readily deposit a uniform and durable semi-bright silver deposit on the nickel surface of the nickel plated leadframe 235 or FPC.

The semi-bright silver plated leadframe or FPC 245 is then subjected to a silver stripping process 250 that removes excess silver from the leadframe/FPC. A silver stripping step is used to ensure a high brightness and provide a good appearance, which can be used to reproducibly provide brightness of from 1.0 to 1.3 GAM.

The silver stripping step is normally accomplished using a silver stripping solution (comprising a strong oxidising agent, an alkaline pH buffer and a solubilizing agent) and an aniodic current. For example the silver stripping solution may be a non-cyanide stripping solution where the oxidizing agent is present in the solution at a concentration of from 65 to 75g/L, the alkaline pH buffer is present at a concentration of from 10 to 40 g/L and is present in sufficient quantity to maintain the pH between from 10.5 to 11.5, and the silver solubilizing agent is present at a concentration of from 400 to 500 mL/L. The conditions for the silver plate stripping may be an anodic current of 1.5 A/dm^2 with a voltage of from 1.0 to 4.0 for a period of from 15 to 30 seconds at room temperature (e.g. from 20 to 25°C). The use of the silver stripping solution and the conditions mentioned herein may result in a silver stripping ability of from about 1 to about 2 µm/min, while not attacking the base metal to which the silver is plated.

Once the silver stripping step has been completed, stripped leadframe or FPC 255 is subjected to a standard neutralization step to remove any remaining materials left on the surface of the leadframe or FPC from the silver stripping and in preparation for the application of the silver anti-tarnish layer.

Subsequent to the stripping and neutralisation steps, the stripped leadframe/FPC 255 is treated in an anti-tarnish step 260, which prevents the tarnishing of metals such as silver and copper under a normal atmosphere. The coating of the metallic surface with an anti-tarnish substance is to maintain the brightness of the silver deposit and its reflectivity for long term storage and/ or high temperature exposure. The coating is generally a thin, transparent film deposit on the metal surface that prevents the attack of sulfur or oxygen on the metal, without affecting the electrical properties of the metallic deposit. A number of anti-tarnish agents are available to prevent the tarnish of silver (and other tarnishable metals). Suitable anti-tarnish agents include, but are not limited to, tetraalkaline phosphates in combination with a metal salt. For example, the anti-tarnish composition may contain an alkaline pyrophosphate 60 wt%, and a metal salt 15 wt% compared to the total weight of the composition. The bath make up is at a concentration of from 120 to 150 mL/L.

Turning to the current invention as depicted in the flow diagram provided in Figure 2, there remains an etching phase, followed by a plating phase and the steps involved in the etching phase are identical to those described hereinbefore for the conventional process (i.e. steps 100-190 remain as set out above). However, there are a number of changes made to the plating phase that results in an increased brightness and may also provide additional advantages, as described hereinbelow.

In an optional first step in the new plating phase, the etched and anti-tarnish coated copper leadframe/FPC is subjected to a pre-clean soaking step 310. This soak cleaning step is intended to remove the major portion of any heavy, oily soils on the leadframe/FPC quickly, effectively, safely and economically. This is because the metal leadframe/FPC may contain a heavy accumulation of oil, grease and other buffing compounds on the metal surface that need to be removed, as well as removing any remaining oxides on the metal surface as well. This may not always be possible to achieve using electrolytic cleaning alone.

The soaking step 310 may be accomplished by placing the leadframe/FPC in an acid bath for a suitable period of time. Suitable acids that may be mentioned herein in relation to the acid bath include sulfur-based acids such as sulfuric acid, polysulfuric acids, dithionic acids, and peroxysulfuric acids. While other acids such as nitric acids, hydrochloric acid and phosphoric acid could potentially be used, they are not preferred. This is because of the potential for these acids to release toxic gasses during the process, thereby causing an increased health risk. Particular acids that may be mentioned herein include sulfuric acid (50 wt% in deionised water).

When the soaking step is conducted, then the precleaned leadframe or FPC 315 is subjected to electrolytic cleaning 320. Alternatively, when the precleaning step is omitted, the anti-tarnish coated copper leadframe or FPC is subjected to electrolytic cleaning. In both cases, the electrolytic cleaning step is conducted in the same manner as outlined hereinbefore for the conventional process.

The electrolytically cleaned leadframe or FPC 325 may then be subjected to a microetching process 330A. This process cleans and chemically microetches the entire copper surface to provide a microetched leadframe or FPC 335A. This is accomplished by spraying the electrolytically cleaned leadframe or FPC 325 with a microetchant solution to further remove any organic materials and/or oxide materials from the surface and provide a finely pitted morphology on the surface of the leadframe/FPC. The microetchant solution may comprise an organic or inorganic peroxy substance (e.g. ammonium persulfate) and sulfuric acid (e.g. a powdered inorganic peroxy material that is mixed with water and sulphuric acid), which together form a mild etch solution for copper metal that when used will provide a clean, uniformly micro-roughened copper surface. In certain embodiments, a further acid etchant may be added to provide a yet further improved micro-roughened topography. The optimum topography yields a higher surface energy for the completed leadframe/FPC, giving better solderability and solder adhesion during assembly of the LED.

As previously mentioned, sulfuric acid is a preferred acid for use in the microetching solution. This is because its common replacements, such as hydrochloric acid and nitric acid, will result in the release of one or more toxic gases, such as chlorine, nitric oxide or nitrogen dioxide.

In an example of a microetching step, the microetching solution comprises a peroxide etchant (e.g. ammonium persulfate) in a concentration of from 60 to 90 g/L, sulfuric acid at a concentration of from 1 to 2 vol% and a contact time of from 30 to 60 seconds. The total copper removal achieved using these conditions is between 0.5 to 1.3 μm. In order to ensure consistency in microetching, the concentration of the microetchant should be maintained.

In an alternative to microetching, but which enables one to obtain the desired product characteristics, the electrolytically cleaned leadframe/FPC 325 may be subjected to a copper plating step 330B instead, which provides a double copper plated leadframe or FPC 335B. The copper plating may be accomplished using any suitable copper plating method that can provide a thin layer (e.g. less than 0.3 μm) of copper plating and an improved grain structure. This new copper layer then acts as the base for the plating surface to provide an enhanced surface finishing. In addition, the double copper plated leadframe or FPC 335B may be subjected to buffing before use in the next processing step. Buffing may increase the brightness of the final product.

The microetched leadframe or FPC 335A or the double copper plated leadframe or FPC 335B are then subjected to a nickel plating 340 to provide a nickel plated leadframe or FPC 345. This process is used to produce a bright and level nickel electrodeposition and is similar to that described hereinbefore for the conventional process 230 in Figure 1 and the associated description. For example, an aqueous acid solution of a nickel electrolyte solution comprises nickel sulfate and nickel chloride that also contains three types of brighteners, and a wetting agent may be used. A particular nickel plating process that may be mentioned herein involves the use of electroplating solution comprising of from about 300 to about 350g/L of nickel sulfate hexahydrate ($NiSO_4.6H_2O$), from about 40 to about 60 g/L of nickel chloride ($NiCl_2.6H_2O$) and from about 40 to about 50 g/L of boric acid (H_3BO_3; pH buffer), with the solution having a pH range of from 4.0 to 4.5, and the electroplating taking place under a current density of from about 5.0 to about 6.5 A/dm^2, at a temperature of from 50 to 65°C, and with soluble nickel anodes operated with cathode movement or air agitation.

As noted above, the nickel plating solution further contains three types of brighteners (additives A-C) and a wetting agent. Additive D is used during chemical make-up of the original solution only.

Additive A may be selected from one or more of the group consisting of a substituted or unsubstituted aryl sulfonamide, a substituted or unsubstituted unsaturated alkyl sulfonamide, a substituted or unsubstituted aryl sulfonate, a substituted or unsubstituted unsaturated alkyl sulfonate, an aryl sulfonic acid and salts and solvates thereof. A particular compound that may be mentioned herein as additive A is the sodium salt of O-sulfobenzimide. Additive A is a primary brightener and may also be responsible for the ductility of the metal deposits. Additive A may be added to the nickel bath solution containing nickel sulfate, nickel chloride and boric acid in an amount of from 1.0 to 2.0%vv.

Additive B may be selected from one or more of the group consisting of trifluoromethane sulfonic acid, halides of trifluoromethane sulfonic acid and aromatic substitted sufonic acids and salts and solvates thereof. Particular compounds that may be mentioned herein as additive B is the ammonium salt of trifluoromethane sulfonic acid and *p*-toluenesulfonic acid. Additive B may be added to the nickel bath solution containing nickel sulfate, nickel chloride and boric acid in an amount of from 0.2 to 0.3%vv.

Additive C may be selected from one or more of the group consisting of 1,2-methyl-4-isothiazoline, carbendaxin, 1,2-benzisothiazole-3(2*H*)-one, 2-phenoxyethanol, benzoic acid, and methyl paraben. Additive C may be added to the nickel bath solution containing nickel sulfate, nickel chloride and boric acid in an amount of from 0.5 to 0.75%vv.

Additive D, when present, may be a mixture of the components mentioned as additives A and B and may be added to the nickel bath solution containing nickel sulfate, nickel chloride and boric acid in an amount of from 0.05 to 0.1%vv. As noted above, additive D is used when seeking to top up the original compositions after use.

Additives B and C act as the secondary brightener for maximum brightening of the leadframe or FPC and they may also act as a leveller to improve the uniformity of the coating, especially for areas of the leadframe/FPC that receive a low current density.

The wetting agent may be sodium lauryl sulfate, which may be used to prevent pits in the nickel deposit and to eliminate hazing of the deposit, which may lead to a reduction in brightness. The wetting agent may also be used to achieve zero porosity/voids in the nickel plating finishing. Porosity or void spaces in the plated area may lead to contamination and porosity or voids occur whenever bubbles become trapped in the floodcell during plating. To prevent such bubbles forming (and hence porosity/voids in the nickel plating) a wetting agent is used in an amount such that the concentration of the wetting agent in the plating solution to reduce the surface tension of the plating solution. For example, wetting agent (e.g. sodium lauryl sulfate) may be added to the nickel bath solution containing nickel sulfate, nickel chloride and boric acid in an amount of around 0.3%vv.

Thus, the nickel plating solution containing nickel sulfate, nickel chloride and the buffer salt boric acid described above may further comprise additive A in an amount of about 1.0%vv, additive B in an amount of about 0.2%vv, additive C in an amount of about 0.75%vv, and a wetting agent in an amount of about 0.3%vv. Said plating solution may be useful in obtaining a bright and ductile nickel plating.

The nickel plated leadframe or FPC 345 is then subjected to silver strike electroplating 350 to provide a silver strike leadframe or FPC 355, having a thin silver layer of from 0.1-0.2 µm. This method involves electroplating silver strike over the nickel layer using a cyanide (i.e. a high-concentration cyanide) electroplating solution to provide a thin layer of silver metal that is deposited as a bright deposit on the nickel metal of leadframe or FPC 345. The addition of a silver strike layer may assist in preparing the surface for the deposition of a thicker layer of silver from the main silver deposition step 360 (see below) and may also prevent any contaminants remaining from the nickel deposition process from causing problems in said main silver deposition step.

Any suitable silver strike composition may be used. For example, the silver strike solution may have a silver content of from 1.0 to 2.0 g/L, a KCN content of from 100 to 300 g/L under conditions that include a current density of around 1.0 to 2.0 A/dm^2 and a deposition time of from 20 to 60 seconds. As will be noted, the composition contains a high concentration of cyanide, which is used to increase the conductivity of the silver strike solution and enhances the deposition of silver.

The main silver electroplating process 360 results in a bright silver leadframe or FPC 365, wherein the GAM value of the silver-plated area is from 1.8-2.0 GAM, which is much higher than that achieved using the conventional plating process described hereinbefore, where the GAM value of a bright silver plated leadframe or FPC is generally less than 1.2 GAM.

In this process step, the aim is to provide a silver plated leadframe or FPC 365 with a brightness of from 1.8 to 2.0 GAM. This is achieved using a cyanide as a silver source with three types of brighteners and with a high current density for the electrodeposition. The silver electrolytic solution used herein may comprise potassium silver cyanide salt at a concentration of from 50 to 100 g/L, potassium cyanide at a concentration of from 100 to 150 g/L, potassium hydoxide (to maintain the pH over 10.0) at a concentration of from about 6 to about 20 g/L, brightener A at a concentration of from 3 to 15 mL/L, brightener B at a concentration of from 2 to 7mL/L and brightener C at a concentration of from 2 to 7mL/L, where the solution has a pH of above 11.5. The electrodeposition may be conducted using a current density from about 5.0 to about 6.5 A/dm^2 at a temperature of from 20 to 40°C. These conditions enable one to readily deposit a uniform and durable highly bright silver deposit on the silver strike surface of leadframe or FPC 355.

Brightener A may be a mixture of organic brightener compounds that contain a ketone group and/or organometallic compounds that can be dissolved in water. Brightener A may be used in an amount of from 0.5 to 0.15 %v/v. Brightener A is used to achieve a mirror-bright silver deposit.

Brightener B may be a mixture of organic brighterner compounds that contain a ketone group, such as ketones that provide an aroma (e.g. mint; such as carvone and/or thujone) and/or organometallic compounds that can be dissolved in water. Brightener B may be used in an amount of from 0.2 to 0.7 %v/v. Brightener B is used to improve the white, bright throwing power of the electrolyte.

Brightener C may be one or more alkyl acrylates, such as 2-hydroxyethyl methacrylate, and butyl acyrlate. Brightener C may be used in an amount of from 0.2 to 0.7 %v/v. Brightener C is may act as a grain refiner.

Brighteners A-C may be pre-prepared as a solution in water before addition to the electrodeposition solution described hereinabove. In addition, potassium hydroxide may be added to these solutions to maintain a pH of over 10.

The bright silver plated leadframe or FPC 365 is then subjected to a silver stripping process 370 that removes excess silver from the leadframe/FPC and provides a mirror bright silver leadframe or FPC 375. A silver stripping step is used to ensure a high brightness and provide a good appearance, which can be used to reproducibly provide brightness of above 2.0 GAM. The silver stripping process 370 is identical to that described hereinbefore for the conventional process (see the description of silver stripping process 250).

Optionally, the mirror-bright silver leadframe or FPC 375 may be subjected to a surface cleaning process 380A using electrolytic cleaning to provide a cleaned silver leadframe or FPC 385A. The electrocleaning may be conducted in a similar manner to that as described hereinbefore (e.g. see the description of process 210). In this electrocleaning step, the leadframe or FPC 375 is used as the cathode and is contacted with a metal anode (usually stainless steel). In this step, alkaline silicate (e.g. sodium silicate) compounds may be used at a concentration of from 15 to 25 g/L using a direct current of from 1 to 5 A/dm^2 and a temperature of from 50 to 60°C. A low current density is preferred. This cleaning process may remove any residue remaining from the silver stripping process 370 and may also remove any ion contamination that is present on the silver plated surface.

The bright silver leadframe or FPC 375 or the cleaned silver leadframe or FPC 385A is then subjected to a post-treatment step involving the application of an anti-tarnish coating 380B, which may be applied in the same manner as described in process 260 for the conventional process.

Following the plating process, the leadframe or FPC 385B will be subjected to further conventional processes to prepare an LED. Said LED will have a GAM value of above 2.0.

Claims

1. A method of manufacturing a leadframe having a GAM value of greater than 2.0, the method comprising the steps of:

(a) providing a copper plated leadframe or FPC, where the copper plating is etched and is coated with an anti-tarnish layer;

(b) subjecting the copper plated leadframe or FPC to a first electrolytic cleaning step to provide an electrolytically cleaned leadframe;

(c) subjecting the electrolytically cleaned leadframe or FPC to a microetching step to provide a microetched leadframe or FPC or subjecting the electrolytically cleaned leadframe or FPC to a copper plating process to provide a double copper plated leadframe or FPC;

(d) subjecting the microetched leadframe or FPC or double copper plated leadframe or FPC to a bright-deposition nickel plating process to provide a nickel plated leadframe or FPC;

(e) subjecting the nickel plated leadframe or FPC to a silver strike electoplating process to provide a silver strike plated leadframe or FPC;

(f) subjecting the silver strike plated leadframe or FPC to a bright silver plating process to provide a bright silver leadframe or FPC;

(g) subjecting the bright silver plated leadframe or FPC to a silver stripping process to provide a mirror bright silver leadframe or FPC; and

(h) applying an anti-tarnish coating to the mirror bright silver plated leadframe or FPC.

2. The method of Claim 1, wherein before step (b) is performed, the copper plated leadframe or FPC of step (a) is subjected to a soaking step in an acid bath to provide an acid-cleaned copper plated leadframe or FPC, optionally wherein the acid is selected from one or more of the group selected from sulfuric acid, polysulfuric acids, dithionic acids, and peroxysulfuric acids.

3. The method of Claim 1 or Claim 2, wherein, when used in step (c), the microetching process comprises spraying a microetchant solution onto the electrolytically cleaned leadframe or FPC in an amount and for a sufficient period of time to remove from 0.5 to 1.3 μm of copper from the copper plating layer.

4. The method of Claim 3, wherein the microetchant solution comprises an organic peroxide (e.g. ammonium persulfate) at a concentration of from 60 to 90 g/L and sulfuric acid at a concentration of from 1 to 2 vol%, optionally wherein the contact time of the microetchant solution with the electrolytically cleaned leadframe or FPC is from 30 to 60 seconds.

5. The method of any one of the preceding claims, wherein in step (c) the copper plating step uses a copper cyanide bath and is conducted using a current density of from about 3.0 to about 4.0 A/dm^2, at a temperature of from about 50 to about 55°C.

6. The method of any one of the preceding claims, wherein in step (d) the nickel plating process uses a nickel electrolyte solution that comprises:

nickel sulfate (e.g. nickel sulfate hexahydrate) in an amount of from about 300 to about 350g/L;

nickel chloride in an amount of from about 40 to about 60 g/L;
boric acid in an amount of from about 40 to about 50 g/L;
a wetting agent in an amount of around 0.3%v/v;
additive A in an amount of from 1.0 to 2.0%vv;
additive B in an amount of from 0.2 to 0.3%vv; and
additive C in an amount of from 0.5 to 0.75%vv; where:

additive A is selected from one or more of the group consisting of a substituted or unsubstituted aryl sulfonamide, a substituted or unsubstituted unsaturated alkyl sulfonamide, a substituted or unsubstituted aryl sulfonate, a substituted or unsubstituted unsaturated alkyl sulfonate, an aryl sulfonic acid and salts and solvates thereof;

additive B is selected from one or more of the group consisting of trifluoromethane sulfonic acid, halides of trifluoromethane sulfonic acid and aromatic substitted sufonic acids and salts and solvates thereof;

additive C is selected from one or more of the group consisting of 1,2-methyl-4-isothiazoline, carbendaxin, 1,2-benzisothiazole-3(2*H*)-one, 2-phenoxyethanol, benzoic acid, and methyl paraben; and

the nickel solution has a pH of from 4.0 to 4.5.

7. The method of claim 6, wherein in step (d) the depleted additives A and B are replenished by the further addition of:

additive D in an amount of from 0.05 to 0.1%vv;

additive D, is a mixture of at least one compound mentioned in the list provided for additive A and at least one compound mentioned in the list provided for additive B.

8. The method of Claim 6, wherein the nickel plating process is conducted using a current density of from about 5.0 to about 6.5 A/dm^2, at a temperature of from 50 to 65°C, and with soluble nickel anodes operated with cathode movement or air agitation.

9. The method of any one of the preceding claims, wherein in step (e) the silver strike electroplating process uses a silver strike electrolyte solution that comprises:

ionic silver in an amount of from 1.0 to 2.0 g/L; and
KCN in an amount of from 100 to 300 g/L.

10. The method of Claim 9, wherein the silver strike electroplating process is conducted using a current density of around 2.0 A/dm^2 and a deposition time of from 20 to 60 seconds.

11. The method of any one of the preceding claims, wherein in step (f) bright silver plating process uses a bright silver plating electrolyte solution that comprises:

potassium silver cyanide salt at a concentration of from 50 to 100 g/L;
potassium cyanide at a concentration of from 100 to 150 g/L;
potassium hydroxide at a concentration of from about 6 to 20 g/L;
brightener A at a concentration of from 3 to 15 mL/L;
brightener B at a concentration of from 2 to 7mL/L; and
brightener C at a concentration of from 2 to 7mL/L, where

brightener A is a mixture of organic brightener compounds that contain a ketone group and/or organometallic compounds;

brightener B is a mixture of organic brighterner compounds that contain a ketone group, such as ketones that provide an aroma and/or organometallic compounds;

brightener C is one or more alkyl acrylates; and

the pH of the solution is over 11.5.

12. The method of Claim 11, wherein the bright silver plating process is conducted using a current density from about 5.0 to about 6.5 A/dm^2 and at a temperature of from 20 to 40°C.

13. The method according to any one of the preceding claims, wherein after step (f) and before step (g), a second electrolytic cleaning process is conducted.

14. The method according to any one of the preceding claims, wherein the electrolytic cleaning process uses an electrolytic cleaning solutions that comprises:

an alkaline material selected from one or more of the group consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal silicates and alkali metal phosphates; and

a sequestering agent selected from one or more of the group consisting of sodium tripolyphosphate, tetrapotassium pyrophosphate, and tetrasodium pyrophosphate, optionally wherein

the alkaline material is present in an amount of from 12 to 25 g/L.

15. The method of Claim 14, wherein the alkaline material is sodium silicate.

16. The method of Claim 14 or Claim 15, wherein the electrolytic cleaning is conducted using the leadframe or FPC as the cathode and a direct current of from 1 to 5 A/dm^2 at a temperature of from 50 to 60°C.

17. An LED leadframe or FPC obtained or obtainable from the method of any one of the proceeding claims, wherein the leadframe or FPC has a GAM value of greater than 2.0.

18. A method of manufacturing an LED comprising the use of an LED leadframe or FPC obtained or obtainable from the method of any one of Claims 1 to 16, wherein the leadframe or FPC has a GAM value of greater than 2.0.

Figures

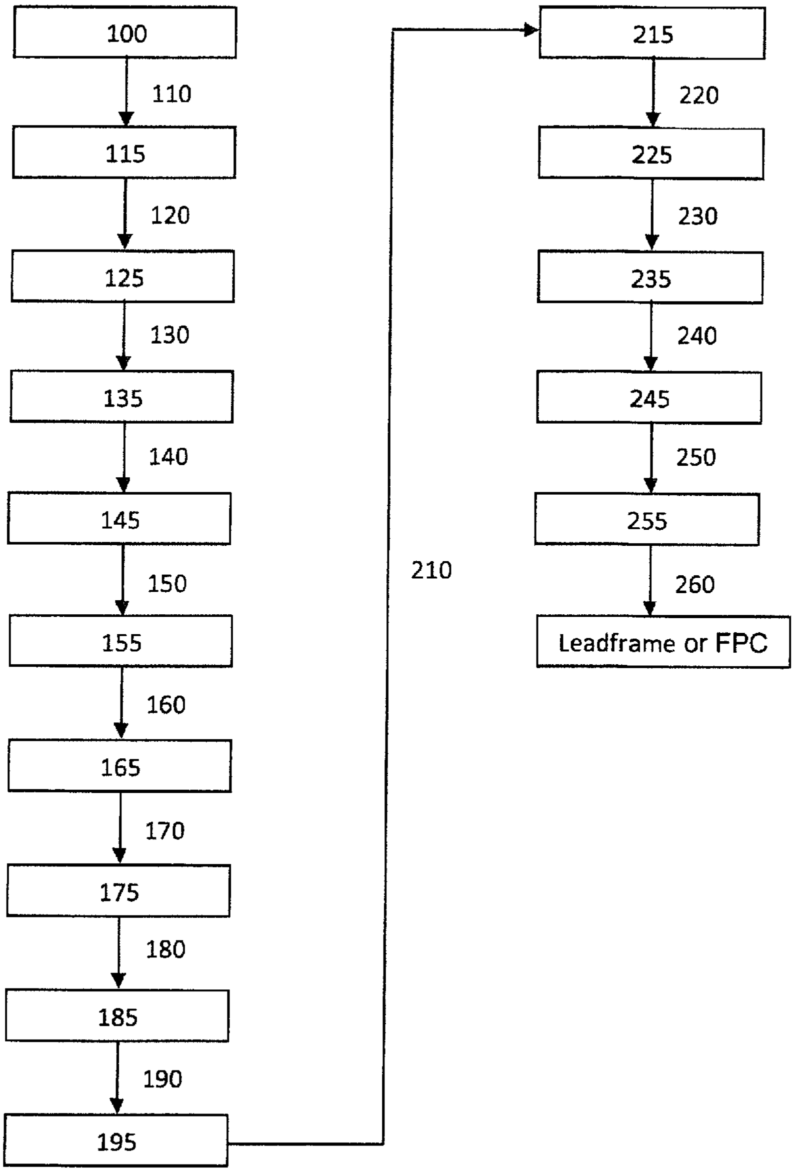
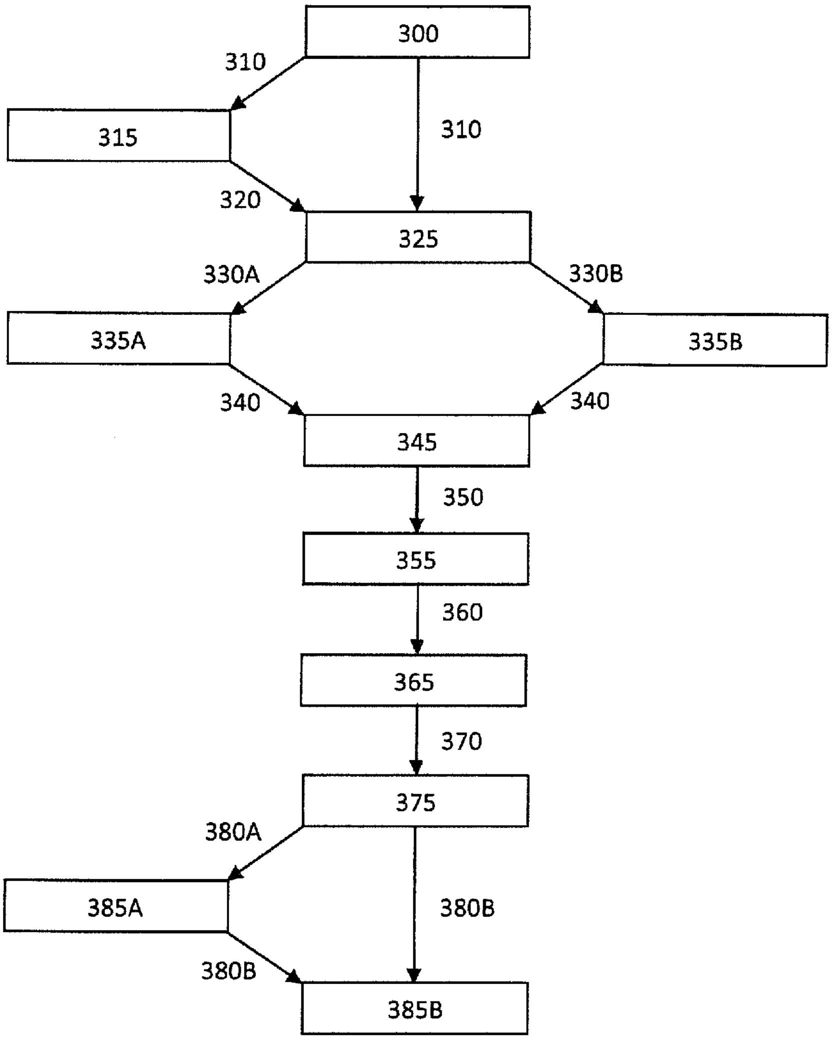


Fig. 1


300
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380A
385A
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380B
385B

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2017/050115

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/00 (2006.01)   H05K 3/00 (2006.01)   C23F 1/00 (2006.01)   C25D 3/12 (2006.01)   C25D 3/40 (2006.01)
C25D 3/46 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PATENW: /IC/C/CNO((H01L 21/-, H05K 1/02/LOW, H05K 1/028, H05K 1/0283, H05K 2201/05, H05K 2201/10106, F21K 9/90) AND (C25D3/02, C25D 3/40) AND (C25F 1/04, C25F 3/00/LOW, C25F 5/00) AND (C23F 1/00/LOW, H05K 3/00/LOW, H05K 3/002)); **PATENW:** /IC/C/CNO((H01L21/-, H05K 1/02/LOW OR H05K1/028, H05K 1/0283, H05K 2201/05, H05K 2201/10106, F21K 9/90) AND (C25D 3/02, C25D 3/40) AND (C25F 1/04, C25F 3/00/LOW, C25F 5/00)); **PATENW:** /IC/C/CNO(H05K 1/00/LOW, H05K 3/00/LOW, H05K 1/0277, H05K 1/0283, H05K 3/0011, H05K 3/0017, H05K 3/002, H05K 3/0023, H05K 2201/05, H05K 2201/10106, F21K 9/90) using keywords (COPPER, NICKEL, SILVER, ELECTROLYTIC, CLEAN) and like terms; **PATENW:** /IC/C/CNO(H01L 21/44/LOW, H01L 23/495, G03F 7/00/LOW) using keywords (COPPER, NICKEL, SILVER, ELECTROLYTIC, CLEAN) and like terms; **PATENW:** /IC/C/CNO(C25D 3/02, C25D 3/40, C25D 3/12/LOW, C25D 3/46)using keywords (LEADFRAME, ELECTROLYTIC, CLEANING, MICROETCHING, STRIPPING) and like terms; **ESPACENET, WIPO, USPTO, GOOGLE**: using keywords (LEADFRAME, ELECTROLYTIC, CLEANING, PLATING, COPPER, NICKEL, SILVER, STRIPPING) and like terms; **ESPACENET, AUSPAT, INTERNAL DATABASES** provided by IP Australia: Applicant and Inventor names searched

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ Further documents are listed in the continuation of Box C   ☒ See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
22 May 2017	22 May 2017

Name and mailing address of the ISA/AU	**Authorised officer**
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INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT	International application No. **PCT/SG2017/050115**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/126018 A1 (ROKKO LEADFRAMES PTE LTD) 29 August 2013 page 1, lines 11 – 13; page 5, line 3 – page 12, line 21; claims 1 - 11; figures 1 – 2	1 - 18
A	Bright Future for Plating LED Lights [retrieved from internet on 26 April 2017] <URL: http://www.pfonline.com/articles/bright-future-for-plating-led-lights> published on 05 September 2015 as per Wayback Machine whole document	1 - 18
A	US 2003/0153129 A1 (ABBOTT) 14 August 2003 abstract; claims 1 - 9	1 - 18
A	CN 103928302 A (SICHUAN JINWAN ELECTRONIC CO LTD) 16 July 2014 & machine translated English version of D4 from Google Patents abstract; claims 1 - 10	1 - 18

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/SG2017/050115**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
WO 2013/126018 A1	29 August 2013	WO 2013126018 A1	29 Aug 2013
		SG 193052 A1	30 Sep 2013
		TW 201341599 A	16 Oct 2013
US 2003/0153129 A1	14 August 2003	US 2003153129 A1	14 Aug 2003
		US 6706561 B2	16 Mar 2004
		US 2004155321 A1	12 Aug 2004
		US 6995042 B2	07 Feb 2006
CN 103928302 A	16 July 2014	CN 103928302 A	16 Jul 2014
		CN 103928302 B	24 Aug 2016

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.