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[Continued on next page]

(54) Title: CONDUCTIVE COMPOSITIONS AND PROCESSES FOR USE IN THE MANUFACTURE OF SEMICONDUCTOR DEVICES

FIG. 1A

FIG. 1B

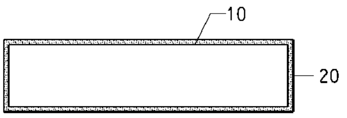


FIG. 1C

FIG. 1D

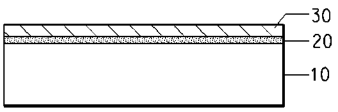


FIG. 1E

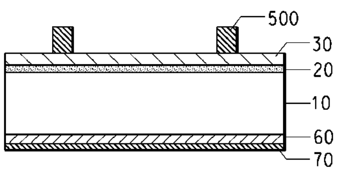
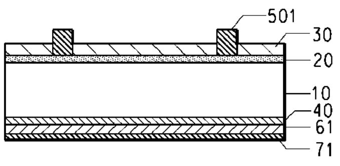


FIG. 1F



(57) Abstract: Embodiments of the invention relate to a silicon semiconductor device, and a conductive paste for use in the front side of a solar cell device.

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TITLE

CONDUCTIVE COMPOSITIONS AND PROCESSES FOR USE IN THE MANUFACTURE OF SEMICONDUCTOR DEVICES

FIELD OF THE INVENTION

The invention relates to a silicon semiconductor device, and a conductive paste for use in the front side of a solar cell device. The conductive paste may contain one or more of a bismuth-containing additive, a copper containing additive, and a phosphorus containing additive.

TECHNICAL BACKGROUND OF THE INVENTION

A conventional solar cell structure with a p-type base has a negative electrode that is typically on the front-side or sun side of the cell and a positive electrode on the backside. It is well-known that radiation of an appropriate wavelength falling on a p-n junction of a semiconductor body serves as a source of external energy to generate hole-electron pairs in that body. Because of the potential difference which exists at a p-n junction, holes and electrons move across the junction in opposite directions and thereby give rise to flow of an electric current that is capable of delivering power to an external circuit. Most solar cells are in the form of silicon wafers that have been metallized, i.e., provided with metal contacts that are electrically conductive.

Although various methods and compositions for forming solar cells exist, there is a need for compositions, structures, and devices which have improved electrical performance, adhesion properties, and methods of making.

SUMMARY OF THE INVENTION

An embodiment of the present invention relates to a thick film conductive composition comprising:

a) electrically conductive powder;

b) one or more additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof;

c) one or more glass frits; dispersed in

d) organic medium.

The additive may be selected from the group consisting of: Bi_2O_3, bismuth resinate, Copper powder, Copper oxide, P_2O_5, phosphorus-containing surfactant, and organic phosphorus.

In one aspect of the embodiment, the glass frit may comprise, based on weight percent of total glass composition: SiO_2 1-36, Al_2O_3 0-7, B_2O_3 1.5-19, PbO 20-83, ZnO 0-42, CuO 0-4, ZnO 0-12, Bi_2O_3 0-35, ZrO_2 0-8, TiO_2 0-7, PbF_2 3-34.

The composition may comprise an additional metal/metal oxide additive selected from (a) a metal wherein said metal is selected from Zn, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu, and Cr; (b) a metal oxide of one or more of the metals selected from Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (c) any compounds that can generate the metal oxides of (b) upon firing; and (d) mixtures thereof. In an aspect of the embodiment, the Zn-containing additive is ZnO.

An embodiment of the invention relates to a structure, wherein the structure comprises the thick film composition and a substrate. The substrate may be one or more insulating layers. The substrate may be one or more semiconductor substrates. In an aspect, the thick film composition may be formed on the one or more insulating layers. In an aspect, the one or more insulating layers may be formed on a semiconductor substrate. In a further aspect, upon firing, the organic vehicle is removed and the silver and glass frits are sintered.

In an embodiment of the invention, an electrode is formed from the composition, and said composition has been fired to remove the organic vehicle and sinter said glass particles.

An embodiment of the invention relates to a method of manufacturing a semiconductor device. The method comprises the steps of:

(a) providing one or more semiconductor substrates, one or more insulating films, and a thick film composition, wherein the thick film composition comprises: a) an electrically conductive silver, b) one or more glass frits, dispersed in c) an organic medium,

(b) applying the insulating film on the semiconductor substrate,

(c) applying the thick film composition on the insulating film on the semiconductor substrate, and

(d) firing the semiconductor, insulating film and thick film composition, wherein, upon firing, the organic vehicle is removed, the silver and glass frits are sintered, and the insulating film is penetrated by components of the thick film composition.

In an aspect of the embodiment, the insulating film comprises one or more components selected from: titanium oxide, silicon nitride, SiNx:H, silicon oxide, and silicon oxide/titanium oxide.

A further embodiment relates to structures including the thick film conductive composition. The structure may include an insulating layer. The structure may include a semiconductor substrate. An aspect of the present invention relates to semiconductor devices that contain the structure. Another aspect of the present invention relates to photovoltaic devices that contain the structure. Another aspect of the present invention relates to solar cells that contain the structure. A further aspect of the present invention relates to solar panels that contain the structure.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a process flow diagram illustrating the fabrication of a semiconductor device.

Reference numerals shown in Figure 1 are explained below.

10: p-type silicon substrate
20: n-type diffusion layer
30: silicon nitride film, titanium oxide film, or silicon oxide film
40: p+ layer (back surface field, BSF)
60: aluminum paste formed on backside
61: aluminum back electrode (obtained by firing back side aluminum paste)
70: silver or silver/aluminum paste formed on backside
71: silver or silver/aluminum back electrode (obtained by firing back side silver paste)
500: silver paste formed on front side according to the invention
501: silver front electrode according to the invention (formed by firing front side silver paste)

Figure 2 illustrates the adhesion properties of paste compositions of Table 2. The adhesion values are an average of 12 data points.

DETAILED DESCRIPTION OF THE INVENTION

The present invention addresses the need for semiconductor compositions with improved electrical performance, semiconductor devices, methods of manufacturing the semiconductor devices, and the like.

An embodiment of the present invention relates to thick film conductor compositions. In one aspect of the embodiment, the thick film conductor compositions may include: a conductive powder, a flux material, and an organic medium. The flux material may be glass frit or mixture of glass frits. The thick film conductor compositions may also include an additive. The thick film conductor compositions may include additional additives or components.

An embodiment of the present invention relates to structures, wherein the structures include the thick film conductor compositions. In an aspect, the structure also includes one or more insulating films. In an aspect, the structure does not include an insulating film. In an aspect, the structure includes a semiconductor substrate. In an aspect, the thick film conductor composition may be formed on the one or more insulating films. In an aspect, the thick film conductor composition may be formed on the semiconductor substrate. In the aspect wherein the thick film conductor composition may be formed on the semiconductor substrate, the structure may not contain an applied insulating film.

In an embodiment, the thick film conductor composition may be printed on the substrate to form busbars. The busbars may be more than two busbars. For example, the busbars may be three or more busbars. In addition to busbars, the thick film conductor composition may be printed on the substrate to form connecting lines. The connecting lines may contact a busbar. The connecting lines contacting a busbar may be interdigitated between the connecting lines contacting a second busbar.

In an exemplary embodiment, three busbars may be parallel to each other on a substrate. The busbars may be rectangular in shape. Each of the sides of the middle busbar may be in contact with connecting lines. On each of the side busbars, only one side of the rectangle may be in contact with connecting lines. The connecting lines contacting the side busbars may interdigitate with the connecting lines contacting the middle busbar. For example, the connecting lines contacting one side busbar may interdigitate with the connecting lines contacting the middle busbar on one side, and the connecting lines contacting the other side busbar may interdigitate with the connecting lines contacting the middle busbar on the other side of the middle busbar.

In an embodiment, the busbar formed on the substrate may consist of two busbars arrayed in a parallel arrangement with conductor lines formed perpendicular to the busbar and arrayed in an interdigitated parallel line pattern. Alternately, the busbars may be three or more busbars. In the case of three busbars, the central busbar may serve as a common between the busbars to each side in a parallel arrangement. In this embodiment, the area coverage of the three busbars may be adjusted to approximately the same as the case for the use of two busbars. In the case of three busbars, the perpendicular lines are adjusted to shorter dimensions appropriate to the spacing between pairs of busbars.

In an embodiment, the components of the thick film conductor composition(s) are electrically functional silver powders, one or more additive(s) , wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof, and a glass frit dispersed in an organic medium. The glass frit may be lead-free. Additional additives may include metals, metal oxides or any compounds that can generate these metal oxides during firing. The components are discussed herein below.

Inorganic Components

An embodiment of the present invention relates to thick film conductor compositions. In an aspect of the embodiment, the thick film conductor compositions may include: a conductive material, a flux material, and an organic medium. The conductive material may include silver. In an embodiment, the conductive material may be a conductive powder. The flux material may include a glass frit or glass frits. The glass frit may be lead-free. The thick film conductor compositions may also include an additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof. An additional additive may be included. The additional additive may be a metal/metal oxide additive selected from (a) a metal wherein said metal is selected from Zn, Mg, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (b) a metal oxide of one or more of the metals selected from Zn, Mg, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (c) any compounds that can generate the metal oxides of (b) upon firing; and (d) mixtures thereof. The thick film conductor compositions may include additional components.

As used herein, “busbars” means a common connection used for collection of electrical current. In an embodiment, the busbars may be rectangular shaped. In an embodiment, the busbars may be parallel.

As used herein, “flux material” means a substance used to promote fusion, or a substance that fuses. In an embodiment, the fusion may be at or below required process temperatures to form a liquid phase.

In an embodiment, the inorganic components of the present invention comprise (1) electrically functional silver powders; (2) one or more additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof; (3) glass frit; and optionally (4) additional metal/metal oxide additive selected from (a) a metal wherein said metal is selected from Zn, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (b) a metal oxide of one or more of the metals selected from Zn, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (c) any compounds that can generate the metal oxides of (b) upon firing; and (d) mixtures thereof. In a non-limiting embodiment, an additive may be selected from the group consisting of: Bi_2O_3, bismuth resinate, Copper powder, Copper oxide, P_2O_5, phosphorus-containing surfactant, and organic phosphorus. In an embodiment, the glass frit may be lead-free.

A. <u>Electrically Conductive Functional Materials</u>

Electrically conductive materials may include Ag, Cu, Pd, and mixtures thereof. In an embodiment, the electrically conductive particle is Ag. However, these embodiments are intended to be non-limiting.

Embodiments in which other conductive materials are utilized are contemplated and encompassed.

The silver may be in a particle form, a powder form, a flake form, spherical form, provided in a colloidal suspension, a mixture thereof, etc. The silver may be silver metal, alloys of silver, or mixtures thereof, for example. The silver may include silver oxide (Ag_2O) or silver salts such as AgCl, $AgNO_3$, or $AgOOCCH_3$ (silver acetate), silver orthophosphate, Ag_3PO_4, or mixtures thereof, for example. Any form of silver compatible with the other thick film components may be used, and will be recognized by one of skill in the art.

The silver may be any of a variety of percentages of the composition of the thick film composition. In a non-limiting embodiment, the silver may be from about 70 to about 99 % of the solid components of the thick film composition. In a further embodiment, the silver may be from about 80 to about 95 wt % of the solid components of the thick film composition. In a further embodiment, the silver may be from about 87 to about 93 wt % of the solid components of the thick film composition.

In an embodiment, the solids portion of the thick film composition may include about 80 to about 90 wt % silver particles and about 1 to about 10 wt % silver flakes. In an embodiment, the solids portion of the thick film composition may include about 75 to about 90 wt % silver particles and about 1 to about 10 wt % silver flakes. In another embodiment, the solids portion of the thick film composition may include about 75 to about 90 wt % silver flakes and about 1 to about 10 wt % of colloidal silver. In a further embodiment, the solids portion of the thick film composition may include about 60 to about 90 wt % of silver powder or silver flakes and about 0.1 to about 20 wt % of colloidal silver.

In an embodiment, a thick film composition includes a functional phase that imparts appropriate electrically functional properties to the composition. The functional phase may include electrically functional powders dispersed in an organic medium that acts as a carrier for the functional phase that forms the composition. In an embodiment, the composition may be applied to a substrate. In a further embodiment, the composition and substrate may be fired to burn out the organic phase, activate the inorganic binder phase and to impart the electrically functional properties.

In an embodiment, the functional phase of the composition may be coated or uncoated silver particles which are electrically conductive. In an embodiment, the silver particles may be coated. In an embodiment, the silver may be coated with various materials such as phosphorus. In an embodiment, the silver particles may be at least partially coated with a surfactant. The surfactant may be selected from, but is not limited to, stearic acid, palmitic acid, a salt of stearate, a salt of palmitate and mixtures thereof. Other surfactants may be utilized including lauric acid, palmitic acid, oleic acid, stearic acid, capric acid, myristic acid and linolic acid. The counter-ion can be, but is not limited to, hydrogen, ammonium, sodium, potassium and mixtures thereof.

The particle size of the silver is not subject to any particular limitation. In an embodiment, an average particle size is less than 10 microns; in a further embodiment, the average particle size is less than 5 microns.

In a further embodiment, silver oxide may be dissolved in the glass during the glass melting/manufacturing process.

B. Additive(s)

An embodiment of the present invention relates to thick film compositions which contain one or more additive. The additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof. In a non-limiting example, the additive may be selected from the group consisting of: Bi_2O_3, bismuth resinate, Copper powder, Copper oxide, P_2O_5, phosphorus-containing surfactant, and organic phosphorus.

An embodiment of the present invention relates to thick film compositions which may contain additional additives. A further embodiment relates to thick film compositions which contain two or more additives. In an aspect of this embodiment, the additional additive may be a metal/metal oxide additive selected from (a) a metal wherein said metal is selected from Zn, Mg, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (b) a metal oxide of one or more of the metals selected from Zn, Mg, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (c) any compounds that can generate the metal oxides of (b) upon firing; and (d) mixtures thereof.

In an embodiment, the particle size of the additives is not subject to any particular limitation. In an embodiment, an average particle size may be less than 10 microns; in an embodiment, an average particle size may be less than 5 microns. In an embodiment, the average particle size may be from 0.1 to 1.7 microns. In a further embodiment, the average particle size may be from 0.6 to 1.3 microns. In an embodiment, the average particle size may be from 7 to 100 nm. In a further embodiment, the particle size of the additives can be at the atomic or molecular level when an organo-metallic compound such as a metal resinate is used.

In an embodiment, the particle size of the metal/metal oxide additive may be in the range of 7 nanometers (nm) to 125 nm. In an embodiment, the particle size of the metal/metal oxide additive may be in the range of 7 nanometers (nm) to 100 nm. In an embodiment, MnO_2 and TiO_2 may be utilized in the present invention with an average particle size range (d_{50}) of 7 nanometers (nm) to 125 nm. In a further embodiment, the particle size of the additives can be at the atomic or molecular level when an organo-metallic compound such as a metal resinate is used.

In an embodiment, the bismuth-containing, copper-containing, or phosphorus-containing additive may be present in the total thick film composition in the range of 0 to 20 wt %; in a further embodiment, 0.05 to 10 wt %; in a further embodiment, 0.1 to 5 wt %; in a further embodiment, 0.1 to 2 wt %; in a further embodiment, 0.1 to 1 wt %; in a further embodiment, 0.15 to 0.5 wt %.

In an embodiment, the additional additive may be a Zn-containing additive. The Zn-containing additive may, for example be selected from (a) Zn, (b) metal oxides of Zn, (c) any compounds that can generate metal oxides of Zn upon firing, and (d) mixtures thereof.

In one embodiment, the Zn-containing additive is ZnO, wherein the ZnO may have an average particle size in the range of 10 nanometers to 10 microns. In a further embodiment, the ZnO may have an average particle size of 40 nanometers to 5 microns. In still a further embodiment, the ZnO may have an average particle size of 60 nanometers to 3 microns. In a further embodiment, the Zn-containing additive may have an average particle size of less than 0.1 μm. In particular the Zn-containing additive may have an average particle size in the range of 7 nanometers to less than 100 nanometers.

In a further embodiment the Zn-containing additive (for example Zn, Zn resinate, etc.) may be present in the total thick film composition in the range of 2 to 16 weight percent. In a further embodiment the Zn-containing additive may be present in the range of 4 to 12 weight percent total composition. In an embodiment, ZnO may be present in the composition in the range of 2 to 10 weight percent total composition. In an embodiment, the ZnO may be present in the range of 4 to 8 weight percent total composition. In still a further embodiment, the ZnO may be present in the range of 5 to 7 weight percent total composition.

In an embodiment, the additional additive may be a Mg-containing additive. The Mg-containing additive may, for example be selected from (a) Mg, (b) metal oxides of Mg, (c) any compounds that can generate metal oxides of Mg upon firing, and (d) mixtures thereof.

In one embodiment, the Mg-containing additive is MgO, wherein the MgO may have an average particle size in the range of 10 nanometers to 10 microns. In a further embodiment, the MgO may have an average particle size of 40 nanometers to 5 microns. In still a further embodiment, the MgO may have an average particle size of 60 nanometers to 3 microns. In a further embodiment, the MgO may have an average particle size of 0.1 to 1.7 microns. In a further embodiment, the MgO may have an average particle size of 0.3 to 1.3 microns. In a further embodiment, the Mg-containing additive may have an average particle size of less than 0.1 μm. In particular the Mg-containing additive may have an average particle size in the range of 7 nanometers to less than 100 nanometers.

MgO may be present in the composition in the range of 0.1 to 10 weight percent total composition. In one embodiment, the MgO may be present in the range of 0.5 to 5 weight percent total composition. In still a further embodiment, the MgO may be present in the range of 0.75 to 3 weight percent total composition.

In a further embodiment the Mg-containing additive (for example Mg, Mg resinate, etc.) may be present in the total thick film composition in the range of 0.1 to 10 weight percent. In a further embodiment the Mg-containing additive may be present in the range of 0.5 to 5 weight percent total composition. In still a further embodiment, the MgO may be present in the range of 0.75 to 3 weight percent total composition.

In a further embodiment, the Mg-containing additive may have an average particle size of less than 0.1 μm. In particular the Mg-containing additive may have an average particle size in the range of 7 nanometers to less than 100 nanometers.

In an embodiment, the additional additive may contain a mixture of additives. The additional additive may be a mixture of metal/metal oxide additives selected from (a) a metal wherein said metal is selected from Zn, Mg, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (b) a metal oxide of one or more of the metals selected from Zn, Mg, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (c) any compounds that can generate the metal oxides of (b) upon firing; and (d) mixtures thereof.

Compounds that can generate metal oxides of Zn, Mg, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu or Cr upon firing include, but are not limited to resonates, octoates, organic functional units, and the like.

In an embodiment, the additional additive may contain a mixture of ZnO and MgO.

In an embodiment, the additives may improve multiple functions of the solar cell. In an embodiment, the one or more additives may improve electrical properties of a solar cell; in an embodiment, the one or more additives may improve solderability on Si substrates; in an embodiment, the one or more additives may improve adhesion on Si substrates; in an embodiment the one or more additives may improve one or more of the properties described above.

C. Glass Frit

In an embodiment of the invention, the thick film composition may include glass materials. In an embodiment, glass materials may include one or more of three groups of constituents: glass formers, intermediate oxides, and modifiers. Exemplary glass formers may have a high bond coordination and smaller ionic size; the glass formers may form bridging covalent bonds when heated and quenched from a melt. Exemplary glass formers include, but are not limited to: SiO_2, B_2O_3, P_2O_5, V_2O_5, GeO_2 etc. Exemplary intermediate oxides include, but are not limited to: TiO_2, Ta_2O_5, Nb_2O_5, ZrO_2, CeO_2, SnO_2, Al_2O_3, HfO_2 and the like. Intermediate oxides may be used to substitute glass formers, as recognized by one of skill in the art. Exemplary modifiers may have a more ionic nature, and may terminate bonds. The modifiers may affect specific properties; for example, modifiers may result in reduction of glass viscosity and/or modification of glass wetting properties, for example. Exemplary modifiers include, but are not limited to: oxides such as alkali metal oxides, alkaline earth oxides, PbO, CuO, CdO, ZnO, Bi_2O_3, Ag_2O, MoO_3, WO_3 and the like.

In an embodiment, the glass materials may be selected by one of skill in the art to assist in the at least partial penetration of oxide or nitride insulating layers. As described herein, this at least partial penetration may lead to the formation of an effective electrical contact to the silicon surface of a photovoltaic device structure. The formulation components are not limited to glass forming materials.

In an embodiment of the invention, glass frit compositions (glass compositions) are provided. Non-limiting examples of glass frit compositions are listed in Table 1 below and described herein. Additional glass frit compositions are contemplated.

It is important to note that the compositions listed in Table 1 are not limiting, as it is expected that one skilled in glass chemistry could make minor substitutions of additional ingredients and not substantially change the properties of the glass composition of this invention. In this way, substitutions of glass formers such as P_2O_5 0-3, GeO_2 0-3, V_2O_5 0-3 in weight % maybe used either individually or in combination to achieve similar performance. It is also possible to substitute one or more intermediate oxides, such as TiO_2, Ta_2O_5, Nb_2O_5, ZrO_2, CeO_2, SnO_2 for other intermediate oxides (i.e., Al_2O_3, CeO_2, SnO_2) present in a glass composition of this invention. It is observed from the data that generally higher SiO_2 content of the glass degrades performance. The SiO_2 is thought to increase glass viscosity and reduce glass wetting. Although not represented in the Table 1 compositions, glasses with zero SiO_2 are expected to perform well, as other glass formers such as P_2O_5, GeO_2 etc. may be used to replace the function of low levels of SiO_2. The CaO, alkaline earth content, can also be partially or fully replaced by other alkaline earth constituents such as SrO, BaO and MgO.

Exemplary, non-limiting glass compositions in weight percent total glass composition are shown in Table 1. In an embodiment, glass compositions may comprise the following oxide constituents in the compositional range of: SiO_2 1-36, Al_2O_3 0-7, B_2O_3 1.5-19, PbO 20-83, ZnO 0-42, CuO 0-4, ZnO 0-12, Bi_2O_3 0-35, ZrO_2 0-8, TiO_2 0-7, PbF2 3-34 in weight percent of total glass composition. In a further embodiment, the glass composition may comprise: SiO_2 20-24, Al_2O_3 0.2-0.5, B_2O_3 5-9, PbO 20-55, Bi_2O_3 0-33, TiO_2 5-7, BiF_3 4-22 in weight percent of total glass composition. The fluoride used in the composition may be sourced from compounds of the available composition such as PbF_2, BiF_3, AlF_3 or other such compounds with appropriate calculations to maintain the same target composition. An example of this calculation equivalency is shown for Glass ID #1 as: SiO_2 22.08, Al_2O_3 0.38, PbO 56.44, B_2O_3 7.49, TiO_2 5.86, Bi_2O_3 6.79, F 1.66 weight % where the fluorine is expressed as elemental fluorine and associated oxides. One skilled in the art would readily make these conversion calculations. In an embodiment, glass compositions may have a total of PbO, Bi_2O_3 and PbF_2 between 60 – 70 % in wt %. In an embodiment, the glass composition may be generally described by the following in weight % of total glass composition: SiO_2 1-36 , PbO 20-83,

B_2O_3 1.5 – 19, PbF_2 4-22 and optional constituents include: Al_2O_3 0-7, ZrO_2 0-8, ZnO 0-12, CuO 0-4, Bi_2O_3 0-35, and TiO_2 0-7. It is also possible to describe the compositional range as a SiO_2, PbO, F, and B_2O_3 with optional additions of Al_2O_3, ZrO_2, ZnO, CuO, Bi_2O_3 ,TiO_2, and compound fluorides as source compound for the supply of fluorine to the composition.

Table 1: Glass Composition(s) in Weight Percent Total Glass Composition

Glass frits useful in the present invention include ASF1100 and ASF1100B which are commercially available from Asahi Glass Company. An average particle size of the glass frit (glass composition) in an embodiment of the present invention may be in the range of 0.5-1.5 μm. In a further embodiment, an average particle size may be in the range of 0.8-1.2 μm. In an embodiment, the softening point of the glass frit (T_g : second transition point of DTA) is in the range of 300-600°C. The T_g is determined by the intersection of the two extension lines drawn on the DTA plot for the specific material where the base line dips into an endotherm associated with the initiation of particle sintering. In an embodiment, the amount of glass frit in the total composition may be in the range of 0.5 to 4 wt. % of the total composition. In one embodiment, the glass composition is present in the amount of 1 to 3 weight percent total

	Glass Component (wt% total glass composition)											°C	Density
ID#	SiO_2	Al_2O_3	PbO	ZrO_2	B_2O_3	ZnO	CuO	Bi_2O_3	TiO_2	PbF_2	CdO	T_g	(g/cc)
1	22.08	0.38	46.68		7.49			6.79	5.86	10.7		510	4.83
2	29.32	3.13	51.55		3.06	2.57	2.74			7.64		525	4.59
3	14.87	6.56	46.66		14.82					17.1		490	4.47
4	9.5	1.46	63.94		13.05	3				9.04		458	5.59
5	1.1		82.7		11.2					5		298	6.2
6	14.64	6.46	30.63		14.6					33.7		465	4.61
7	20.94	1.97	25.93	7.95	17.98	10.5	2.05			12.7		503	3.8
8	21.84	0.38	21.48		7.41			32.5	5.79	10.6		485	4.69
9	21.87	0.38	36.57		7.42			6.73	5.8	21.2		455	4.81
10	22.14	0.39	53.34		7.51				5.87	10.8		478	4.84
11	30.61	2.55	55.02		1.83	2.7				7.29		524	4.63
12	32.54	3.77	23.35		10.71	10				19.6		523	3.78
13	34.99	5.09	42.87		3.36	5.22				8.46		5.26	4.04
14	23	0.4	58.8		7.8				6.1		3.9	505	4.2

composition. In a further embodiment, the glass composition is present in the range of 1.5 to 2.5 weight percent total composition.

The glasses described herein are produced by conventional glass making techniques. The glasses were prepared in 500-1000 gram quantities. The ingredients may be weighed and mixed in the desired proportions and heated in a bottom-loading furnace to form a melt in platinum alloy crucibles. As is well-known in the art, heating was conducted to a peak temperature (1000°C-1200°C) and for a time such that the melt becomes entirely liquid and homogeneous. The molten glass was quenched between counter rotating stainless steel rollers to form a 10-20 mil thick platelet of glass. The resulting glass platelet was then milled to form a powder with its 50% volume distribution set between 0.8-1.5 microns.

The T_g data in Table 1 was derived from thermo-mechanic analysis (TMA) measurements using a TA instruments Q400 using a dynamic force of 0.05 Newton on a pressed powder pellet 2.0-2.5 mm in thickness. The samples were heated at a rate of 10 °C/min. from room temperature to a temperature where viscous flow is dominant in its thermal deformation.

In an embodiment, one or more additives described herein, such as ZnO, MgO, etc, may be contained in a glass. The glass frits which contain the one or more additives are useful in the embodiments described herein.

In an embodiment, the glass frit may include Bi_2O_3, B_2O_3 8-25 weight percent of total glass composition, and further comprises one or more components selected from the group consisting of: SiO_2, P2O5, GeO_2, and V_2O_5.

In an embodiment, the glass frit may include one or more of Al_2O_3, CeO_2, SnO_2, and CaO. In an aspect of this embodiment, based on weight percent of total glass composition, the amount of Al_2O_3, CeO_2, SnO_2, and CaO may be less than 6. In an aspect of this embodiment, based on weight percent of total glass composition, the amount of Al_2O_3, CeO_2, SnO_2, and CaO may be less than 1.5.

In an embodiment, the glass frit may include one or more of BiF_3 and Bi_2O_3. In an aspect of this embodiment, based on weight percent of total glass composition, the amount of BiF_3 and Bi_2O_3 may be less than 83. In an aspect of this embodiment, based on weight percent total of glass composition, the amount of BiF_3 and Bi_2O_3 may be less than 72.

In an embodiment, the glass frit may include one or more of Na_2O, Li_2O, and Ag_2O. In an aspect of this embodiment, based on weight percent of total glass composition, the amount of Na_2O, Li_2O, and Ag_2O may be less than 5. In an aspect of this embodiment, based on weight percent of total glass composition, the amount of Na_2O, Li_2O, and Ag_2O may be less than 2.0.

In an embodiment, the glass frit may include one or more of Al_2O_3, Si_2O_2, and B_2O_3. In an aspect of this embodiment, based on weight percent of total glass composition, the amount of Si_2O_2, Al_2O_3, and B_2O_3 may be less than 31.

In an embodiment, the glass frit may include one or more of Bi_2O_3, BiF_3, Na_2O, Li_2O, and Ag_2O. In an embodiment, based on weight percent of total glass composition, the amount of $(Bi_2O_3 + BiF_3) / (Na_2O + Li_2O + Ag_2O)$ may be greater than 14.

As used herein, “lead-free” means that no lead has been added. In an embodiment, trace amounts of lead may be present in a composition and the composition may still be considered lead-free if no lead was added. In an embodiment, a lead-free composition may contain less than 1000 ppm of lead. In an embodiment, a lead-free composition may contain less than 300 ppm of lead. One of skill in the art will recognize that compositions containing lesser amounts of lead are encompassed by the term lead-free. In an embodiment, a lead-free composition may not only be free of lead, but may also be free of other toxic materials, including Cd, Ni, and carcinogenic toxic materials, for example. In an embodiment, a lead-free composition may contain less than 1000 ppm of lead, less than 1000 ppm of Cd, and less than 1000 ppm of Ni. In an embodiment, the lead-free composition may contain trace amounts of Cd and/or Ni; in an embodiment, no Cd, Ni, or carcinogenic toxic materials are added to a lead-free composition.

Flux Materials

An embodiment of the present invention relates to a thick film composition, structures and devices including, and methods of making the structures and devices, wherein the thick film includes flux materials. The flux materials, in an embodiment, may have properties similar to the glass materials, such as possessing lower softening characteristics. For example, compounds such as oxide or halogen compounds may be used. The compounds may assist penetration of an insulating layer in the structures described herein. Non-limiting examples of such compounds include materials that have been coated or encased in organic or inorganic barrier coating to protect against adverse reactions with organic binder components of the paste medium. Non-limiting examples of such flux materials may include PbF_2, BiF_3, V_2O_5, alkali metal oxides and the like.

Glass Blending

In an embodiment, one or more glass frit materials may be present as an admixture in the thick film composition. In an embodiment, a first glass frit material may be selected by one of skill in the art for its capability to rapidly digest the insulating layer; further the glass frit material may have strong corrosive power and low viscosity.

In an embodiment, the second glass frit material may be designed to slowly blend with the first glass frit material while retarding the chemical activity. A stopping condition may result which may effect the partial removal of the insulating layer but without attacking the underlying emitter diffused region potentially shunting the device is the corrosive action proceeds unchecked. Such a glass frit material may be characterized as having a sufficiently higher viscosity to provide a stable manufacturing window to remove insulating layers without damage to the diffused p-n junction region of the semiconductor substrate.

In a non-limiting exemplary admixture, the first glass frit material may be SiO_2 1.7 wt%, ZrO_2 0.5 wt%, B_2O_3 12 wt% , Na_2O 0.4

wt%, Li_32O 0.8 wt%, and Bi_2O_3 84.6 wt% and the second glass frit material may be as SiO_2 27 wt%, ZrO_2 4.1 wt%, Bi_2O_3 68.9 wt%. The proportions of the blend may be used to adjust the blend ratio to meet optimal performance of the thick film conductor paste, under conditions recognized by one of skill in the art..

Analytical Glass Testing

Several testing methods may be used to characterize glass materials as candidates for application to photovoltaic Ag conductor formulation, and are recognized by one of skill in the art. Among these measurements are Differential Thermal Analysis, DTA and Thermo-mechanical Analysis, TMA for the determination of Tg and glass flow kinetics. As needed, many additional characterization methods may be employed such as dilatometry, thermogravimetric analysis, XRD, XRF, and ICP

Inert Gas Firing

In an embodiment, the processing of photovoltaic device cells utilize nitrogen or other inert gas firing of the prepared cells. The firing temperature profile is typically set so as to enable the burnout of organic binder materials from dried thick film paste or other organic materials present. In an embodiment, the temperature may be between 300-525 Celsius. The firing may be conducted in a belt furnace using high transport rates, for example between 40- 200 inches per minute. Multiple temperature zones may be used to control the desired thermal profile. The number of zones may vary between 3 to 9 zones, for example. The photovoltaic cells may be fired at set temperatures between 650 and 1000 C, for example. The firing is not limited to this type of firing, and other rapid fire furnace designs known to one of skill in the art are contemplated.

Organic Medium

The inorganic components may be mixed with an organic medium by mechanical mixing to form viscous compositions called “pastes”, having suitable consistency and rheology for printing. A wide variety of inert viscous materials can be used as organic medium. The organic medium may be one in which the inorganic components are dispersible with an adequate degree of stability. The rheological properties of the medium must be such that they lend good application properties to the composition, including: stable dispersion of solids, appropriate viscosity and thixotropy for screen printing, appropriate wet ability of the substrate and the paste solids, a good drying rate, and good firing properties. In an embodiment of the present invention, the organic vehicle used in the thick film composition of the present invention may be a nonaqueous inert liquid. Use can be made of any of various organic vehicles, which may or may not contain thickeners, stabilizers and/or other common additives. The organic medium may be a solution of polymer(s) in solvent(s). Additionally, a small amount of additives, such as surfactants, may be a part of the organic medium. The most frequently used polymer for this purpose is ethyl cellulose. Other examples of polymers include ethylhydroxyethyl cellulose, wood rosin, mixtures of ethyl cellulose and phenolic resins, polymethacrylates of lower alcohols, and monobutyl ether of ethylene glycol monoacetate can also be used. The most widely used solvents found in thick film compositions are ester alcohols and terpenes such as alpha- or beta-terpineol or mixtures thereof with other solvents such as kerosene, dibutylphthalate, butyl carbitol, butyl carbitol acetate, hexylene glycol and high boiling alcohols and alcohol esters. In addition, volatile liquids for promoting rapid hardening after application on the substrate can be included in the vehicle. Various combinations of these and other solvents are formulated to obtain the viscosity and volatility requirements desired.

The polymer present in the organic medium is in the range of 8 wt. % to 11 wt.% of the total composition. The thick film silver composition of the present invention may be adjusted to a predetermined, screen-printable viscosity with the organic medium.

The ratio of organic medium in the thick film composition to the inorganic components in the dispersion is dependent on the method of applying the paste and the kind of organic medium used, and it can vary. Usually, the dispersion will contain 70-95 wt % of inorganic components and 5-30 wt % of organic medium (vehicle) in order to obtain good wetting.

An embodiment of the present invention relates to a thick film composition, wherein the thick film composition includes:

(a) an electrically conductive silver powder;

(b) one or more additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof; and a second additive, wherein the second additive is selected from the group consisting of: (i) a metal oxide additive; (ii) a compound that can generate a metal oxide upon firing;

(c) one or more glass frits; dispersed in

(d) an organic medium;

wherein the glass frit includes: Bi_2O_3, B_2O_3 8-25 weight percent of the total glass frit, and further comprises one or more components selected from the group consisting of: SiO_2, P_2O_5, GeO_2, and V_2O_5. In an aspect of this embodiment, the glass frits may be lead-free. In an aspect of this embodiment, the glass frit includes: Bi_2O_3 28-85, B_2O_3 8-25, and one or more of: SiO_2 0-8, P_2O_5 0-3, GeO_2 0-3, V_2O_5 0-3. In an aspect of this embodiment, the glass frit includes SiO_2 0.1-8. In an aspect of this embodiment, the glass frit may include one or more intermediate oxides. Exemplary intermediate oxides include, but are not limited to: Al_2O_3, CeO_2, SnO_2, TiO_2, Ta_2O_5, Nb_2O_5, and ZrO_2. In an aspect of this embodiment, the glass frit may include one or more alkaline earth constituents. Exemplary alkaline earth constituents include, but are not limited to: CaO, SrO, BaO, MgO. In an embodiment, the glass frit may include one or more components selected from the group consisting of: ZnO, Na_2O, Li_2O, AgO_2, and BiF_3.

In an aspect of this embodiment, the composition may also include a second additive. Exemplary additives include: a metal additive, or a metal-containing additive, and wherein the metal additive or metal-containing additive forms an oxide under processing conditions. The additive may be a metal oxide additive. For example, the additive may be a metal oxide of one or more of the metals selected from Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, and Cr.

An embodiment of the invention relates to a semiconductor device including the composition including:

(a) an electrically conductive silver powder;

(b) one or more additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof; and a second additive, wherein the second additive is selected from the group consisting of: (i) a metal oxide additive; (ii) a compound that can generate a metal oxide upon firing;

(c) one or more glass frits; dispersed in

(d) an organic medium;

wherein the glass frit includes: Bi_2O_3, B_2O_3 8-25 weight percent of the total glass frit, and further comprises one or more components selected from the group consisting of: SiO_2, P_2O_5, GeO_2, and V_2O_5. An aspect of this embodiment relates to a solar cell including the semiconductor device.

An embodiment of the invention relates to a structure including:

(a) the thick film composition including:

(a) an electrically conductive silver powder;

(b) one or more additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and

(iv) mixtures thereof; and a second additive, wherein the second additive is selected from the group consisting of: (i) a metal oxide additive; (ii) a compound that can generate a metal oxide upon firing;

(c) one or more glass frits; dispersed in

(d) an organic medium;

wherein the glass frit includes: Bi_2O_3, B_2O_3 8-25 weight percent of the total glass frit, and further comprises one or more components selected from the group consisting of: SiO_2, P_2O_5, GeO_2, and V_2O_5; and

(b) an insulating film

wherein the thick film composition is formed on the insulating film, and wherein, upon firing, the insulating film is penetrated by components of the thick film composition and the organic medium is removed.

Structures

An embodiment of the present invention relates to structure including a thick film composition and a substrate. In an embodiment, the substrate may be one or more insulating films. In an embodiment, the substrate may be a semiconductor substrate. In an embodiment, the structures described herein may be useful in the manufacture of photovoltaic devices. An embodiment of the invention relates to a semiconductor device containing one or more structures described herein; an embodiment of the invention relates to a photovoltaic device containing one or more structures described herein; an embodiment of the invention relates to a solar cell containing one or more structures described herein; an embodiment of the invention relates to a solar panel containing one or more structures described herein.

An embodiment of the present invention relates to an electrode formed from a thick film composition described herein. In an embodiment, the thick film composition has been fired to remove the organic vehicle and sinter the silver and glass particles. An embodiment of the present invention relates to a semiconductor device containing an electrode formed from the thick film composition. In an embodiment, the electrode is a front side electrode.

An embodiment of the present invention relates to structures described herein, wherein the structures also include a back electrode.

An embodiment of the present invention relates to structures, wherein the structures include thick film conductor compositions. In an aspect, the structure also includes one or more insulating films. In an aspect, the structure does not include an insulating film. In an aspect, the structure includes a semiconductor substrate. In an aspect, the thick film conductor composition may be formed on the one or more insulating films. In an aspect, the thick film conductor composition may be formed on the semiconductor substrate. In the aspect wherein the thick film conductor composition may be formed on the semiconductor substrate, the structure may not contain an insulating film.

Thick film conductor and insulating film structure

An aspect of the present invention relates to a structure including a thick film conductor composition and one or more insulating films. The thick film composition may include: (a) an electrically conductive silver powder; (b) one or more glass frits; dispersed in c) an organic medium. In an embodiment, the glass frits may be lead-free. In an embodiment, the thick film composition may also include an additive, as described herein. The structure may also include a semiconductor substrate. In an embodiment of the invention, upon firing, the organic vehicle may be removed and the silver and glass frits may be sintered. In a further aspect of this embodiment, upon firing, the conductive silver and frit mixture may penetrate the insulating film.

The thick film conductor composition may penetrate the insulating film upon firing. The penetration may be partial penetration. The penetration of the insulating film by the thick film conductor composition may result in an electrical contact between the conductor of the thick film composition and the semiconductor substrate.

The thick film conductor composition may be printed on the insulating film in a pattern. The printing may result in the formation of busbars with connecting lines, as described herein, for example.

The printing of the thick film may be by plating, extrusion, inkjet, shaped or multiple printing, or ribbons, for example.

A layer of silicon nitride may be present on the insulating film. The silicon nitride may be chemically deposited. The deposition method may be CVD, PCVD, or other methods known to one of skill in the art.

Insulating films

In an embodiment of the invention, the insulating film may include one or more component selected from: titanium oxide, silicon nitride, SiNx:H, silicon oxide, and silicon oxide/titanium oxide. In an embodiment of the invention, the insulating film may be an anti-reflection coating (ARC). In an embodiment of the invention, the insulating film may be applied; the insulating film may be applied to a semiconductor substrate. In an embodiment of the invention, the insulting film may be naturally forming, such as in the case of silicon oxide. In an embodiment, the structure may not include an insulating film that has been applied, but may contain a naturally forming substance, such as silicon oxide, which may function as an insulating film.

Thick film conductor and semiconductor substrate structure

An aspect of the present invention relates to a structure including a thick film conductor composition and a semiconductor substrate. In an embodiment, the structure may not include an insulating film. In an embodiment, the structure may not include an insulating film which has been applied to the semiconductor substrate. In an embodiment, the surface of the semiconductor substrate may include a naturally occurring substance, such as SiO_2. In an aspect of this embodiment, the naturally occurring substance, such as SiO_2, may have insulating properties.

The thick film conductor composition may be printed on the semiconductor substrate in a pattern. The printing may result in the formation of busbars with connecting lines, as described herein, for example. An electrical contact may be formed between the conductor of the thick film composition and the semiconductor substrate.

A layer of silicon nitride may be present on the semiconductor substrate. The silicon nitride may be chemically deposited. The deposition method may be CVD, PCVD, or other methods known to one of skill in the art.

Structure in which the silicon nitride may be chemically treated

An embodiment of the invention relates to a structure in which the silicon nitride of the insulating layer may be treated resulting in the removal of at least a portion of the silicon nitride. The treatment may be chemical treatment. The removal of at least a portion of the silicon nitride may result in an improved electrical contact between the conductor of the thick film composition and the semiconductor substrate. The structure may have improved efficiency.

In an aspect of this embodiment, the silicon nitride of the insulating film may be part of the anti-reflective coating (ARC). The silicon nitride may be naturally forming, or chemically deposited, for example. The chemical deposition may be by CVD or PCVD, for example.

Structure in which the thick film composition includes flux materials that are not glass frit

An embodiment of the invention relates to a structure including a thick film composition and one or more insulating films, in which the thick film composition includes an electrically conductive silver powder, one or more flux materials, and an organic medium, and wherein the structure further comprises one or more insulating films. In an aspect of this embodiment, the flux materials are lead-free. In an aspect, the flux materials are not glass frit. In an embodiment, the structure may further include a semiconductor substrate.

The thick film conductor composition may penetrate the insulating film upon firing. The penetration may be partial penetration. For example, a percentage of the surface of the insulating film may be penetrated by the thick film conductor composition. The penetration of the insulating film by the thick film conductor composition may result in an electrical contact between the conductor of the thick film composition and the semiconductor substrate.

In an embodiment of the present invention, a method and structure are provided in which a conductor has been applied directly to the semiconductor substrate. In an aspect of this embodiment, a mask may have been applied to the semiconductor substrate in a pattern correlating to the pattern of the conductor. An insulating may have then been applied, with subsequent removal of the mask. The conductor composition may have then been applied to the semiconductor substrate in a pattern correlating to the area from which the mask was removed.

An embodiment of the present invention relates to a semiconductor device which includes a composition, wherein, prior to firing, the composition includes:

an electrically conductive silver powder;

one or more additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof; and a second additive, wherein the second additive is selected from the group consisting of: (i) a metal oxide additive; (ii) a compound that can generate a metal oxide upon firing;

one or more glass frits wherein said glass frits are lead-free; dispersed in an organic medium.

In an aspect of this embodiment, the composition may include an additive. Exemplary additives are described herein. An aspect of this embodiment relates to a solar cell including the semiconductor device. An aspect of this embodiment relates to a solar panel including the solar cell.

Busbars

In an embodiment, the thick film conductor composition may be printed on the substrate to form busbars. The busbars may be more than two busbars. For example, the busbars may be three or more busbars. In addition to busbars, the thick film conductor composition may be printed on the substrate to form connecting lines. The connecting lines may contact a busbar. The connecting lines contacting a busbar may be interdigitated between the connecting lines contacting a second busbar.

In an exemplary embodiment, three busbars may be parallel to each other on a substrate. The busbars may be rectangular in shape. Each of the longer sides of the middle busbar may be in contact with connecting lines. On each of the side busbars, only one side of the longer rectangle may be in contact with connecting lines. The connecting lines contacting the side busbars may interdigitate with the connecting lines contacting the middle busbar. For example, the connecting lines contacting one side busbar may interdigitate with the connecting lines contacting the middle busbar on one side, and the connecting lines contacting the other side busbar may interdigitate with the connecting lines contacting the middle busbar on the other side of the middle busbar.

Description of Method of Manufacturing a Semiconductor Device

An embodiment of the invention relates to a method of manufacturing a semiconductor device. An aspect of this embodiment includes the steps of:

(a) providing a semiconductor substrate, one or more insulating films, and a thick film composition, wherein the thick film composition comprises: a) an electrically conductive silver powder, b) one or more additive, wherein the additive is selected from the group consisting of: (i) bismuth-containing additive, copper-containing additive, and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, copper, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof; and a second additive, wherein the second additive is selected from the group consisting of: (i) a metal oxide additive; (ii) a compound that can generate a metal oxide upon firing;

c) one or more glass frits, dispersed in d) an organic medium,

(b) applying one or more insulating films on the semiconductor substrate,

(c) applying the thick film composition on the one or more insulating films on the semiconductor substrate, and

(d) firing the semiconductor, one or more insulating films and thick film composition,

wherein, upon firing, the organic vehicle is removed, the silver and glass frits are sintered, and the insulating film is penetrated by components of the thick film composition.

In an aspect of this embodiment, the glass frits may be lead-free. In an aspect of this embodiment, the one or more insulating films may be selected from the group including: silicon nitride film, titanium oxide film, SiNx:H film, silicon oxide film and a silicon oxide/titanium oxide film.

An embodiment of the invention relates to semiconductor device formed by a method described herein. An embodiment of the invention relates to a solar cell including a semiconductor device formed by a method described herein. An embodiment of the invention relates to a solar cell including an electrode, which includes a silver powder and one or more glass frits, wherein the glass frits are lead-free.

An embodiment of the present invention provides a novel composition(s) that may be utilized in the manufacture of a semiconductor device. The semiconductor device may be manufactured by the following method from a structural element composed of a junction-bearing semiconductor substrate and a silicon nitride insulating film formed on a main surface thereof. The method of manufacture of a semiconductor device includes the steps of applying (for example, coating and printing) onto the insulating film, in a predetermined shape and at a predetermined position, the conductive thick film composition of the present invention having the ability to penetrate the insulating film, then firing so that the conductive thick film composition melts and passes through the insulating film, effecting electrical contact with the silicon substrate. In an embodiment, the electrically conductive thick film composition may be a thick-film paste composition, as described herein, which is made of a silver powder, Zn-containing additive, a glass or glass powder mixture having a softening point of 300 to 600°C, dispersed in an organic vehicle and optionally, additional metal/metal oxide additive(s).

In an embodiment, the composition may include a glass powder content of less than 5% by weight of the total composition and a Bismuth-containing and Zn-containing additive combined with optional additional metal/metal oxide additive content of no more than 6% by weight of the total composition. An embodiment of the invention also provides a semiconductor device manufactured from the same method.

In an embodiment of the invention, silicon nitride film or silicon oxide film may be used as the insulating film. The silicon nitride film may be formed by a plasma chemical vapor deposition (CVD) or thermal CVD process. In an embodiment, the silicon oxide film may be formed by thermal oxidation, thermal CFD or plasma CFD.

In an embodiment, the method of manufacture of the semiconductor device may also be characterized by manufacturing a semiconductor device from a structural element composed of a junction-bearing semiconductor substrate and an insulating film formed on one main surface thereof, wherein the insulating layer is selected from a titanium oxide silicon nitride, SiNx:H, silicon oxide, and silicon oxide/titanium oxide film, which method includes the steps of forming on the insulating film, in a predetermined shape and at a predetermined position, a metal paste material having the ability to react and penetrate the insulating film, forming electrical contact with the silicon substrate. The titanium oxide film may be formed by coating a titanium-containing organic liquid material onto the semiconductor substrate and firing, or by a thermal CVD. In an embodiment, the silicon nitride film may be formed by

PECVD (plasma enhanced chemical vapor deposition). An embodiment of the invention also provides a semiconductor device manufactured from this same method.

In an embodiment of the invention, the electrode formed from the conductive thick film composition(s) of the present invention may be fired in an atmosphere composed of a mixed gas of oxygen and nitrogen. This firing process removes the organic medium and sinters the glass frit with the Ag powder in the conductive thick film composition. The semiconductor substrate may be single-crystal or multicrystalline silicon, for example.

FIG. 1(a) shows a step in which a substrate is provided, with a textured surface which reduces light reflection. In an embodiment, a semiconductor substrate of single-crystal silicon or of multicrystalline silicon is provided. In the case of solar cells, substrates may be sliced from ingots which have been formed from pulling or casting processes. Substrate surface damage caused by tools such as a wire saw used for slicing and contamination from the wafer slicing step may be removed by etching away about 10 to 20 μm of the substrate surface using an aqueous alkali solution such as aqueous potassium hydroxide or aqueous sodium hydroxide, or using a mixture of hydrofluoric acid and nitric acid. In addition, a step in which the substrate is washed with a mixture of hydrochloric acid and hydrogen peroxide may be added to remove heavy metals such as iron adhering to the substrate surface. An antireflective textured surface is sometimes formed thereafter using, for example, an aqueous alkali solution such as aqueous potassium hydroxide or aqueous sodium hydroxide. This gives the substrate, 10.

Next, referring to FIG. 1(b), when the substrate used is a p-type substrate, an n-type layer is formed to create a p-n junction. The method used to form such an n-type layer may be phosphorus (P) diffusion using phosphorus oxychloride ($POCl_3$). The depth of the diffusion layer in this case can be varied by controlling the diffusion temperature and time, and is generally formed within a thickness range of about 0.3 to 0.5 μm. The n-type layer formed in this way is represented in the diagram by reference numeral 20. Next, p-n separation on the front and backsides may be carried out by the method described in the background of the invention. These steps are not always necessary when a phosphorus-containing liquid coating material such as phosphosilicate glass (PSG) is applied onto only one surface of the substrate by a process, such as spin coating, and diffusion is effected by annealing under suitable conditions. Of course, where there is a risk of an n-type layer forming on the backside of the substrate as well, the degree of completeness can be increased by employing the steps detailed in the background of the invention.

Next, in FIG. 1(d), a silicon nitride film or other insulating films including SiNx:H (i.e., the insulating film comprises hydrogen for passivation during subsequent firing processing) film, titanium oxide film, and silicon oxide film, 30, which functions as an antireflection coating is formed on the above-described n-type diffusion layer, 20. This silicon nitride film, 30, lowers the surface reflectance of the solar cell to incident light, making it possible to greatly increase the electrical current generated. The thickness of the silicon nitride film, 30, depends on its refractive index, although a thickness of about 700 to 900Å is suitable for a refractive index of about 1.9 to 2.0. This silicon nitride film may be formed by a process such as low-pressure CVD, plasma CVD, or thermal CVD. When thermal CVD is used, the starting materials are often dichlorosilane ($SiCl_2H_2$) and ammonia (NH_3) gas, and film formation is carried out at a temperature of at least 700°C. When thermal CVD is used, pyrolysis of the starting gases at the high temperature results in the presence of substantially no hydrogen in the silicon nitride film, giving a compositional ratio between the silicon and the nitrogen of Si_3N_4 which is substantially stoichiometric. The refractive index falls within a range of substantially 1.96 to 1.98. Hence, this type of silicon nitride film is a very dense film whose characteristics, such as thickness and refractive index, remain unchanged even when subjected to heat treatment in a later step. The starting gas used when film formation is carried out by plasma CVD is generally a gas mixture of SiH_4 and NH_3. The starting gas is decomposed by the plasma, and film formation is carried out at a temperature of 300 to 550°C. Because film formation by such a plasma CVD process is carried out at a lower temperature than thermal CVD, the hydrogen in the starting gas is present as well in the resulting silicon nitride film. Also, because gas decomposition is effected by a plasma, another distinctive feature of this process is the ability to greatly vary the compositional ratio between the silicon and nitrogen. Specifically, by varying such conditions as the flow rate ratio of the starting gases and the pressure and temperature during film formation, silicon nitride films can be formed at varying compositional ratios between silicon, nitrogen and hydrogen, and within a refractive index range of 1.8 to 2.5. When a film having such properties is heat-treated in a subsequent step, the refractive index may change before and after film formation due to such effects as hydrogen elimination in the electrode firing step. In such cases, the silicon nitride film required in a solar cell can be obtained by selecting the film-forming conditions after first taking into account the changes in film qualities that will occur as a result of heat treatment in the subsequent step.

In FIG. 1(d), a titanium oxide film may be formed on the n-type diffusion layer, 20, instead of the silicon nitride film, 30, functioning as an antireflection coating. The titanium oxide film is formed by coating a titanium-containing organic liquid material onto the n-type diffusion layer, 20, and firing, or by thermal CVD. It is also possible, in FIG. 1(d), to form a silicon oxide film on the n-type diffusion layer, 20, instead of the silicon nitride film 30 functioning as an antireflection layer. The silicon oxide film is formed by thermal oxidation, thermal CVD or plasma CVD.

Next, electrodes are formed by steps similar to those shown in FIGS. 1(e) and (f). That is, as shown in FIG. 1(e), aluminum paste, 60, and back side silver paste, 70, are screen printed onto the back side of the substrate, 10, as shown in FIG. 1(e) and successively dried. In addition, a front electrode-forming silver paste is screen printed onto the silicon nitride film, 30, in the same way as on the back side of the substrate, 10, following which drying and firing are carried out in an infrared furnace; the set point temperature range may be 700 to 975°C for a period of from one minute to more than ten minutes while a mixed gas stream of oxygen and nitrogen are passed through the furnace.

As shown in FIG. 1(f), during firing, aluminum diffuses as an impurity from the aluminum paste into the silicon substrate, 10, on the back side, thereby forming a p+ layer, 40, containing a high aluminum dopant concentration. Firing converts the dried aluminum paste, 60, to an aluminum back electrode, 61. The backside silver paste, 70, is fired at the same time, becoming a silver back electrode, 71. During firing, the boundary between the backside aluminum and the backside silver assumes the state of an alloy, thereby achieving electrical connection. Most areas of the back electrode are occupied by the aluminum electrode, partly on account of the need to form a p+ layer, 40. The silver or silver/aluminum back electrode is formed on limited areas of the backside as an electrode for interconnecting solar cells by means of copper ribbon or the like.

On the front side, the front electrode silver paste, 500, of the invention is composed of silver, a first additive containing one or more of a bismuth, copper, or phosphorus-containing additive, a Zn-containing additive, glass frit, organic medium and optional metal oxides, and is capable of reacting and penetrating through the silicon nitride film, 30, during firing to achieve electrical contact with the n-type layer, 20 (fire through). This fired-through state, i.e., the extent to which the front electrode silver paste melts and passes through the silicon nitride film, 30, depends on the quality and thickness of the silicon nitride film, 30, the composition of the front electrode silver paste, and on the firing conditions. The conversion efficiency and moisture resistance reliability of the solar cell clearly depend, to a large degree, on this fired-through state.

EXAMPLES

Non-limiting examples of thick film composition(s) described herein are provided in Table 2.

Paste Preparation

Paste preparations were, in general, accomplished with the following procedure: The appropriate amount of solvent, medium and surfactant was weighed then mixed in a mixing can for 15 minutes, then glass frits and metal additives were added and mixed for another 15 minutes. Since Ag is the major part of the solids of the present invention, it was added incrementally to ensure better wetting. When well mixed, the paste was repeatedly passed through a 3-roll mill for at progressively increasing pressures from 0 to 400 psi. The gap of the rolls was adjusted to 1 mil. The degree of dispersion was measured by fineness of grind (FOG). The FOG value may be equal to or less than 20/10 for conductors.

The ASF1100 glass frit (available from Asahi Glass Company) used in the following examples was not used as supplied. It was milled to a D_{50} in the range of 0.5-0.7 microns prior to use.

Test Procedure-Efficiency

The solar cells built according to the method described above were placed in a commercial IV tester for measuring efficiencies (ST-1000). The Xe Arc lamp in the IV tester simulated the sunlight with a known intensity and radiated the front surface of the cell. The tester used a four contact method to measure current (I) and voltage (V) at approximately 400 load resistance settings to determine the cell's I-V curve. Both fill factor (FF) and efficiency (Eff) were calculated from the I-V curve.

Paste efficiency and fill factor values were normalized to corresponding values obtained with cells contacted with industry standard PV145 (E. I. du Pont de Nemours and Company).

Test Procedure-Adhesion

After firing, a solder ribbon (copper coated with 62Sn/36Pb/2Ag or 96.5Sn/3.5 Ag) was soldered to the bus bars printed on the front of the cell. In an embodiment, solder reflow was achieved at 330 - 365°C for 5 seconds. Flux was no-clean Alpha-100, or MF200. The soldered area was approximately 2mm x 2mm. The adhesion strength was obtained by pulling the ribbon at an angle of 90° to the surface of the cell. Normalized adhesion strength was calculated to compare vs. a minimum adhesion value.

Efficiency and Adhesion Data

The compositions in Table 2 are given in percent total thick film composition (paste). Experiments showed that the electrical efficiency did not decrease with the addition of the additives of either Bi_2O_3 or Cu. However, adhesion showed significant improvement with the addition of the additives. FIG. 2 illustrates the adhesion values of the compositions described in Table 2.

Table 2 Compositions Containing Additives

Paste ID	Glass #14	Glass #1	Ag %*	ZnO %	Bi_2O_3 %	Cu %
A	0	1.4	78.95	6.5	0	0
B	0	1.4	78.95	6.3	0.2	0
C	0	1.4	78.95	6.3	0	0.2
D	0	1.4	78.95	6.1	0.4	0
E	2.90	0	77.49	5.81	0	0
F	2.90	0	77.49	5.41	0.4	0

The components in Table 2 are given in weight percent of total thick film composition (paste).

* Ag content for A-D is 90.9 wt% of the solids in the total thick film composition

* Ag content for E-F is 89.9 wt% of the solids in the total thick film composition

CLAIMS

What is claimed is:

1. A thick film conductive composition comprising:
   - a) electrically conductive powder;
   - b) two or more additives, wherein the first additive is selected from the group consisting of: (i) bismuth-containing additive and phosphorus-containing additive; (ii) a metal oxide of one or more of bismuth, and phosphorus; (iii) any compound that can generate the metal oxides of (ii) upon firing; and (iv) mixtures thereof; and wherein the second additive is selected from the group consisting of: (i) a metal oxide additive; (ii) a compound that can generate a metal oxide upon firing;
   - c) one or more glass frits; dispersed in
   - d) organic medium.

2. The composition of claim 1, wherein the bismuth-containing additive is selected from the group consisting of: Bi_2O_3, and bismuth resinate; and wherein the phosphorus-containing additive is selected from the group consisting of: P_2O_5, phosphorus-containing surfactant, and organic phosphorus.

3. The composition of claim 1, wherein the first additive is a bismuth-containing additive.

4. The composition of claim 1, wherein the first additive is 0.05 to 10 wt % of the thick film composition.

5. The composition of claim 1, wherein the first additive is 0.15 to 0.5 wt % of the thick film composition.

6. The composition of claim 1, wherein the second additive is 4 to 8 wt % of the thick film composition.

7. The composition of claim 1, wherein the conductive powder comprises Ag.

8. The composition of claim 1, wherein the second additive is selected from the group consisting of: (a) a metal wherein said metal is selected from Zn, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (b) a metal oxide of one or more of the metals selected from Zn, Gd, Ce, Zr, Ti, Mn, Sn, Ru, Co, Fe, Cu and Cr; (c) any compounds that can generate the metal oxides of (b) upon firing; and (d) mixtures thereof.

9. The composition of claim 8, wherein the Zn-containing additive is ZnO.

10. The composition of claim 1, wherein the Ag is 70 to 99 wt % of the total solid components of the thick film composition.

11. A method of manufacturing a semiconductor device comprising the steps of:

(a) providing one or more semiconductor substrates, one or more insulating films, and the thick film composition of claim 1;

(b) applying the insulating film to the semiconductor substrate,

(c) applying the thick film composition to the insulating film on the semiconductor substrate, and

(d) firing the semiconductor, insulating film and thick film composition, wherein, upon firing, the organic vehicle is removed, the silver and glass frits are sintered, and the insulating film is penetrated by components of the thick film composition.

12. The method of claim 11, wherein the insulating film comprises one or more components selected from: titanium oxide, silicon nitride, SiNx:H, silicon oxide, and silicon oxide/titanium oxide.

13. A semiconductor device made by the method of claim 11.

14. A semiconductor device comprising an electrode, wherein the electrode, prior to firing, comprises the composition of claim 1.

15. A solar cell comprising the semiconductor device of claim 14.

FIG. 1A

FIG. 1B

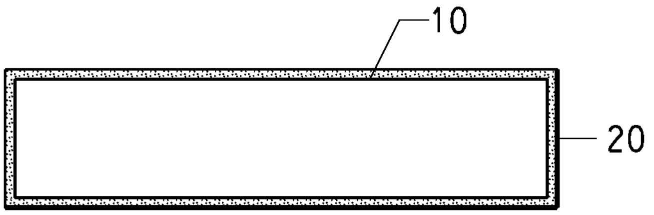


FIG. 1C

FIG. 1D

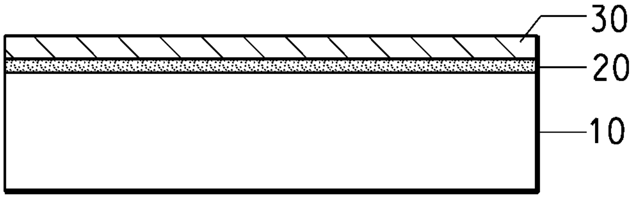


FIG. 1E

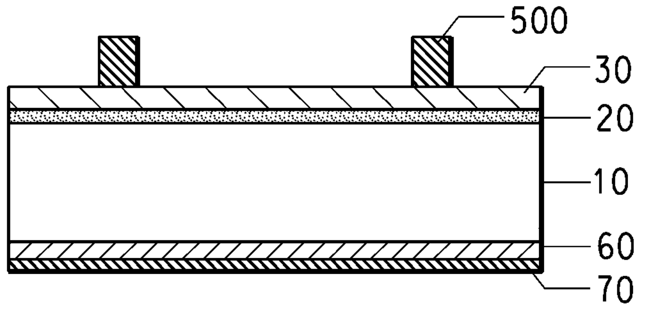
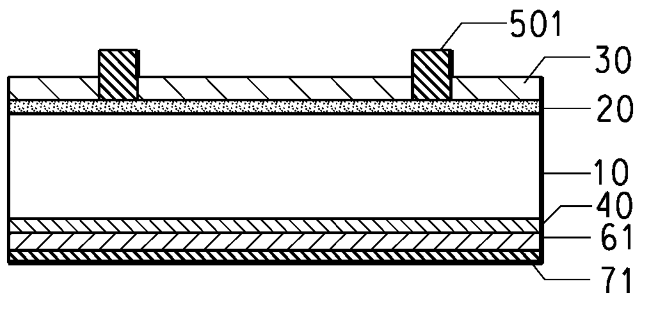


FIG. 1F



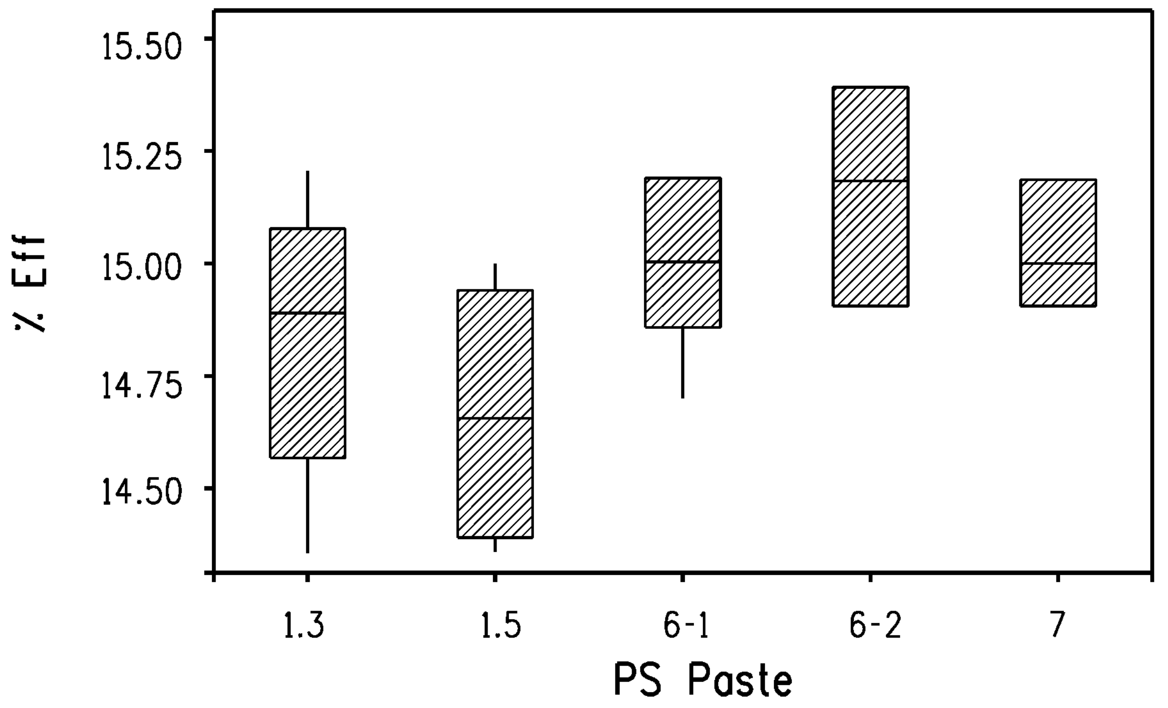


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/041333

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B1/16 H01B1/22 H01L31/0224

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)
H01L H01B H05K

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/125879 A (SHARP KK [JP]; NAMICS CORP [JP]; MACHIDA TOMOHIRO; TONOMURA YOSHIFUMI;) 8 November 2007 (2007-11-08) paragraphs [0057], [0074] - [0079], [0125]; example 10 -----	1,2,4-15
X	US 2005/277550 A1 (BROWN ORVILLE W [US] ET AL BROWN ORVILLE WASHINGTON [US] ET AL) 15 December 2005 (2005-12-15) paragraph [0015]; claims 22,23; example 1; table 2 -----	1-6,8, 14,15
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	-/--	

☒ 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

"E" earlier document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 7 August 2009	Date of mailing of the international search report 31/08/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Delaporte, P

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No

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