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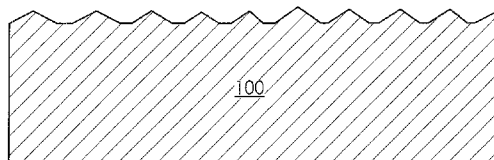
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(54) **Title:** NON FIRE-THROUGH ALUMINUM CONDUCTOR REFLECTOR PASTE FOR BACK SURFACE PASSIVATED CELLS WITH LASER FIRED CONTACTS

**FIG. 1**

(57) **Abstract:** This invention relates an aluminum (Al) conductor paste formulation and its method of application on rear side passivated locally laser fired contacts (LFC). Such Back Surface Passivated (BSP) Si-solar cells include aluminum conductor paste formulations and methods of application on rear side passivated locally opened vias; dot or line geometry or combination thereof employing laser ablation or chemical etching methods. Such Back Surface Passivated Si- solar cells include dielectric layers of Al_2O_3 , SiN_x , SiO_2 , SiC , α -Si, SiO_2/SiN_x , Al_2O_3/SiN_x , SiO_2Al_2/SiN_x . The Al-conductor paste of this invention achieves; (i) non-degradation of passivation stack, (ii) defect free surfaces and void free vias, (iii) a strong and uniform Back Surface Field (BSF) layer within dot vias and line vias.



NON FIRE-THROUGH ALUMINUM CONDUCTOR REFLECTOR PASTE FOR BACK SURFACE PASSIVATED CELLS WITH LASER FIRED CONTACTS

TECHNICAL FIELD

[0001] The subject disclosure generally relates to paste compositions, methods of making a paste composition, photovoltaic cells, and methods of making a photovoltaic cell contact.

BACKGROUND

[0002] Solar cells are generally made of semiconductor materials, such as Silicon (Si), Cadmium Telluride (CdTe), Copper Indium Gallium Selenium (CIGSe) etc. which convert sunlight into useful electrical energy using the photoelectric effect. Si solar cells are typically made of wafers of Si in which the required PN junction is formed by diffusing phosphorus (P) from a suitable phosphorus source into a P-type Si wafer. The side of silicon wafer on which sunlight is incident is in general coated with a silicon nitride layer as an anti-reflective coating (ARC) with excellent surface and bulk passivation properties to prevent reflective loss of incoming sunlight and recombination loss, respectively and thus to increase the efficiency of the solar cell. A two dimensional electrode grid pattern known as a front contact makes a connection to the N-side of silicon, and a coating of aluminum (Al) on the other side (back contact) makes connection to the P-side of the silicon. These contacts are the electrical outlets from the PN junction to the outside load.

[0003] Front and back contacts of silicon solar cells are typically formed by screen-printing a thick film conductor paste. Typically, the front contact paste contains fine silver particles, glass particles, and an organic vehicle. After screen-printing, the wafer and paste are fired in air, typically at infra-red (IR) furnace peak set temperatures of about 650 –1000°C. During the firing, glass softens, melts, reacts and etches the anti-reflective coating, and facilitates the formation of intimate silicon-silver contact. Silver deposits on silicon as islands. The shape, size, number and distribution of silicon-silver islands determine the efficiency of photo-generated electron transfer from silicon to the outside circuit.

[0004] Conventional Si-solar cell design includes full Al metallization on the back surface of silicon wafer which is fired along with the front contact silver paste (“co-fired”) in a furnace set at 600–1000 °C, with 120–300 inch per minute (ipm) belt speeds. This generally causes melting of Al, Al–Si reaction and formation of eutectic layer and a back surface field (BSF)

layer, contributing to high open-circuit voltage (V_{oc}), high short-circuit current (I_{sc}) and high cell efficiency (η). The BSF formed provides a reasonable back surface passivation and acts as an optical and electrical reflection layer. One drawback of this technology is that the BSF formed is not uniform across the entire back wafer surface and its layer thickness, and extent of Al doping is a function of the paste chemistry, nature of silicon wafer (single or poly crystal), type of surface texture, wafer thickness and size, and firing conditions, among other factors. Moreover, due to co-firing of the front silver and back Al pastes, the firing conditions are more dictated by the front silver composition and the wafer properties (such as total phosphorus concentration phosphorus doping profile, etc.) as measured by sheet resistivity and pn junction depth rather than the back Al paste. This produces considerable variability in electrical performance which has direct impact on V_{oc} , I_{sc} and the cell efficiency. Furthermore, full Al paste printing with a strong reaction with Si surface causes wafer warpage (bow), thus, limiting the use of thinner wafers and increases in the solar module manufacturing yield losses.

[0005] In conventional Si solar cells with no back surface dielectric passivation, Al conductor paste is applied on back surface (P- side) of crystalline silicon solar wafer, which on firing, forms Al-Si eutectic alloy along with Back Surface Field (BSF) that gives good electrical performance. The BSF layer provides good Ohmic contacts, reasonable passivation on the back side of the cell and optical and electronic reflection, thus enhancing open circuit voltage (V_{oc}) and short circuit current (I_{sc}), determine the efficiency of cells.

SUMMARY

[0006] In the interest of improving energy conversion efficiency, a process scheme that incorporates a high quality back surface passivation and provides a good optical confinement is needed, especially if the cell thickness is reduced. In advanced cell designs, the back surface passivation is provided by a dielectric stack which can include any or all of Al_2O_3 , SiN_x , SiO_2/SiN_x , SiC , α -Si, Al_2O_3/SiN_x or $SiO_2/Al_2O_3/SiN_x$ having an overall thickness in the range of 5–360 nm range. The advantages of rear side passivation are twofold: (i) the passivation dielectric layer reduces the surface recombination of minority carriers at the rear surface, and (ii) the presence of a dielectric layer enhances the internal reflectivity at the rear surface while preventing the absorption diminution of infrared energy photons due to bulk thickness reduction. Therefore, rear passivated solar cells exhibit higher open circuit voltages (V_{oc}) and short circuit

currents (I_{sc}) resulting in higher conversion efficiencies in comparison to back unpassivated conventional Si-solar cells.

[0007] A passivated rear surface requires patterned (local) contacts to silicon through the dielectric film. Two different techniques can be employed for the fabrication of rear point contacts. One approach is full area screen printing of aluminum paste on the passivation layer followed by laser firing through the dielectric layer to form a local contact. The other method is to locally open the passivation layer followed by full area screen printing of aluminum paste and subsequent thermal (furnace heated) alloying to form contacts. In both cases the intact region of the passivation layer protects the silicon surface and maintains the passivation quality. During these processes, underneath the alloyed local contact points, a thin aluminum doped silicon layer known as local back surface field (Al-BSF) is formed. This Al-BSF layer repels the minority carriers reducing the surface recombination. There are several important factors which affect the formation of robust local contacts. The nature of the passivation film stack, the geometry of the local contact pattern, the chemical composition of the aluminum paste and the firing parameters of the alloying process all strongly contribute to forming robust local contact. For a given dielectric passivation film stack with fixed contact pattern and firing profile, the extent of robust local contacts formation substantially varies from one paste formulation to another. In formulating a screen printable aluminum paste for rear local contact application several factors should be taken into consideration. The paste should have a low contact resistance to silicon and a low bulk resistivity to allow for the cell to function in a soldered string with minimum series resistance losses. Also, the fired paste must strongly bond to the passivation dielectric layer without reacting with passivation (non fire-through) so that the integrity of the passivation quality is maintained after contact formation. Furthermore, paste composition should be such that it should be able to reflect infrared energy photons back to the wafer, to form a sufficiently thick and uniform BSF layer over a range of contact sizes with different furnace/laser firing conditions. The V_{oc} of the cells is strongly related to Fermi level position to both edges of the solar cells. On the back side of the cell its position is related to the surface passivation and the back surface field (BSF) presence. This invention describes paste formulations for back surface passivated cells with local contacts made by laser firing process and method of application of this paste in order to achieve this goal.

[0008] The following presents a simplified summary of the invention in order to provide a basic understanding of some aspects of the invention. This summary is not an extensive overview of the invention. It is intended to neither identify key or critical elements of the invention nor delineate the scope of the invention. Its sole purpose is to present some concepts of the invention in a simplified form as a prelude to the more detailed description that follows.

[0009] In accordance with one aspect, a paste composition is provided. More particularly, in accordance with this aspect, the paste composition includes one or more conductive metal components, a glass component, and a vehicle. The paste may further include organic and/or inorganic additives.

[0010] In accordance with another aspect, a photovoltaic cell structure is provided. More particularly, in accordance with this aspect, the photovoltaic cell includes a silicon wafer and a back contact thereon, the back contact including locally opened dielectric passivation stack fully coated with a back side Al paste. The back side paste includes, prior to firing, one or more conductive metal components, one or more glass frits, organic and inorganic additives, and vehicles.

[0011] In accordance with yet another aspect, a method of making a paste composition is provided. More particularly, in accordance with this aspect, the method involves mixing and dispersing a conductive metal components, non-leaded glass frits, organic or inorganic additives, and vehicle.

[0012] In accordance with still yet another aspect, a method of forming a photovoltaic cell contact is provided. More particularly, in accordance with this aspect, the method involves providing a silicon substrate, dielectric passivation stack, applying Al paste composition on the full passivation layer, the paste including a conductive metal components, one or more glass frits, organic and inorganic additives, and vehicles; and heating the paste locally by laser to sinter the conductive metal component and fuse the glass. The conductive metal component forming a strong and uniform local BSF by reacting with silicon substrate within locally heated areas, thereby electrically contacting the silicon substrate. The paste provides; adequate fired adhesion on passivation layer upon co-firing without damaging the superior passivation properties.

[0013] In another aspect, the invention provides a method of making a solar cell contact, comprising, (a) providing a p-type silicon wafer having at least two sides wherein a first (front) side is texturized, (b) depositing a phosphorus compound on the texturized side to form an

emitter, (c) depositing a passivation layer on at least a second (back) side of the silicon wafer, (d) applying an antireflective/passivation surface to both sides of the silicon wafer, (e) applying a back side tabbing Ag or Ag/Al paste to at least a portion of the passivation layer, (f) applying a back Al paste of this invention to the back passivation layer to cover at least a some portion of the back side tabbing Ag or Ag/ Al paste, (g) applying a front paste to at least a portion of the antireflection coating on the first side, (h) firing the silicon wafer such that the pastes sinter where front Ag makes contact to silicon while reacting with antireflective coatings, and (i) firing a laser upon at least a portion of the back side paste to drive Al metal through the passivation layer and into the silicon wafer.

[0014] To the accomplishment of the foregoing and related ends, the invention, then, involves the features hereinafter fully described and particularly pointed out in the claims. The following description and the annexed drawings set forth in detail certain illustrative embodiments of the invention. These embodiments are indicative, however, of but a few of the various ways in which the principles of the invention can be employed. Other objects, advantages and novel features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Figs. 1-7 provide a process flow diagram schematically illustrating the fabrication of a semiconductor solar device. Reference numerals shown in Figs. 1-7 are explained below.

[0016] 100: p-type silicon substrate

[0017] 200: n-type diffusion layer on texturized substrate

[0018] 300: back side passivation layer (*e.g.*, AlO_x, TiO₂, SiO₂, SiC, α -Si or combinations)

[0019] 400: front side passivation/anti-reflection layer (*e.g.*, SiN_x, TiO₂, SiO₂ film)

[0020] 402: back side passivation/capping layer (*e.g.*, SiN_x film)

[0021] 500: silver or silver/aluminum back paste formed on backside

[0022] 502: non fire-through reflector aluminum back paste formed on backside

[0023] 504: silver paste formed on front side

[0024] 600: silver or silver/aluminum back electrode (obtained by firing silver or silver/aluminum back paste)

[0025] 602: non fire-through reflector aluminum back electrode after firing

[0026] 604: silver front electrode after firing through ARC

[0027] 700: local p+ layer (back surface field (BSF)) by laser firing

DETAILED DESCRIPTION

[0028] In the Back Surface Passivated (BSP) cells with laser fired contacts, the silicon passivation function of the full layer Al BSF is performed by the dielectric stack layers that include SiNx, SiO₂, Al₂O₃, SiC, α -Si, SiO₂/SiNx, Al₂O₃/SiNx, SiO₂/Al₂O₃/SiNx etc., that have a thickness of 5–360 nm. More recently, single dielectric layer of ALD (atomic layer deposited) Al₂O₃ of 5–60 nm thickness has also shown to be an effective in back passivation compared to the stack of SiO₂/SiNx or Al₂O₃/SiNx. In order to derive the benefit of superior back passivation from these advanced cell designs, electrical local contact is necessary on the back surface since the alloying of Al and Si is prevented by the presence of the dielectric layer(s). One effective method of making this contact is to apply an Al paste to the entire wafer surface, during co-firing steps, without chemically etching or degrading the dielectric stack, i.e., non fire-through, to make laser fired local contacts of various diameter and pitch in the dielectric stack, to provide better reflectivity of photons, and to form a uniform and strong local Back Surface Field (BSF). In this invention, we describe an Al paste that can achieve this goal. The paste needs to have adequate fired adhesion on above-mentioned passivation layer, to provide better reflectivity of photons (higher J_{sc}), and to form good local BSF with perfections (higher Voc). The current invention describes such an inventive paste and its method of application in BSP cells with locally contacts by laser heating.

[0029] The subject invention can overcome the shortcomings of the conventional methods of making the back contacts. The subject invention generally relates to paste compositions, photovoltaic cells including fired paste compositions, methods of making a paste composition, methods of making a photovoltaic cell. The paste compositions can be used to form a contact to solar cells and, other related components. The subject invention can provide one or more of the following advantages: (1) photovoltaic cells with an excellent back passivation due to dielectric layer AlO_x, SiO₂, SiC, α -Si, SiNx, SiO₂/SiNx, AlO_x/SiO₂/SiNx; (2) novelty of Al paste that does not degrade the passivation (non fire-through) thus, but forms good bonds with the SiNx layer (good fired adhesion), leaves the passivation of dielectric effective; (3) the reflector property of the passivation dielectric layer is further enhanced by having this reflector Al paste on top of the

dielectric layer; (4) BSF formation and/or Al-Si eutectic formation is uniform and fully developed within the laser heating zone; and therefore (5) there are no wide variations in the efficiency of cells achieved.

[0030] The paste composition can include one or more conductive metal components, one or more glass frits, organic and inorganic additives, and vehicles. Metals of interest include Boron, Gallium, Indium, Titanium and combination thereof, which may be obtained from O M Group, Cleveland, Ohio. Non-limiting examples include: Borate esters such as trimethyl borate, triethylborate, (Borosilica Film) (C_xH_yO , $x=1-9$, $Y=2x+1$) and Alkoxides of Titanium (Ti-Ethoxides, Ti propoxides, Ti butoxides, Ti pentoxides, Ti aryloxides etc.), Alkoxides of Zirconia etc. Paste can include Organo metallic compounds such as but not limited to Ni, Co, Zn and V. For example, metal carboxylates such as Ni-Hex Cem, Cur-Rex etc., acetates of Cu, Ni etc.

[0031] The paste composition should have a low contact resistance to silicon and a low bulk resistivity to allow for the cell to function in a soldered string with minimum series resistance losses. Also, the paste must strongly adhere to the passivation dielectric layer so that the integrity of the passivation quality is maintained after contact formation. Furthermore, paste composition should be such that it should enable to form robust contacts with sufficiently thick BSF layer over a range of contact sizes with different laser firing conditions. The dielectric passivation can include any or all of SiN_x , Al_2O_3 , SiO_2 , SiC , α -Si, TiO_2 , Al_2O_3/SiN_x , or $SiO_2/Al_2O_3/SiN_x$ etc. deposited using various methods such as plasma enhanced chemically vapor deposition (PECVD), plasma assisted atomic layer deposition (ALD), induced coupled plasma deposition (ICPD), thermal oxidation etc. The SiN_x dielectric layer is usually made by a CVD process that allows for very uniform conformal coating, that enables good reflector properties. The SiN_x layer also contains some H content (since SiN_x is made from reaction of silane (SiH_4) and NH_3) which diffuse into bulk silicon during firing and passivates defects.

[0032] Paste formulations are generally screen printable and suitable for use in photovoltaic devices. However, other application procedures can be used such as spraying, hot melt printing, pad printing, ink-jet printing, and tape lamination techniques with suitable modifications of the vehicle component.

[0033] The pastes herein can be used to form conductors in applications other than solar cells, and employing other substrates, such as, for example, glass, ceramics, enamels, alumina, and metal core substrates. For example, the paste is used in devices including MCS heaters, LED

lighting, thick film hybrids, fuel cell systems, automotive electronics, and automotive windshield busbars.

[0034] The pastes can be prepared either by mixing individual components (*i.e.*, metals, glass frits, organic/inorganic compounds, and vehicles) or by blending pastes that are Al based (major component) with organic/inorganic additives that achieve the desired objectives. Broadly construed, the inventive pastes include a conductive metal including at least aluminum, glass, organic/inorganic additives, and a vehicle. Each ingredient is detailed hereinbelow.

[0035] **Metal Component.** The conductive metal component can include aluminum. In one embodiment, the major metal component of the paste is aluminum. Aluminum is used because it forms a low contact resistance p⁺/p surface on p-type silicon and provides a BSF for enhancing solar cell performance. In one embodiment, the backside pastes of the invention include about 40 to about 80 wt% aluminum, preferably about 60 to about 80 wt% aluminum and more preferably about 65 to about 75 wt% aluminum. The conductive metal component can include aluminum alloys, aluminum silicon alloys and mixtures of aluminum metal and aluminum alloys.

[0036] The paste can also include other metals and/or alloys to preserve the dielectric passivation layer. The other metals and alloys can include any suitable conductive metal(s) other than aluminum. In one embodiment, the other metals and/or alloying elements can be at least one other metal selected from the group consisting of sixteen elements: palladium, silver, platinum, gold, boron, gallium, indium, zinc, tin, antimony, magnesium, potassium, titanium, vanadium, nickel, and copper.

[0037] The conductive metal component can include the other metals or alloys at any suitable amount so long as the other metals or alloys can aid in achieving optimum bulk resistivity and contact to silicon without affecting the passivation layer. In one embodiment, the conductive metal component includes about 0.1 to about 50 wt % the other metals or alloys. In another embodiment, the metal component includes about 0.5 to about 50 wt%, 1 to about 25 wt%, more preferably about 2 to about 10 wt% of silver. In yet another embodiment, the metal component includes about 3 to about 50 wt%, preferably about 3 to about 15 wt%, more preferably about 3 to about 10 wt% copper. In still yet another embodiment, the metal component includes about 1 to about 50 wt%, preferably about 5 to about 25 wt%, and more preferably about 5 to about 15 wt% nickel. Contacts and solar cells including the above metals are envisioned herein.

[0038] The conductive metal component can have any suitable form. The particles of the conductive metal component can be spherical, flaked, colloidal, amorphous, or combinations thereof. In one embodiment, the conductive metal component can be coated with various materials such as phosphorus. Alternately, the conductive metal component can be coated on glass.

[0039] The conductive metal component can have any suitable size particle. Generally, the sizes of the conductive metal component particles are about 0.1 to about 40 microns, preferably about 0.1 to about 10 microns, given as D₅₀ particle sizes. In one embodiment, the Al particles are generally about 2 to about 20 microns, preferably, about 3 to about 10 microns. In another embodiment, the other metal particles are about 2 to about 20 microns, more preferably about 2 to about 8 microns. In yet another embodiment, the metal particle sizes are in line with the sizes of aluminum and silver particles herein, in a back contact. In still yet another embodiment, Al and other metals/alloys have 99+% purity.

[0040] In one embodiment, the metal component include about 80 to about 99 wt% spherical metal particles or alternatively about 35 to about 70 wt% metal particles and about 29 to about 55 wt% metal flakes. In another embodiment, the metal component includes about 75 to about 90 wt% metal flakes and about 5 to about 9 wt% of colloidal metal, or about 60 to about 95 wt % of metal powder or flakes and about 4 to about 20 wt % of colloidal metal. The foregoing combinations of particles, flakes, and colloidal forms of the foregoing metals are not intended to be limiting, where one skilled in the art would know that other combinations are possible.

Suitable commercial examples of aluminum particles are available from Alcoa, Inc., Pittsburgh, PA; Ampal Inc., Flemington, NJ; and ECKA Granulate GmbH & Co. KG, of Fürth, Germany.

[0041] In one embodiment, the metal component includes (as an alloying element or as an additive) other conductive metals from groups such as (a) palladium, silver, platinum, gold, and combinations thereof (highly conductive or electrical conduction modifier); (b) boron, gallium, indium, and combinations thereof (trivalent dopants for P type silicon); (c) zinc, tin, antimony, and combinations thereof (low melting metals); and (d) magnesium, titanium, potassium, vanadium, nickel, copper, and combinations thereof (grain modifiers/refiners). Mixtures of the sixteen metals can also be used for the pastes, contacts, and solar cells herein.

[0042] In one embodiment, the conductive metal may further includes up to 20 wt% of at least one selected from the group consisting of an Al-Si eutectic, zinc, tin, antimony, silicon, bismuth,

indium, molybdenum, palladium, silver, platinum, gold, titanium, vanadium, nickel, copper, and combinations thereof.

[0043] In one embodiment, a minimum of one organometallic component is used in the paste formulation. The organic and organometallic compounds may include boron, gallium, indium, titanium, nickel, cobalt, zinc and vanadium and combination thereof. Examples: Borate esters such as trimethyl borate, triethylborate, (Borosilica Film) (C_xH_yO , $x=1-9$, $Y=2x+1$) and alkoxides of titanium such as Ti-ethoxides, Ti-propoxides, Ti-butoxides, Ti- pentoxides, Ti-aryloxides; alkoxides of zirconia etc. Metal carboxylates such as Hex-Cem and Cur-Rex are suitable as well as acetates of any named metal, especially Cu, Ni, V, and Zn.

[0044] Suitable organometallics include HEX-CEM® (Octoates) from OM Group, Inc., Cleveland, Ohio. Other Hex Cem products include Cobalt Hex-Cem®; Calcium Hex-Cem®; Potassium Hex-Cem®; Manganese Hex-Cem®; Rare Earth Hex-Cem®; Zinc Hex-Cem®; Zirconium Hex-Cem®; Strontium Hex-Cem®. Also suitable are TEN-CEM® Driers which are neodecanoates or versatates. Suitable Ten-Cem products include: Cobalt Ten-Cem®; Calcium Ten-Cem®; Manganese Ten-Cem®; Rare Earth Ten-Cem®; Lithium Ten-Cem®. Also suitable are CEM-ALL®, synthetic acid metal carboxylates such as Cobalt Cem-All®; Calcium Cem-All®; Manganese Cem-All®; Manganese Cem-All® Light-Color; Lead Cem-All®; Zinc Cem-All®; NAP-ALL® Driers (Naphthenates) such as Cobalt Nap-All®; Calcium Nap-All®; Manganese Nap-All®; Zinc Nap-All and Lead Nap-All®.

[0045] Inorganic Oxide Component. In one embodiment, the inorganic oxide components can be provided in the form of a oxide of the following elements: silicon, palladium, silver, boron, gallium, indium, zinc, tin, antimony, magnesium, potassium, titanium, vanadium, nickel, and copper. Ionic salts, such as halides, carbonates, hydroxides, phosphates, nitrates, sulfates, and sulfites, of the metal of interest which upon decomposition provide oxide of the metal can be also used.

[0046] Organometallic Component. Organometallic compounds of the following elements: boron, titanium, nickel, vanadium, silicon, zinc, tin, antimony, magnesium, potassium, vanadium, nickel, and copper. Organometallic compounds of any of the metals can be used, including acetates, formates, carboxylates, phthalates, isophthalates, terephthalates, fumarates, salicylates, tartrates, gluconates, or chelates such as those with ethylenediamine or

ethylenediamine tetraacetic acid (EDTA). The organometallic component of the paste may include ethoxides of silicon, boron and titania, and/or the acetonates of nickel and vanadium.

[0047] Paste Glasses. The glass can contain one or more suitable glass frits, for example, 2, 3, 4, or more distinct frit compositions. In one embodiment, the glass used herein is zinc alkali borosilicate glasses. As an initial matter, the glass frits used in the pastes herein can intentionally contain lead and/or cadmium, or they can be devoid of intentionally added lead and/or cadmium. In one embodiment, the glass component comprises substantially to completely lead-free and cadmium-free glass frits as shown in Table 1. The glasses can be partially crystallizing or non-crystallizing. In one embodiment partially crystallizing glasses are preferred. Broad categories of suitable glasses include bismuth, bismuth-zinc; zinc, borosilicate, alkali borosilicate, alkali titanate, and leaded-glasses. The details of the composition and manufacture of the glass frits can be found in, for example, commonly-assigned U.S. Patent Application Publication Nos. 2006/0289055 and 2007/0215202, which are hereby incorporated by reference. In all glass tables, a glass composition may be assembled by taking oxide amounts from different columns within a table. In all ranges bounded by zero at the lower end, an alternate disclosed embodiment is the same range having a lower bound of 0.1.

[0048] Table 1. Alkali silicate glasses in mole percent of glass component.

Oxide (mole %)	1-1	1-2	1-3	1-4	1-5	1-6
ZnO	0-65	5-65	7-50	10-32	0-40	0-10
B ₂ O ₃ + Al ₂ O ₃	0-55	5-55	7-40	10-25	0-25	0-10
SiO ₂	0.5-65	10-50	10-45	10-30	15-55	10-40
Li ₂ O+Na ₂ O+K ₂ O +Rb ₂ O+Cs ₂ O	0.5-45	0.5-40	5-33	10-20	15-42	15-39
TiO ₂ +ZrO ₂	0-25	0.5-25	1-20	2-15	5-25	7-22
V ₂ O ₅ +Ta ₂ O ₅ +Sb ₂ O ₅ +P ₂ O ₅	0-20	1-15	0-15	0-10	0-15	1-9
MgO+CaO+BaO+SrO	0-20	0-15	0-13	0-10	1-10	0-10
TeO ₂ +Tl ₂ O+GeO ₂	0-40	0-25	0-20	0-10	0-10	0-10
F	0-25	0-20	1-10	1-15	0-10	0-8

[0049] In one embodiment, the glass component includes, prior to firing, Zn glasses. Table 2 below shows some exemplary Zn glasses, both Zn-B, and Zn-B-Si glasses. The oxide constituent amounts for an embodiment need not be limited to those in a single column such as 2-1 to 2-6 and can be chosen from different columns in the table.

[0050] Table 2. Zn glasses in mole percent of glass component.

Oxide (mole %)	2-1	2-2	2-3	2-4	2-5	2-6
ZnO	5-65	5-65	7-50	10-32	6-18	5-14
SiO ₂	0-65	10-65	20-60	22-58	35-58	41-66
B ₂ O ₃ + Al ₂ O ₃	5-55	5-55	7-35	10-25	11-20	7.5-19.4
Li ₂ O+Na ₂ O+K ₂ O +Rb ₂ O+Cs ₂ O	0-45	0-45	2-25	1-20	11-20	11-23
MgO+CaO+BaO+SrO	0-20	0-20	0-15	0-10	0.1-5	0-5
TiO ₂ +ZrO ₂	0-25	0-25	0-15	0.5-15	0-10	0-10
V ₂ O ₅ +Ta ₂ O ₅ +Sb ₂ O ₅ +P ₂ O ₅	0-20	0-15	0-10	0-5	0.05-3	0.01-5
TeO ₂ +Tl ₂ O+GeO ₂	0-40	0-30	0-20	0-20	0-5	0-5
F	0-25	0-20	0-15	0-8	0.1-6	1-10

[0051] In still yet another embodiment, the glass component includes, prior to firing, alkali-B-Si glasses. Table 3 below shows some exemplary alkali-B-Si glasses. The oxide constituent amounts for an embodiment need not be limited to those in a single column such as 3-1 to 3-5.

[0052] Table 3. Alkali-B-Si glasses in mole percent of glass component.

Ingredient (mole %)	3-1	3-2	3-3	3-4	3-5
Li ₂ O + Na ₂ O + K ₂ O	5-55	15-50	30-40	15-50	30-40
TiO ₂ +ZrO ₂	0.5-30	0.5-20	0.5-15	1-10	1-5
B ₂ O ₃ + SiO ₂	5-75	25-70	30-52	25-70	30-52
V ₂ O ₅ + Sb ₂ O ₅ + P ₂ O ₅ +Ta ₂ O ₅	0-30	0.25-25	5-25	0.25-25	5-25
MgO + CaO + BaO + SrO	0-20	0-15	0-10	0-15	0-10
TeO ₂ +Tl ₂ O+GeO ₂	0-40	0-30	0.05-20	0-20	0-5
F	0-20	0-15	5-13	0-15	5-13

[0053] In one embodiment, the glass component includes, prior to firing, Bi-Zn-B glasses. Table 4 below shows some exemplary Bi-Zn-B glasses. The oxide constituent amounts for an embodiment need not be limited to those in a single column such as 4-1 to 4-5.

[0054] Table 4. Bi-Zn-B glasses in mole percent of glass component.

Oxide (mole %)	4-1	4-2	4-3	4-4	4-5
Bi ₂ O ₃	25-65	30-60	32-55	35-50	37-45
ZnO	3-60	10-50	15-45	20-40	30-40
B ₂ O ₃	4-65	7-60	10-50	15-40	18-35

[0055] In another embodiment, the glass component includes, prior to firing, Bi-B-Si glasses. Table 5 below shows some exemplary Bi-B-Si glasses. The oxide constituent amounts for an embodiment need not be limited to those in a single column such as 5-1 to 5-5.

[0056] Table 5. Bi-B-Si glasses in mole percent of glass component.

Oxide (mole %)	5-1	5-2	5-3	5-4	5-5
Bi ₂ O ₃	25-65	30-60	32-55	35-50	37-45
B ₂ O ₃	4-65	7-60	10-50	15-40	18-35
SiO ₂	5-35	5-30	5-25	5-20	5-15

[0057] In another embodiment, the glass component includes, prior to firing, Bi-Si-V/Zn glasses. Table 6 below shows some exemplary Bi-Si-V/Zn glasses. The oxide constituent amounts for an embodiment need not be limited to those in a single column such as 6-1 to 6-5.

[0058] Table 6. Bi glasses in mole percent of glass component.

Oxide (mole %)	6-1	6-2	6-3	6-4	6-5	6-6	6-7	6-8
Bi ₂ O ₃	5-85	15-80	20-80	30-80	40-80	30-42	39-52	0-21
B ₂ O ₃ + SiO ₂	5-35	5-30	5-25	5-20	5-15	27-48	17-24	41-62
ZnO	0-55	0-40	0.1-25	1-20	1-15	0-38	25-39	0-17
V ₂ O ₅	0-55	0.1-40	0.1-25	1-20	1-15	0-5	0-12	0-12
Li ₂ O+Na ₂ O+K ₂ O+ Rb ₂ O+ Cs ₂ O	0-8	0-7	0-11	0-12	14-24	14-24	1-7	1-7
MgO+CaO+BaO+SrO	0-12	0-9	0-13	0-5	0-13	0-9	0-8	26-49

[0059] In yet another embodiment, the glass component includes, prior to firing, Pb-Al-B-Si glasses. Table 7 below shows some exemplary Pb-Al-B-Si glasses. The oxide constituent amounts for an embodiment need not be limited to those in a single column such as 7-1 to 7-12.

[0060] Table 7. Pb glasses in mole percent of glass component.

Oxide (mole %)	7-1	7-2	7-3	7-4	7-5	7-6
PbO	15-75	25-72	40-70	50-70	60-70	55-80
B ₂ O ₃ + SiO ₂	5-38	20-38	20-38	5-30	5-15	4-13
Al ₂ O ₃	0-25	0.1-23	1-10	4-19	15-23	11-22
ZnO	0-35	5-30	1-10	5-10	0-5	0-5
TiO ₂ +ZrO ₂ +HfO ₂	0-20	0-10	0.1-3	0.1-3	0.1-3	0.1-3
V ₂ O ₅ +Sb ₂ O ₅ +P ₂ O ₅ +Ta ₂ O ₅ +Nb ₂ O ₅	0-25	0.05-5	0-5	0-15	0.1-5	0-5
MgO+CaO+BaO+SrO	0-20	0-15	0-10	0-10	0-8	0-7
Li ₂ O+Na ₂ O+K ₂ O+Rb ₂ O+ Cs ₂ O	0-40	0-30	0-20	0-10	0-10	0-8
TeO ₂ +Tl ₂ O+GeO ₂	0-70	0-50	0-40	0-30	0-20	0-10
F	0-15	0-10	0-8	0-8	0-6	0-6

[0061] Table 7a. Further Pb glasses.

Oxide (mole %)	7-7	7-8	7-9	7-10	7-11	7-12
PbO	57-77	59-71	24-38	27-36	25.5-37	28-35
B ₂ O ₃ + SiO ₂	5-11	6-10	21-37	22.3-33.9	22-35	23.9-33.2
Al ₂ O ₃	13-20	14-19	5-12	6.1-10.7	5.7-11.3	6.2-10.8
ZnO	0-25	0-31	0-17	0-13	24-36	25.2-34.7
TiO ₂ +ZrO ₂ +HfO ₂	0.5-2.2	0.7-1.9	0-3	0-8	0.1-3	0.1-3
V ₂ O ₅ +Sb ₂ O ₅ +P ₂ O ₅ +Ta ₂ O ₅ +Nb ₂ O ₅	0.8-4	1-3.5	0.1-3	0.3-2.5	0.4-2.8	0.6-2.5
MgO+CaO+BaO+SrO	0-7	0-15	0-10	0-10	0-8	0-7
Li ₂ O+Na ₂ O+K ₂ O+Rb ₂ O+ Cs ₂ O	0-6	0-30	0-20	0-10	0-10	0-8

TeO ₂ +Ti ₂ O+GeO ₂	0-70	0-50	0-40	0-30	0-20	0-10
F	0-5	0-10	0-8	0-8	0-6	0-6

[0062] Table 7b. Further Pb Glasses.

Oxide (mole %)	7-13	7-14	7-15	7-16	7-17
PbO	1-90	10-70	20-50	20-40	25-65
V ₂ O ₅	1-90	10-70	25-65	45-65	20-50
P ₂ O ₅	5-80	5-80	5-40	5-25	5-40

[0063] It is also envisioned that glass component can contain additions of predominantly vanadate glasses, phosphate glasses, telluride glasses and germanate glasses to impart specific electrical and reactivity characteristics to the resultant contacts.

[0064] It is also envisioned that glass frits of Tables 1 to 7 can contain one or more transition metal oxide, wherein the metal of the transition metal oxide is selected from the group consisting of Mn, Fe, Co, Ni, Cu, Cr, W, Nb, Ta, Hf, Mo, Rh, Ru, Pd and Pt, to provide specific adhesion and/or electrical and /or flow properties to the glass component.

[0065] The glass frits can be formed by any suitable techniques. In one embodiment, the glass frits are formed by blending the starting materials (*e.g.*, aforementioned oxides) and melting together at a temperature of about 800 to about 1450 °C for about 40 to 60 minutes to form a molten glass having the desired composition. Depending on the raw materials used, amount of glass being melted, and the type of furnace used these ranges will vary. The molten glass formed can then be suddenly cooled by any suitable technique including water quenching to form a frit. The frit can then be ground using, for example, milling techniques to a fine particle size, from about 0.1 to 25 microns, preferably 0.1 to about 20 microns, more preferably 0.2-10 microns, still more preferably 0.4-3.0 microns, most preferably less than 1.3 microns. It is envisioned that the finer particle sizes such as mean particle size less than 1.2 micron and more preferably less than 1.0 micron, and most preferably less than 0.8 micron are the preferred embodiments for this invention. Alternately the mean particle size can preferably be 1 to about 10 microns, alternatively 2 to about 8 microns, and more preferably 2 to about 6 microns. All particle sizes noted herein are the D₅₀ particle size.

[0066] It is also envisioned that the glass component can contain multiple glass frits with different mean particle sizes, each as defined elsewhere herein, and in particular in the preceding paragraph.

[0067] The glass frits can have any suitable softening temperature. In one embodiment, the glass frits have glass softening temperatures of about 650 °C or less. In another embodiment, the glass frits have glass softening temperature of about 550 °C or less. In yet another embodiment, the glass frits have glass softening temperature of about 500 °C or less. The glass softening point may be as low as 450 °C.

[0068] The glass frits can have suitable glass transition temperatures. In one embodiment, the glass transition temperatures range between about 250° C to about 600° C, preferably between about 300° C to about 500° C, and most preferably between about 300° C to about 475° C.

[0069] The paste composition can contain any suitable amount of the glass component. In one embodiment, the paste composition contains the glass component at about 0.5 wt % or more and about 15 wt % or less. In another embodiment, the paste composition contains the glass component at about 1 wt % or more and about 10 wt % or less. In yet another embodiment, the paste composition contains the glass component at about 2 wt % or more and about 7 wt % or less. In still yet another embodiment, the paste composition contains the glass component at about 2 wt % or more and about 6 wt % or less.

[0070] Although generally avoided for various reasons, substantial additions of Tl_2O or TeO_2 or GeO_2 can be present in these glass compositions to attain lower flow temperatures.

[0071] **Organometallic Compound.** The organometallic compounds useful herein in addition to the foregoing include organo-vanadium compounds, organo-antimony compounds, and organo-yttrium compounds. The organometallic compound is a compound where metal is bound to an organic moiety. For example, the organometallic compound is an organic compound containing metal, carbon, and/or nitrogen in the molecule. Further, in addition to the foregoing metal compounds, a second metal additive selected from the group consisting of an organo-cobalt compound, an organo-tin compound, an organo-zirconium compound, an organo-zinc compound and an organo-lithium compound may be included in the paste composition.

[0072] The organometallic compound can include any suitable organic moieties such as those that are $C_1 - C_{50}$ linear or branched, saturated or unsaturated, aliphatic, alicyclic, aromatic, araliphatic, halogenated or otherwise substituted, optionally having one or more heteroatoms

such as O, N, S, or Si, and/or including hydrocarbon moieties such as alkyl, alkyloxy, alkylthio, or alkylsilyl moieties.

[0073] Specific examples of organometallic compounds include metal alkoxides. The metal can be boron, silicon, vanadium, antimony, phosphorous, yttrium, titanium or combinations thereof. It is understood that some authorities consider boron and silicon be metalloids, while phosphorus is a non-metal. For the purposes of this document, and without any intention to attribute foreign properties to them, the term “organometallic” may at times be used to include organoboron compounds, organosilicon compounds and organophosphorus compounds. The alkoxide moiety can have a branched or unbranched alkyl group of, for example, 1 to 20 carbon atoms. The respective alkoxides envisioned herein include, nickel alkoxides, boron alkoxides, phosphorus alkoxides, silicon alkoxides, vanadium alkoxides, vanadyl alkoxides, antimony alkoxides, yttrium alkoxides, cobaltic alkoxides, cobaltous alkoxides, stannic alkoxides, stannous alkoxides, zirconium alkoxides, zinc alkoxides, titanium alkoxides and lithium alkoxides.

[0074] Examples of titanium alkoxides include titanium methoxide, titanium ethoxide, titanium propoxide, and titanium butoxide. Analogous examples can be envisioned for nickel alkoxides, boron alkoxides, phosphorus alkoxides, antimony alkoxides, yttrium alkoxides, cobaltic alkoxides, cobaltous alkoxides, nickel alkoxides, zirconium alkoxides, tin alkoxides, zinc alkoxides and lithium alkoxides can be used.

[0075] Other examples of organo-metal compounds include metal acetylacetonates, where the metal can be nickel, boron, phosphorus, vanadium, antimony, yttrium, or combinations thereof. Examples of organo-vanadium compounds include nickel acetylacetonates such as $\text{Ni}(\text{AcAc})_3$ (also called nickel (III) 2,4-pentanedionate) where (AcAc) is an acetyl acetate (also called 2,4-pentanedionate).

[0076] In the same way, antimony acetylacetonate, yttrium acetylacetonate, cobaltic acetylacetonate, cobaltous acetylacetonate, nickel acetylacetonate, zirconium acetylacetonate, dibutyltin acetylacetonate, zinc acetylacetonate and lithium acetylacetonate can be used. For example, antimony 2,4-pentanedionate, yttrium 2,4-pentanedionate, or combinations thereof can be used.

[0077] Yet other examples of organo-metal compounds include metal 2-methylhexanoates, metal 2-ethylhexanoates, and metal 2-propylhexanoates. Specific examples include boron 2-methylhexanoate, phosphorus 2-methylhexanoate, silicon 2-methylhexanoate, vanadium 2-

methylhexanoate, antimony 2-methylhexanoate, yttrium 2-methylhexanoate, cobalt 2-methylhexanoate, nickel 2-methylhexanoate, zirconium 2-methylhexanoate, tin 2-methylhexanoate, zinc 2-methylhexanoate lithium 2-methylhexanoate, boron 2-ethylhexanoate, phosphorus 2-ethylhexanoate, silicon 2-ethylhexanoate, vanadium 2-ethylhexanoate, antimony 2-ethylhexanoate, yttrium 2-ethylhexanoate, cobalt 2-ethylhexanoate, nickel 2-ethylhexanoate, zirconium 2-ethylhexanoate, tin 2-ethylhexanoate, zinc 2-ethylhexanoate, lithium 2-ethylhexanoate, vanadium 2-propylhexanoate, boron 2-propylhexanoate, phosphorus 2-propylhexanoate, silicon 2-propylhexanoate, antimony 2-propylhexanoate, yttrium 2-propylhexanoate, cobalt 2-propylhexanoate, nickel 2-propylhexanoate, zirconium 2-propylhexanoate, tin 2-propylhexanoate, zinc 2-propylhexanoate and lithium 2-propylhexanoate.

[0078] Yet other examples of organo-metal compounds include metal carboxylates, where the metal can be nickel, vanadium, zinc, or cobalt or combination thereof. Examples of organo-nickel or organo-vanadium compounds include nickel Hex-Cem or Cur-Rex. Suitable commercial examples of organo-metal compounds are available from OMG Group, Cleveland, and American Elements, USA.

[0079] Yet other examples of organo-metal compounds include metal acrylate and metal methacrylate, where the metal can be nickel, boron, phosphorus, vanadium, antimony, yttrium, cobalt, nickel, zirconium, tin, zinc or lithium. Acids including boron can be used also to introduce boron into the intermetallic, for example boric acid, H_3BO_3 ; 2-acetamidopyridine-5-boronic acid, 5-acetyl-2,2-dimethyl-1,3-dioxane-dione; 2-acetylphenylboronic acid; 3-acetylphenylboronic acid; 4-acetylphenylboronic acid; 3-aminocarbonylphenylboronic acid; 4-aminocarbonylphenylboronic acid, 3-amino-4-fluorophenylboronic acid; 4-amino-3-fluorophenylboronic acid, and others commercially available from Boron Molecular, Research Triangle, NC.

[0080] **Vehicle.** The pastes herein include a vehicle or carrier which is typically a solution of a resin dissolved in a solvent and, frequently, a solvent solution containing both resin and a thixotropic agent. The glass frits can be combined with the vehicle to form a printable paste composition. The vehicle can be selected on the basis of its end use application. In one embodiment, the vehicle adequately suspends the particulates and burn off easily upon firing of the paste on the substrate. Vehicles are typically organic. Examples of solvents used to make organic vehicles include alkyl ester alcohols, terpeneols, and dialkyl glycol ethers, pine oils,

vegetable oils, mineral oils, low molecular weight petroleum fractions, and the like. In another embodiment, surfactants and/or other film forming modifiers can also be included.

[0081] The amount and type of organic vehicles utilized are determined mainly by the final desired formulation viscosity, rheology, fineness of grind of the paste, substrate wettability and the desired wet print thickness. In one embodiment, the paste includes about 15 to about 40 wt% of the vehicle. In another embodiment, the paste includes about 20 to about 35 wt% of the vehicle.

[0082] The vehicle typically includes (a) up to 80 wt % organic solvent; (b) up to about 15 wt % of a thermoplastic resin; (c) up to about 4 wt % of a thixotropic agent; and (d) up to about 15 wt % of a wetting agent. The use of more than one solvent, resin, thixotrope, and/or wetting agent is also envisioned. Ethyl cellulose is a commonly used resin. However, resins such as ethyl hydroxyethyl cellulose, wood rosin, mixtures of ethyl cellulose and phenolic resins, polymethacrylates of lower alcohols and the monobutyl ether of ethylene glycol monoacetate can also be used. Solvents having boiling points (1 atm) from about 130°C to about 350°C are suitable. Widely used solvents include terpenes such as alpha- or beta-terpineol or higher boiling alcohols such as Dowanol® (diethylene glycol monoethyl ether), or mixtures thereof with other solvents such as butyl Carbitol® (diethylene glycol monobutyl ether); dibutyl Carbitol® (diethylene glycol dibutyl ether), butyl Carbitol® acetate (diethylene glycol monobutyl ether acetate), hexylene glycol, Texanol® (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), as well as other alcohol esters, kerosene, and dibutyl phthalate.

[0083] The vehicle can contain organometallic compounds, for example those based on aluminum, boron, zinc, vanadium, or cobalt, nickel, titanium and combinations thereof, to modify the contact. N-Diffusol® is a stabilized liquid preparation containing an n-type diffusant with a diffusion coefficient similar to that of elemental phosphorus. Various combinations of these and other solvents can be formulated to obtain the desired viscosity and volatility requirements for each application. Other dispersants, surfactants and rheology modifiers, which are commonly used in thick film paste formulations, can be included. Commercial examples of such products include those sold under any of the following trademarks: Texanol® (Eastman Chemical Company, Kingsport, TN); Dowanol® and Carbitol® (Dow Chemical Co., Midland, MI); Triton® (Union Carbide Division of Dow Chemical Co., Midland, MI), Thixatrol® (Elementis Company, Hightstown NJ), and Diffusol® (Transene Co. Inc., Danvers, MA).

[0084] Among commonly used organic thixotropic agents is hydrogenated castor oil and derivatives thereof. A thixotrope is not always necessary because the solvent coupled with the shear thinning inherent in any suspension can alone be suitable in this regard. Furthermore, wetting agents can be employed such as fatty acid esters, *e.g.*, N-tallow-1,3-diaminopropane di-oleate; N-tallow trimethylene diamine diacetate; N-coco trimethylene diamine, beta diamines; N-oleyl trimethylene diamine; N-tallow trimethylene diamine; N-tallow trimethylene diamine dioleate, and combinations thereof.

[0085] **Other Additives.** Other inorganic additives can be added to the paste to the extent of about 0.5 to about 30 wt%, preferably about 2 to about 25 wt% and more preferably about 5 to about 20 wt% based on the weight of the paste prior to firing. Other additives such as clays, fine silicon, silica, or carbon, or combinations thereof can be added to control the reactivity of the aluminum with silicon. Common clays which have been calcined are suitable. Fine particles of low melting metal additives (*i.e.*, elemental metallic additives as distinct from metal oxides) such as Pb, Bi, In, Zn, and Sb, and alloys of each can be added to provide a contact at a lower firing temperature, or to widen the firing window.

[0086] Other suitable additives include a mixture of (a) glasses or (b) crystalline additives and glasses or (c) one or more crystalline additives can be used to formulate a glass component in the desired compositional range. The goal is to improve the solar cell electrical performance. For example, second-phase crystalline ceramic materials such as SiO₂, ZnO, MgO, ZrO₂, TiO₂, Al₂O₃, Bi₂O₃, V₂O₅, MoO₃, WO₃, Co₂O₃, MnO, Sb₂O₃, SnO, Tl₂O, TeO₂, GeO₂ and In₂O₃, reaction products thereof and combinations thereof can be added to the glass component to adjust contact properties. Ceramic additives include particles such as hectorite, talc, kaolin, attapulgite, bentonite, smectite, quartz, mica, feldspar, albite, orthoclase, anorthite, silica, and combinations thereof. Both crystalline and amorphous silica are suitable.

[0087] **Paste Preparation.** To prepare the paste compositions of the invention, the necessary frit or frits are ground to a fine powder using conventional techniques including milling. In one embodiment, the glass is then mixed with organic components and paste (glass intermediate) can be prepared by three-roll milling. The frit component is then combined with the other components including aluminum. The solids are then mixed with the vehicle and the organic/inorganic additive compounds to form the paste. In other embodiment, the paste can be prepared by a planetary mixer.

[0088] The viscosity of the paste can be adjusted as desired. In preparing the paste compositions, the particulate inorganic solids and the phosphorus compound are mixed with a vehicle and dispersed with suitable equipment, such as a planetary mixer, to form a suspension, resulting in a composition for which the viscosity will be in the range of about 50-1000 Poise (5-100 Pa.s), preferably about 50-800 Poise (5-80 Pa.s), more preferably from 50 to about 600 poise (5 to 60 Pa.s), yet more preferably about 100-500 poise (10-50 Pa.s), more preferably 150-400 poise (1-40 Pa.s) at a shear rate of 9.6 sec^{-1} as determined on a Brookfield viscometer HBT, spindle 14, measured at 25°C. Generally, when the back contact is only partially covered with the paste, the viscosity should be higher.

[0089] Printing and Firing of the Pastes. The inventive method of making a solar cell back contact involves providing a silicon substrate and a passivation layer thereon, applying full area screen printing of non fire-through reflector aluminum paste composition on the passivation layer, subsequent furnace heating to form front contact, followed by laser firing to make local openings for alloying to form local back contact (BSF).

[0090] In particular, the local openings can be made by laser ablation or chemical etching to form dots or lines, wherein the dot diameter ranges from 20 - 200 microns and a trench is 100-700 microns wide, or the dot diameter ranges from 20-200 microns and a trench is 0.5-2.0 mm wide.

[0091] In one embodiment, the method further involves making an Ag or Ag/Al back contact by applying an Ag or Ag/Al back contact paste on the back surface of the silicon substrate and furnace heating the Ag or Ag/Al back contact paste. In another embodiment, the method further involves making an Ag front contact by applying an Ag front contact paste on the front surface of the silicon substrate and furnace heating the Ag front contact paste. The pastes can be applied by any suitable techniques including screen printing, ink jet printing, decal application, spraying, brushing, roller coating or the like. In one embodiment, screen printing is preferred. After application of the paste to a substrate the applied coating is then dried and furnace fired to adhere the paste to the substrate. The firing temperature is generally determined by the frit maturing temperature, and preferably is in a broad temperature range. In one embodiment, the solar cell printed with the subject Al back contact paste, the Ag back contact paste, and the Ag front contact paste can be simultaneously fired at a suitable temperature, such as about 650-1000°C furnace set temperature; or about 550-850°C wafer temperature. During firing, the front side

ARC is attacked and corroded by the front Ag paste; *i.e.*, “fire-through”; however, the back side Ag or Ag/Al and Al back contact paste strongly bond to the passivation dielectric layer so that the integrity of the passivation quality is maintained after contact formation. Also during firing as the wafer temperature rises above 660 °C melting and fusion of Al occurs. The glass in the Al back contact optimally interacts with both Al and Si without unduly affecting the passivation layer. In another embodiment, the solar cell printed with the subject reflector Al back contact paste is laser pulse fired locally in a pattern (dot, or line or combination thereof). During the laser firing, the laser pulse drives the Al metal through the dielectric and into the Silicon, locally alloying with the Silicon and forming p+ layer providing low-resistance Ohmic contact. For an example, a 1064 nm Q-switched laser is used due to the necessity of long pulses to melt silicon with aluminum.

[0092] A p+ layer is believed to provide a BSF, which in turn increases the solar cell performance. The preferred embodiment for these pastes is non fire-through the passivation layer such as SiNx while achieving low contact resistance to silicon and a low bulk resistivity to allow for the cell to function in a soldered string with minimum series resistance losses. Also, the paste must strongly bond to the passivation dielectric layer so that the integrity of the passivation quality is maintained after contact formation. Furthermore, paste composition should be such that it should be able to form a sufficiently thick BSF layer over a range of contact sizes with different laser firing conditions. The reflector property of the passivation dielectric layer is further enhanced by having this reflector Al paste on top of the dielectric layer.

[0093] **Method of Front and Back Contact Production.** Referring now to Figs. 1-7, one of many exemplary methods of making a solar cell Al back contact according to the present invention is illustrated. In this example, the method also involves making an Ag or Ag/Al back contact and an Ag front contact.

[0094] Fig. 1 schematically shows providing a substrate **100** of single-crystal silicon or multicrystalline silicon. The substrate typically has a textured front surface which reduces light reflection. In the case of solar cells, substrates are often used as 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 are typically removed by etching away about 10 to 20 microns of the substrate surface using an aqueous alkali solution such as KOH or NaOH, or using a mixture of HF and HNO₃. The substrate optionally

can be washed with a mixture of HCl and H₂O₂ to remove heavy metals such as iron that can adhere 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, **100**, depicted with exaggerated thickness dimensions. The substrate is typically a p-type silicon layer having about 200 microns or less of thickness.

[0095] Fig. 2 schematically illustrates that, when a p-type substrate is used, an n-type layer **200** is formed to create a p-n junction. Examples of n-type layers include a phosphorus diffusion layer. The phosphorus diffusion layer can be supplied in any of a variety of suitable forms, including phosphorus oxychloride (POCl₃), and organophosphorus compounds. The phosphorus source can be selectively applied to only one side of the silicon wafer, *e.g.*, a front side of the wafer. The depth of the diffusion layer can be varied by controlling the diffusion temperature and time, is generally about 0.2 to 0.5 microns, and has a sheet resistance of about 40 to about 120 ohms per square. The phosphorus source can include phosphorus-containing liquid coating material. In one embodiment, phosphosilicate glass (PSG) is applied onto only one surface of the substrate by a process such as spin coating, where diffusion is effected by annealing under suitable conditions.

[0096] Fig. 3 schematically illustrates forming back side dielectric passivation layer(s) **300**, which also usually serves as an optical reflection layer for low energy (infrared) photons. The passivation layer typically includes SiN_x, TiO₂, SiC, α-Si, or SiO₂, Al₂O₃ or combination thereof. The thickness of passivation layers **300** is about 50 to 3000 Å.

[0097] The passivation layers **300** can be formed by a variety of procedures including low-pressure CVD, plasma CVD, or thermal CVD, or ALD. When thermal CVD is used to form a SiN_x coating, the starting materials are often dichlorosilane (SiCl₂H₂) and ammonia (NH₃) 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 substantially stoichiometric compositional ratio between the silicon and the nitrogen, *i.e.*, Si₃N₄.

[0098] Fig. 4 schematically illustrates anti-reflection coating (ARC) and passivation layer **400** on the above-described n-type diffusion layer **200**. A back passivation capping layer **402** is similarly applied on the above-described back side passivation layers **300** to the back side of the

silicon wafer **100**. Silicon nitride is sometimes expressed as $\text{SiN}_x\text{:H}$ to emphasize passivation by hydrogen. The ARC **400** reduces the surface reflectance of the solar cell to incident light, thus increasing the amount of light absorption, and thereby increasing the electrical current generated. The thickness of passivation layers **400** and **402** depends on the refractive index of the material applied, although a thickness of about 500 to 3200 Å is suitable for a refractive index of about 1.9 to 2.0. Broadly, the refractive index of the ARC, in particular, SiN_x , ranges from 1.8-2.8.

[0099] Fig. 5 schematically illustrates applying an Ag or Ag/Al back paste **500** and a subject non fire-through reflector Al back paste **502** on the back side of the substrate **100**. The preferred non fire-through reflector Al back paste includes one or more Al powders, organic/inorganic additive compounds herein and one or more glass frits from Tables 1 to 7. The pastes can be applied fully, to a wet thickness of about 10 to 50 microns, by screen printing and successively dried on the back side of the substrate. An Ag front paste **504** for a front electrode is next screen printed and dried over the ARC **400**. Co-firing is then carried out in an infrared belt furnace in a temperature range of approximately 700° C to 1000° C for a period of from about one to several minutes.

[00100] Fig. 6 schematically illustrates co-firing of an Ag or Ag/Al back paste **500**, non fire-through reflector Al paste **502** and front Ag pastes **504**, becoming a Ag or Ag/Al back contact **600**, non fire-through reflector Al back conductor **602** and front Ag contact **604**, respectively. During co-firing, the boundary between the non fire-through reflector Al back contact and the Ag or Ag/Al back contact can assume an alloy state, and can be also connected electrically. The back passivation layer **300** and **400** remains essentially undamaged, non fire-through, during co-firing in those areas where it was covered by Ag or Ag/Al back paste **500** in Fig. 5. The Ag or Ag/Al back contact can be used for tab attachment during module fabrication. In addition, the front electrode-forming silver paste **504** sinters and penetrates through (*i.e.*, fires through) the silicon nitride film **400** during firing, and can be thereby able to electrically contact the n-type layer **200**, as shown by front electrodes **604** in Fig. 6.

[00101] Fig. 7 schematically illustrates laser pulse firing of an Al conductor **602** and forming a BSF layer **700**. During the laser firing, the laser pulse drives the Al metal locally through the dielectric and into the Silicon, locally alloying with the Silicon and forming p+ layer providing low-resistance Ohmic contact. For an example, a 1064 nm Q-switched laser is used due to the

necessity of long pulses to melt silicon with aluminum. This p+ layer is generally called the back surface field (BSF) layer, and helps to improve the energy conversion efficiency of the solar cell.

[00102] In an alternate embodiment from that described in conjunction with the drawings, the invention provides a method of making a solar cell contact, comprising (a) providing a p-type silicon wafer having at least two sides with texturized first (front) side, (b) depositing a phosphorus compound (emitter) on the texturized side, (c) depositing a passivation layer on at least a second (back) side of the silicon wafer, (d) applying an antireflective/passivation surface to a both side of the silicon wafer, (e) applying a back side tabbing Ag or Ag/Al paste to at least a portion of the passivation layer, (f) applying a back Al paste of this invention to a full area (overlaps some portion of back side tabbing Ag or Ag/ Al paste) of the back passivation layer, (g) applying a front paste to at least a portion of the antireflection coating, (h) firing the silicon wafer such that the pastes sinter where front Ag make contact to silicon while reacting with antireflective coatings, and (i) firing a laser upon at least a portion of the back side paste to drive Al metal through the passivation layer and into the silicon wafer.

[00103] A solar cell back contact according to the present invention can be produced by applying any non fire-through reflector Al paste disclosed herein, produced by mixing aluminum powders, with the organic or inorganic additive compounds and the glass compositions of tables 1 to 7, to the P-side of the silicon substrate, for example by screen printing, to a desired wet thickness, *e.g.*, from about 10 to 50 microns. To make a front contact, front contact Ag pastes can be printed on the front side.

[00104] Automatic screen-printing techniques can be employed using a 200-400 mesh screen to apply the Al back paste on the back surface of the substrate. The printed pattern is then dried at about 200°C or less, preferably at about 120°C for about 5-15 minutes before firing. The dry printed Al back contact paste of the present invention can be co-fired with the silver rear contact and the front contact silver pastes for as little as 1 second up to about 5 minutes at peak temperature, in a belt conveyor furnace in air.

[00105] Nitrogen (N₂) or another inert atmosphere can be used if desired when firing. The firing is generally according to a temperature profile that will allow burnout of the organic matter at about 300 °C to about 550 °C, a period of peak furnace set temperature of about 650 °C to about 1000 °C, lasting as little as about 1 second, although longer firing times as high as 1, 3, or 5 minutes are possible when firing at lower temperatures. For example a three-zone firing

profile can be used, with a belt speed of about 1 to about 4 meters (40-160 inches) per minute. Naturally, firing arrangements having more than 3 zones are envisioned by the present invention, including 4, 5, 6, or 7, zones or more, each with zone lengths of about 5 to about 20 inches and firing temperatures of 650 to 1000 °C, for example 660-940 °C. In one embodiment, the Al back paste is fired using a typical firing profile of 550°C - 550°C - 550°C - 700°C - 800°C - 940°C set in a 6-zone furnace with the belt speed of 180 inches per minute.

[00106] Examples. The following examples illustrate the subject invention. Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Celsius, and pressure is at or near atmospheric pressure.

[00107] Exemplary aluminum paste compositions are shown in Table 8. The performance from various Al pastes screen printed on SiO₂/Al₂O₃/SiN_x back passivated wafers (type B (no back texture) and type C (back texture)) and fired in a six-zone infrared belt furnace using standard firing profile 400-400-500-700-800-920 C with the conveyor belt speed 200 inch per minute (ipm) are shown in Table 9. The lengths of the zones of the six-zone infrared belt furnace are 45.7, 45.7, 22.9, 22.9, 22.9, and 22.9 cm long, respectively. Five pastes which were divided into two groups. Pastes A1 and A2 contain the borosilica based additive and clearly show higher electrical performance as well as good fired adhesion. SEM cross section studies do indicate that these pastes do not fire-through the SiN_x passivation stack. The adhesion is measured by lamination pull test after firing. Sun Voc is measured using Sinton equipment. Pastes A1 and A2 containing borosilica additive show good electrical performance as well show good lamination adhesion. Pastes A3-A5 in this study do not contain borosilica additive and show poor laminated adhesion.

[00108] Table 8: Exemplary reflector Al paste compositions.

Material	Weight % A
Al powders	40-80
Glass powders	0.1-10
Organic Vehicle and Solvents	5-30
Organometallic Additives	0-10
Inorganic Additives	0-10

[00109] Table 9: Reflector paste performance on type B and type C passivation stacks.

Paste	A1	A2	A3	A4	A5
Al powder (4-6 μm)	71.96	71.96	71.96	60.0	50.0
Al powder (2 μm)	-	-	-	11.96	11.96
Al-Si Alloy Powder (3-5 μm)	-	-		-	10.0
Glass Powder(s) (2-5 μm)	0.51	0.51	0.51	0.51	0.51
No of Glasses	1	2	1	1	1
Ethoxide Organometallic (B,Ti)	1.41	1.41	-	-	-
Borosilica	3.00	3.00	-	-	-
Total Organometallic	4.41	4.41	0	0	0
Total Inorganic Oxide Additives (SiO_2)	0.066	0.066	0.066	0.066	0.066
% Solids	76.95	76.95	72.54	72.54	72.54
% Vehicle	23.05	23.05	27.46	27.46	27.46
Properties					
Sun V_{oc} (B wafers)	0.628	0.631	0.631	0.632	0.628
Sun V_{oc} (C wafers)	0.623	0.625	0.623	0.620	0.630
Eff (B wafers)	0.773	0.825	0.798	0.797	0.817
Eff (C wafers)	0.811	0.823	0.799	0.785	0.812
Adhesion – N- (B wafers)	31.25	39.44	9.15	9.67	5.68
Adhesion – N- (C wafers)	20.90	44.48	4.16	4.82	0.44

[00110] In Table 9, a commercially available organic vehicle was used. In Table 9, Pastes A1 and A3-A5 contain a glass falling within the ranges of Table 1-6. In glass A2, it is an even 50/50 blend of Glass 1-6 and Glass 2-4.

[00111] Figure 8 shows a comparative representative reflectance measurement on the back passivated wafers (type B) with the non-fire-through reflector Al paste A2 and without the reflector Al paste indicating higher reflectance properties due to the paste composition of this invention. The Al paste was screen printed on $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{SiN}_x$ back passivated wafers (type B

(no back texture)) and fired in a six-zone infrared belt furnace using standard firing profile 400-400-500-700-800-920 °C setting the belt speed 200 inch per minute (ipm). Spectrophotometers were utilized to measure the reflectance properties.

[00112] A fired contact of the invention includes a dielectric layer underneath the fired reflector Al paste of type B indicating the non-etching/corrosion of dielectric layers. The Al paste was screen printed on SiO₂/Al₂O₃/SiN_x back passivated wafers (type B (no back texture)), fired in a six-zone infrared belt furnace using standard firing profile 400-400-500-700-800-920 °C setting the belt speed 200 inch per minute (ipm) and subsequently the fired paste was etched using an appropriate solvent.

[00113] What has been described above includes examples of the subject invention. It is, of course, not possible to describe every conceivable combination of components or methodologies for purposes of describing the subject invention, but one of ordinary skill in the art may recognize that many further combinations and permutations of the subject invention are possible. Accordingly, the subject invention is intended to embrace all such alterations, modifications and variations that fall within the spirit and scope of the appended claims. Furthermore, the foregoing ranges (*e.g.*, compositional ranges and conditional ranges) are preferred and it is not the intention to be limited to these ranges where one of ordinary skill in the art would recognize that these ranges may vary depending upon specific applications, specific components and conditions for processing and forming the end products. Disclosure of a range constitutes disclosure of each discrete value within such range, and subranges within the range. One range can be combined with another range. Disclosure of a Markush group supports each individual member of such group and any subgrouping within such group. To the extent that the terms “contain,” “have,” “include,” and “involve” are used in either the detailed description or the claims, such terms are intended to be inclusive in a manner similar to the term “comprising” as “comprising” is interpreted when employed as a transitional word in a claim. In some instances, however, to the extent that the terms “contain,” “have,” “include,” and “involve” are used in either the detailed description or the claims, such terms are intended to be partially or entirely exclusive in a manner similar to the terms “consisting of” or “consisting essentially of” as “consisting of” or “consisting essentially of” are interpreted when employed as a transitional word in a claim.

CLAIMS

What is claimed is:

1. A paste composition comprising, prior to firing:
a conductive metal component;
a glass component; and
a vehicle.
2. The paste composition of claim 1, further comprising, prior to firing, at least one organometallic compound selected from metal boron, silicon, vanadium, antimony, phosphorous, yttrium, titanium, nickel, cobalt, zirconium, zinc, lithium and combinations thereof.
3. The paste composition of claim 2, wherein the organometallic compound includes at least one $C_1 - C_{50}$ organic moiety that is linear or branched, saturated or unsaturated, aliphatic, alicyclic, aromatic, araliphatic, halogenated or otherwise substituted, optionally having one or more heteroatoms such as O, N, S, or Si, and/or including hydrocarbon moieties such as alkyl, alkyloxy, alkoxide, alkylthio, or alkylsilyl moieties.
4. The paste composition of claim 2, wherein the organometallic compounds are selected from the group consisting of metal ethoxides, metal acetates, metal acetylacetonates, metal carboxylates, metal 2-methylhexanoates, metal 2-ethylhexanoates, and metal 2-propylhexanoates, metal acrylates, metal methacrylates, and combinations thereof, wherein the metal is selected from the group consisting of titanium, zirconium, nickel, cobalt, zinc, vanadium, and combinations thereof.
5. The paste composition of claim 1, wherein the conductive metal comprises aluminum.
6. The paste composition of claim 5, further comprising an Al-Si alloy.
7. The paste composition of claim 5, further comprising an Al-Si eutectic alloy.

8. The paste composition of claim 1, wherein the conductive metal further includes up to 20 wt% of at least one selected from the group consisting of an Al-Si eutectic, zinc, tin, antimony, silicon, bismuth, indium, molybdenum, palladium, silver, platinum, gold, titanium, vanadium, nickel, copper, and combinations thereof.
9. The paste of claim 1, wherein the glass component comprises 5-65 mol% ZnO, 5-55 mol% $B_2O_3 + Al_2O_3$, 10-65 mol% SiO_2 , 0.5-40 mol% $Li_2O + Na_2O + K_2O + Rb_2O + Cs_2O$, 0.5-25 mol% $TiO_2 + ZrO_2$, and 0-15 mol% F.
10. The paste of claim 1, wherein the glass component comprises 7-50 mol% ZnO, 7-40 mol% $B_2O_3 + Al_2O_3$, 10-45 mol% SiO_2 , 5-33 mol% $Li_2O + Na_2O + K_2O + Rb_2O + Cs_2O$, 1-20 mol% $TiO_2 + ZrO_2$, and 1-15 mol% F.
11. The paste of claim 1, wherein the glass component comprises 10-32 mol% ZnO, 22-58 mol% SiO_2 , 10-25 mol% $B_2O_3 + Al_2O_3$, 1-20 mol% $Li_2O + Na_2O + K_2O + Rb_2O + Cs_2O$, 0-10 mol% $MgO + CaO + BaO + SrO$, 0.5-15 mol% $TiO_2 + ZrO_2$, 0-5 mol% $V_2O_5 + Ta_2O_5 + Sb_2O_5 + P_2O_5$, 0-20 mol% $TeO_2 + Tl_2O + GeO_2$, and 0-15 mol% F.
12. The paste of claim 1, wherein the glass component comprises 5-55 mol% $Li_2O + Na_2O + K_2O$, 0.5-30 mol% $TiO_2 + ZrO_2$, 5-75 mol% $B_2O_3 + SiO_2$, and 5-20 mol% $V_2O_5 + Ta_2O_5 + Sb_2O_5 + P_2O_5$.
13. The paste of claim 1, wherein the glass component comprises 25-65 mol% Bi_2O_3 , 3-60 mol% ZnO, and 4-65 mol% B_2O_3 .
14. The paste of claim 1, wherein the glass component comprises 25-65 mol% Bi_2O_3 , 5-35 mol% SiO_2 , and 4-65 mol% B_2O_3 .
15. The paste of claim 1, wherein the glass component comprises 5-85 mol% Bi_2O_3 , and 5-35 mol% $B_2O_3 + SiO_2$.
16. The paste of claim 1, wherein the glass component comprises 15-75 mol% PbO and 5-38 mol% $B_2O_3 + SiO_2$.

17. The paste of claim 1, wherein the glass component comprises 60-70 mol% PbO and 5-15 mol% B₂O₃ + SiO₂, 15-23 mol% Al₂O₃, 0-5 mol% ZnO, 0.1-3 mol% TiO₂+ZrO₂+HfO₂, 0.1-5 mol% V₂O₅+Sb₂O₅+P₂O₅+Ta₂O₅+Nb₂O₅, 0-8 mol% MgO+CaO+BaO+SrO, 0-10 mol% Li₂O+Na₂O+K₂O+Rb₂O+ Cs₂O, 0-20 mol% TeO₂+Tl₂O+GeO₂ and 0-6 mol% F.
18. The paste of claim 1, wherein the glass component comprises 10-40 mol% SiO₂, 15-39 mol% Li₂O+Na₂O+K₂O+Rb₂O+Cs₂O, 7-22 mol% TiO₂+ZrO₂, 1-9 mol% V₂O₅+Ta₂O₅+Sb₂O₅+P₂O₅, 0-10 mol% MgO+CaO+BaO+SrO, 0-10 mol% TeO₂+Tl₂O+GeO₂ and 0-8 mol% F.
19. The paste of claim 1, wherein the glass component comprises 30-40 mol% Li₂O + Na₂O + K₂O, 1-5 mol% TiO₂+ZrO₂, 30-52 mol% B₂O₃ + SiO₂, 5-25 mol% V₂O₅ + Sb₂O₅ + P₂O₅+Ta₂O₅, 0-10 mol% MgO + CaO + BaO + SrO, 0-5 mol% TeO₂+Tl₂O+GeO₂ and 5-13 mol% F.
20. The paste composition of claim 1:
wherein the conductive metal component comprises about 40 to about 80 wt% of an aluminum source;
wherein the glass component is present to an extent of about 0.1 to about 10 wt%; and
wherein the vehicle is present to an extent of about 5 to about 30 wt%.
21. The paste composition of claim 2, wherein the paste composition comprises, prior to firing:
about 40 to about 80 wt% of aluminum;
about 0.1 to about 10 wt% of the glass component;
about 5 to about 30 wt% of the vehicle; and
about 0.1 to about 10 wt% of the organic/inorganic additive compound.
22. The paste composition of claim 1, wherein the glass component comprises one or more glasses.

23. The paste composition of claim 1, wherein the D_{50} particle size of the glass component is about 0.1 microns to about 20 microns.
24. The paste composition of claim 5, wherein the aluminum is provided in powder form having a bimodal particle size distribution.
25. The paste composition of claim 24, wherein a first D_{50} average aluminum particle size is in the range of 0.5 to 3 microns and a second D_{50} average aluminum particle size is 3 – 40 micron range, wherein no overlap is intended.
26. The paste composition of claim 1, wherein the viscosity of the paste is in the range of 5-100 Pa.s.
27. The paste composition of claim 1, wherein the metal component comprises both flake and spherical morphologies.
28. A photovoltaic cell comprising a silicon wafer and a back contact thereon, the back contact comprising dielectric passivation layer(s) at least fully coated with a non fire-through Al back paste, the Al back side paste comprising, prior to laser firing:
a conductive metal component;
a glass component; and
a vehicle.
29. The photovoltaic cell of claim 28, wherein the back side paste further comprises, prior to firing, at least one at least one organometallic compound selected from metal boron, silicon, vanadium, antimony, phosphorous, yttrium, titanium, nickel, cobalt, zirconium, zinc, lithium or combinations thereof.
30. The photovoltaic cell of claim 28, wherein the organometallic compound includes at least one $C_1 - C_{50}$ organic moiety that is linear or branched, saturated or unsaturated, aliphatic, alicyclic, aromatic, araliphatic, halogenated or otherwise substituted, optionally having one or more heteroatoms such as O, N, S, or Si, and/or including hydrocarbon moieties such as alkyl, alkyloxy, alkoxide, alkylthio, or alkylsilyl moieties.

31. The photovoltaic cell of claim 30, wherein the organometallic compounds are selected from the group consisting of metal ethoxides, metal acetonates, metal acetylacetonates, metal carboxylates, metal 2-methylhexanoates, metal 2-ethylhexanoates, and metal 2-propylhexanoates, metal acrylates, metal methacrylates, and combinations thereof, wherein the metal is selected from the group consisting of titanium, zirconium, nickel, cobalt, zinc, vanadium, and combinations thereof.
32. A method of making a paste composition, comprising: providing a conductive metal component, a glass component, and a vehicle; and dispersing the conductive metal component, and the glass component in the vehicle.
33. The method of claim 32, wherein the organometallic compound is selected from the group consisting of $C_1 - C_{50}$ organic moieties that are linear or branched, saturated or unsaturated, aliphatic, alicyclic, aromatic, araliphatic, halogenated or otherwise substituted, optionally having one or more heteroatoms such as O, N, S, or Si, and/or including hydrocarbon moieties such as alkyl, alkyloxy, alkoxide, alkylthio, or alkylsilyl moieties.
34. A method of making a photovoltaic cell contact, comprising:
- providing a silicon substrate and a locally pre-opened rear passivation layer thereon;
 - applying a paste composition on the locally opened rear passivation layer, the paste comprising a conductive metal component, a glass component, and a vehicle; and
 - heating the paste to sinter the conductive metal component.
35. The method of claim 34, wherein the paste further comprises at least one organometallic additive compound, a phosphate glass and a phosphorus compound dispersed in the vehicle; wherein the organometallic compound is selected from boron, silicon, vanadium, antimony, phosphorous, yttrium, titanium, nickel, cobalt, zirconium, zinc, lithium and combinations thereof, wherein the organometallic compound can include $C_1 - C_{50}$ organic moieties that are linear or branched, saturated or unsaturated, aliphatic, alicyclic, aromatic, araliphatic, halogenated or

otherwise substituted, optionally having one or more heteroatoms such as O, N, S, or Si, and/or including hydrocarbon moieties such as alkyl, alkyloxy, alkoxide, alkylthio, or alkylsilyl moieties.

36. The method of claim 35, wherein the organometallic additive is selected from the group consisting of metal acetylacetonates, metal carboxylates, metal 2-methylhexanoates, metal 2-ethylhexanoates, metal 2-propylhexanoates, metal acrylates, metal methacrylates, and combinations thereof.

37. The method of claim 34, wherein the glass component is lead-free.

38. The method of claim 34, wherein the passivation layer comprises at least one selected from the group consisting of SiNx, Al₂O₃, SiO₂, SiC, amorphous Si, TiO₂, Al₂O₃/SiNx, SiO₂/SiNx, SiO₂/Al₂O₃/SiNx in a combined thickness of about 5 to about 360 nm thick.

39. The method of claim 34, wherein the local openings are made by laser ablation or chemical etching to form dots or lines, wherein the dot diameter ranges from 20 - 200 microns and a trench is 100-700 microns wide, or the dot diameter ranges from 20-200 microns and a trench is 0.5-2.0 mm wide.

40. The method of claim 39, wherein the local openings are made by chemical etching using an etchant comprising phosphorus.

41. The method of claim 34, wherein heating includes heating to a peak wafer temperature of 660-940 °C.

42. The method of claim 34, wherein the refractive index of SiNx ranges from 1.8-2.8.

43. A method of making a solar cell contact, comprising,
- a. providing a p-type silicon wafer having at least two sides wherein a first (front) side is texturized ,
 - b. depositing a phosphorus compound on the texturized side to form an emitter,
 - c. depositing a passivation layer on at least a second (back) side of the silicon wafer,
 - d. applying an antireflective/passivation surface to both sides of the silicon wafer,
 - e. applying a back side tabbing Ag or Ag/Al paste to at least a portion of the passivation layer,
 - f. applying a back Al paste of this invention to the back passivation layer to cover at least a some portion of the back side tabbing Ag or Ag/ Al paste,
 - g. applying a front paste to at least a portion of the antireflection coating on the first side,
 - h. firing the silicon wafer such that the pastes sinter where front Ag makes contact to silicon while reacting with antireflective coatings, and
 - i. firing a laser upon at least a portion of the back side paste to drive Al metal through the passivation layer and into the silicon wafer.

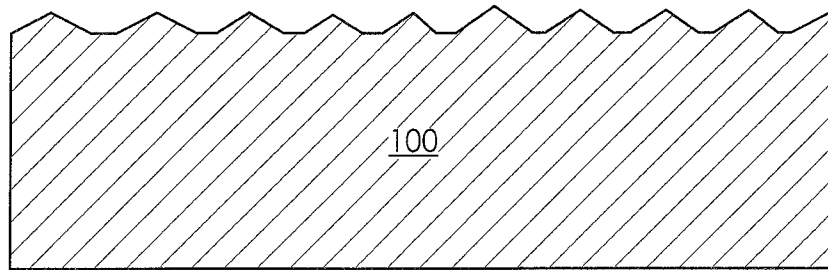


FIG. 1

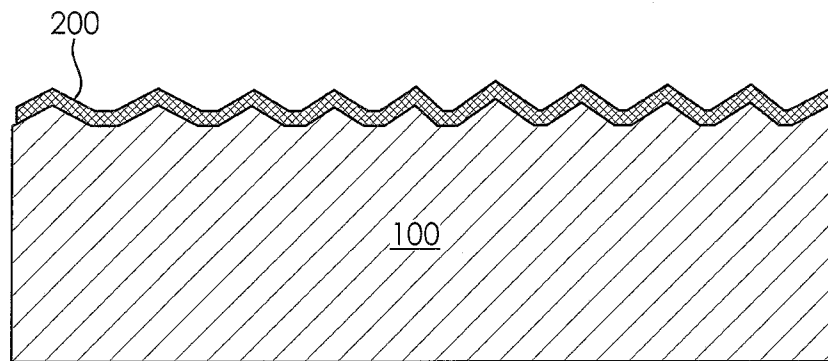


FIG. 2

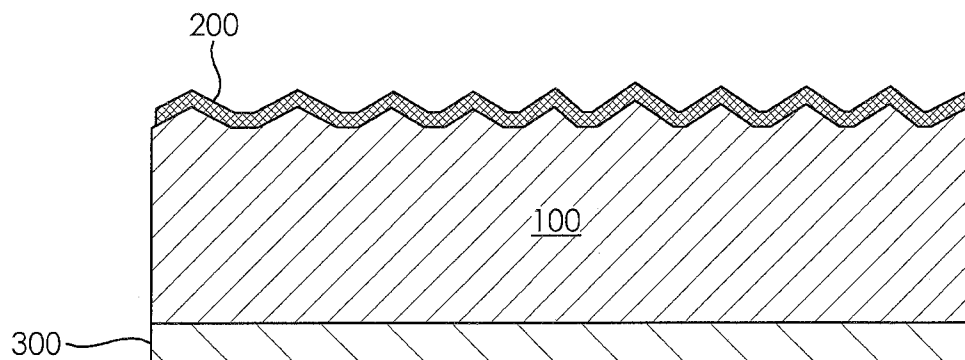


FIG. 3

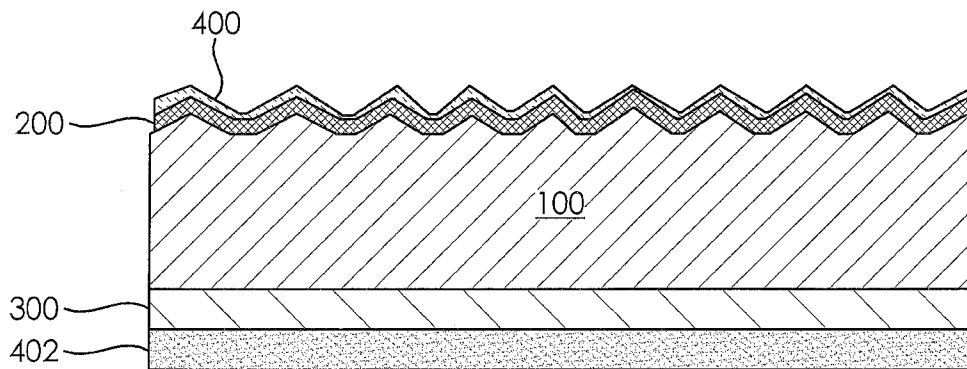


FIG. 4

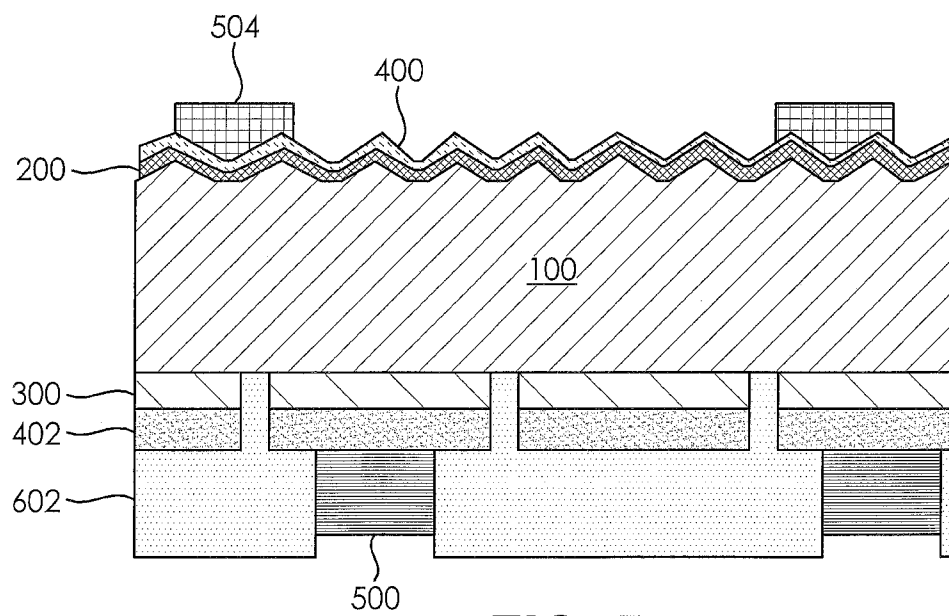


FIG. 5

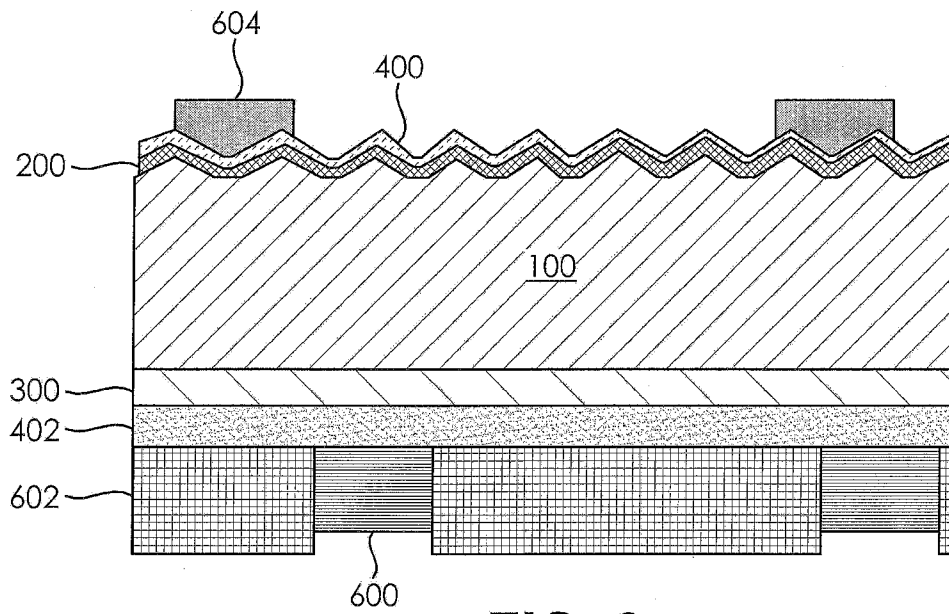


FIG. 6

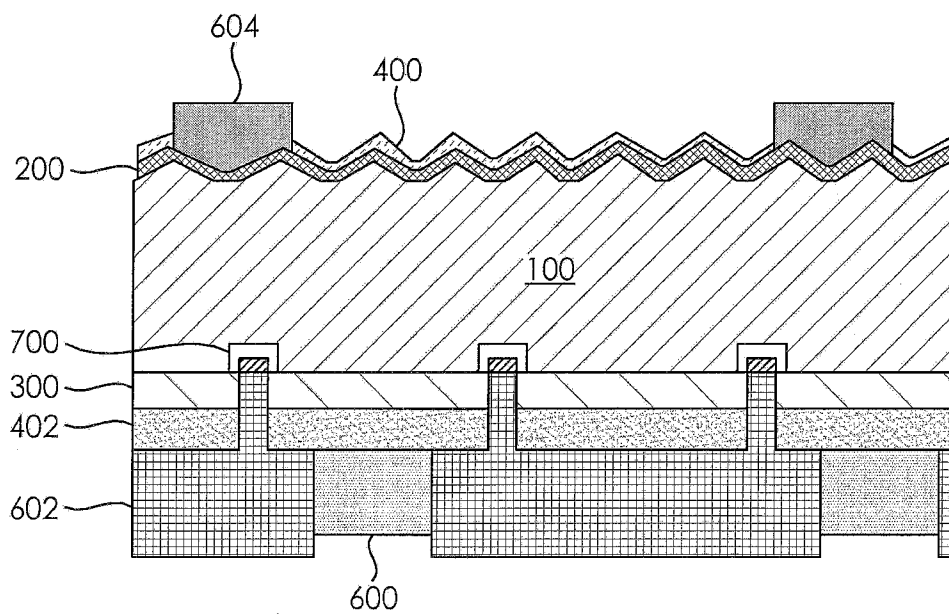
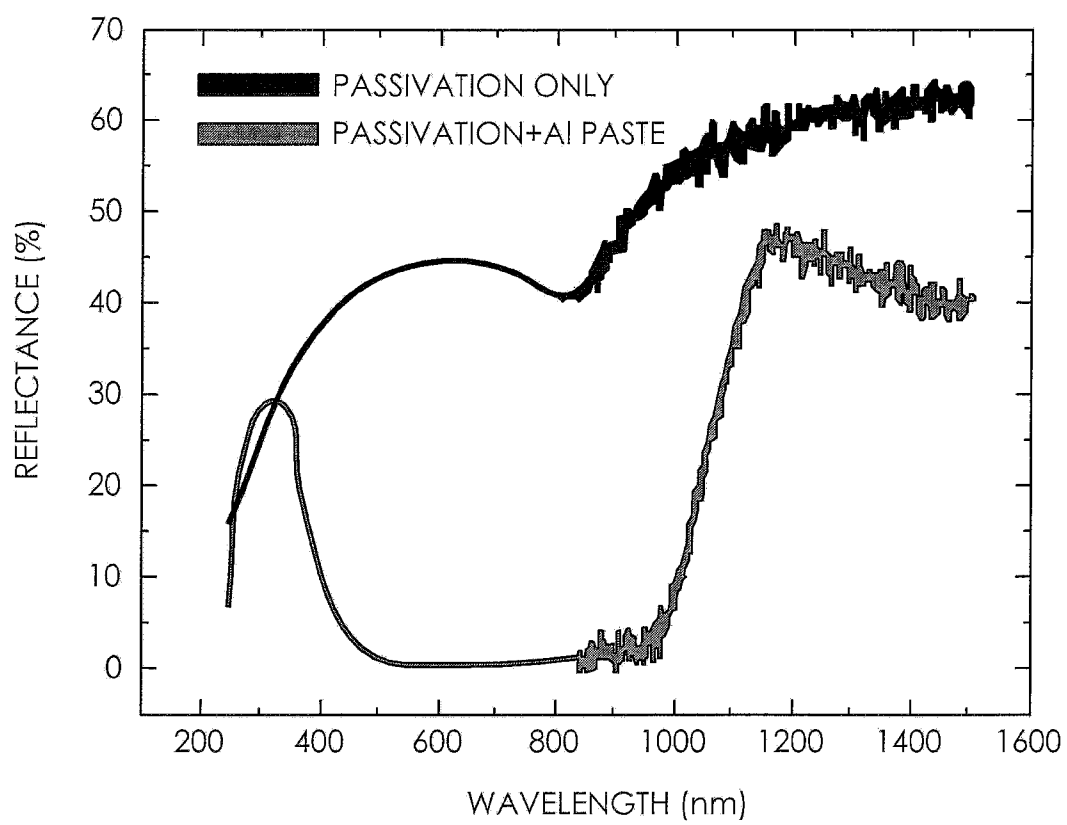


FIG. 7

**FIG. 8**