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(71) Applicant: **SUN CHEMICAL CORPORATION**
[US/US]; 35 Waterview Boulevard, Parsippany, NJ 07054 (US).(72) Inventor: **MOYER, Jerome**; 1 Avenue at Port Imperial, Apt. 1345, West New York, NJ 07073 (US).(74) Agents: **ACHKAR, Charles C.** et al.; Ostrolenk Faber LLP, 1180 Avenue Of The Americas, New York, NY 10036 (US).

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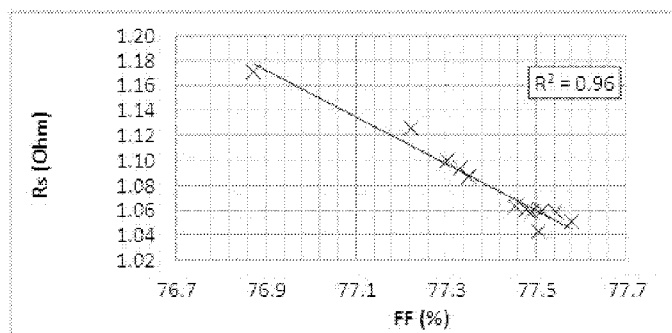
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(54) Title: SILVER CONDUCTIVE PASTE COMPOSITION

Figure 1



(57) **Abstract:** Described herein is a conductive composition that includes a silver powder, an organic medium, an optional inorganic additive, elemental thallium and/or a thallium containing compound, elemental tellurium and/or a tellurium containing compound, and optionally, a glass frit. The composition may be a paste. Other inorganic additives and glass may be present in the composition. Further described are devices such as semiconductors, photovoltaic devices, and solar cells in which the substrates thereof are coated with the conductive compositions. Such devices exhibit improved efficiency.

SILVER CONDUCTIVE PASTE COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application Serial No. 62/265,461 filed December 10, 2015 which is incorporated herein by reference in its entirety and for all purposes.

FIELD OF THE INVENTION

[0002] The present invention is directed to a silver conductive paste that may be used in photovoltaic devices such as solar cells, optically reflective applications, sealing glass pastes, etchant pastes, conductive pastes used for shielding purposes and for carrying electrical current in electronic circuit or inductive applications.

BACKGROUND OF THE INVENTION

[0003] Electrical contacts for solar cells are provided by the formation of electrodes on a silicon wafer by applying and firing a silver paste thereon. In order to minimize the circuit's electrical resistance, maximize the electrical current and voltage output and thus increase the cell power output and efficiency, typically a glass is incorporated into the silver paste such that the glass can enable an electrical contact with the silicon by etching away an insulating coating present on the silicon wafer.

[0004] US 2014/0021417 describes a silver electrode-forming paste that contains a silver powder, a glass component and an organic medium wherein the glass component contains a tellurium loaded glass frit.

[0005] EP 2 617 689, US 8,969,709 B2, and US 8,497,420 B2 describe the use of lead and tellurium oxides in conductive compositions and pastes.

[0006] US 8,889,980 discloses thick film pastes containing lead, tellurium and lithium oxides and their use in the manufacture of semiconductor devices.

[0007] US 8,308,993 discloses conductive inks substantially free of glass frit and containing metallo-organic components including thallium.

SUMMARY OF THE INVENTION

[0008] Described herein is a conductive composition that includes a silver powder, an organic medium, an optional inorganic additive, elemental thallium and/or a thallium containing compound, elemental tellurium and/or a tellurium containing compound, and optionally, glass frit.

[0009] Further described is an inventive device having a substrate coated with the conductive composition described herein.

[00010] Still further, described is a process for preparing a device comprising:

- a) applying the coating composition described herein to a surface of a substrate of a device; and
- b) drying the composition.

[00011] In one aspect, the conductive composition is a conductive paste. In a particular aspect, the paste may be a sealing glass paste, an etchant paste, a conductive paste used for shielding purposes and for carrying electrical current in electronic circuit or inductive applications.

[00012] In one aspect, the device is a photovoltaic device such as solar cell.

[00013] In another aspect, the device is a semiconductor device.

[00014] In one aspect, a lesser amount of glass is present in the conductive composition described herein than compared to state of the art compositions. This may result from including inorganic additive in the conductive composition, which may reduce the contact resistance between the conductive composition and the device, e.g., a silicon solar cell.

[00015] These and other objects, advantages, and features of the invention will become apparent to those persons skilled in the art upon reading the details of the methods and formulations as more fully described below.

[00016] Commonly owned International Application No. PCT/US16/38010, filed under the Patent Cooperation Treaty (PCT) on June 17, 2016, is incorporated herein by reference in its entirety.

BRIEF DESCRIPTION OF THE DRAWINGS

[00017] Figure 1 shows the high R^2 value, correlating the R_s to the FF for the conductive paste compositions of Example 3 indicating that cell efficiencies were driven by the series resistance associated to paste formulation.

[00018] Figure 2 shows the adhesion properties vs. the %wt of glass frits for conductive compositions of Example 4.

DETAILED DESCRIPTION

[00019] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only, and are not restrictive of any subject matter claimed.

[00020] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which the inventions belong. All patents, patent applications, published applications and publications, websites and other published materials referred to throughout the entire disclosure herein, unless noted otherwise, are incorporated-by-reference into the present disclosure in their entirety for any purpose.

DEFINITIONS

[00021] In this application, the use of the singular includes the plural unless specifically stated otherwise. As used herein, the singular forms “a,” “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[00022] “Or” means “and/or”, unless stated otherwise.

[00023] “Comprises” and/or “comprising” specify the presence of the stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or

addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. Furthermore, to the extent that the terms “includes,” “having,” “has,” “with,” “composed,” “comprised” or variants thereof 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.”

[00024] Ranges and amounts can be expressed as “about” a particular value or range. “About” is intended to also include the exact amount. For example, “about 5 percent” means “about 5 percent” and also “5 percent” of the thing in issue (e.g., the amount a component is present in weight%). “About” means within typical experimental error for the application or purpose intended.

[00025] The present invention is directed to conductive compositions, such as conductive paste compositions, that provide thick film electrodes in a solar cell.

[00026] It has been found that high efficiency cells can be produced by using the inventive conductive compositions, e.g., pastes that include inorganic additive, when compared to the efficiency of cells prepared from conductive compositions that require greater amounts of glass in the compositions. Particular advantages may be achieved when the inorganic additive includes elemental thallium and/or a thallium compound and/or elemental tellurium and/or a tellurium compound.

[00027] In one aspect, the inventive conductive compositions, e.g., pastes, comprise an electrically conductive metal, e.g., silver, an organic medium, an optional inorganic additive, elemental thallium and/or a thallium containing compound, elemental tellurium and/or a tellurium containing compound, and optionally, glass frit. While the conductive compositions may be glass free, in another aspect, the compositions may include glass, e.g., glass frit. When present, glass frit may be present in an amount of about 0.01wt% to about 5.0wt%, preferably in an amount of about 0.05wt% to about 2.5wt%, and more preferably in an amount of about 0.1wt% to about 2.0 wt%, and most preferably about 0.1wt% to < about 0.5wt%, based on the total weight of the conductive paste composition. In a further aspect, the conductive compositions described herein may be essentially glass free.

[00028] In one aspect, the glass frit includes elemental thallium and/or a thallium containing compound (referred to hereafter in some instances as “thallium component”) as a glass frit component. In another aspect, the glass frit includes elemental tellurium and/or a tellurium containing compound (referred to hereafter in some instances as “tellurium component”) as a glass frit component. In yet another aspect, the glass frit includes a thallium component and a tellurium component as glass frit components.

[00029] In one aspect, the inorganic additive includes a thallium component as an inorganic additive component. In another aspect, the inorganic additive includes a tellurium component as an inorganic additive component. In yet another aspect, the inorganic additive includes a thallium component and a tellurium component as inorganic additive components.

[00030] In yet another aspect a thallium component and a tellurium component are components of the inorganic additive and glass frit.

[00031] In one aspect, the conductive composition may be in the form of a paste, although other compositions forms may be prepared. For the sake of simplicity, the inventive conductive composition shall be hereinafter described as conductive paste compositions.

[00032] In one aspect, the inorganic additive may include one or more of a lead compound and a bismuth compound. Examples of such compounds include the oxides and salts of lead and bismuth. The inclusion of these components in the conductive paste may improve silicon solar cell performance by improving the contact of an electrode to the cell and increasing the conversion efficiency, e.g., the light conversion efficiency of the solar cell.

[00033] In one aspect, the ratio, on a weight percent (wt%) basis, of the tellurium component to the thallium component in the inventive conductive paste compositions is about 0.6 to about 93 (the molar ratio for same is about 2 to about 265).

[00034] In one aspect, inorganic additives may be crystalline forms of oxides and salts. The term “inorganic additive” refers to one or more additives that are not associated, incorporated or “bound” within a glass. Thus, while the raw materials that go into making glass may

consist of inorganic compounds, the final glass form, wherein some degree of an amorphous material is present, are not to be considered inorganic additives as used herein. It is not intended that the term “inorganic additive” embrace the silver component of the present compositions.

[00035] The term “glass” refers to a milled “glass frit” powder that may be employed in preparing the conductive paste compositions described herein. Molten glass is quenched in water and the resulting quenched beads of glass are referred to as “glass frit” or “frit”, which is further milled to reduce it into a fine powder. The milled powder is also referred to herein as “glass” or “glass frit”.

[00036] Also glassy materials, e.g., those materials that constitute the glass may be described herein as “bound” and typically have an amorphous to semi-amorphous structure, which may or may not be stoichiometric in nature.

[00037] Consequently, the thallium component, the tellurium component, the lead compound and/or the bismuth compound, for example, when bound and co-mingled in glass, may provide the glass with properties that are distinct and measurably different from their non-bound, or “free” forms. In one aspect, the oxides of these components/compounds are present in the glass, and improve the glass properties, and by extension, the properties of the conductive paste compositions.

[00038] The inclusion of the thallium component and the tellurium component in glass frits that are included in the conductive paste composition may improve the electrical contact between the composition and a silicon solar cell, e.g., the substrate of the solar cell, which may improve solar cell efficiency. In one aspect the thallium component is thallium oxide and tellurium component is tellurium oxide.

[00039] Still further, the inclusion of the lead oxide, bismuth oxide, the thallium component and tellurium component in the glass of the conductive paste composition may improve the electrical contact between the paste and a silicon solar cell, which may improve efficiency of the solar cell. In one aspect the thallium component is thallium oxide and tellurium component is tellurium oxide.

[00040] In one aspect, the weight percent of glass/glass frits in the inventive conductive paste compositions are less than the amount at which glasses are included in state of the art compositions, which include at least 0.5wt% glass.

[00041] In one aspect, the compositions of the present invention are essentially glass-free. Furthermore it has been found that good solar cell efficiency is attained in which inventive conductive pastes include lithium-free glass, in an amount of about 0.27wt%.

[00042] Comparable cell efficiencies are achieved using conductive paste compositions based on free state material forms of TeO_2 , TiO_2 , PbO , and Bi_2O_3 to pastes made with highly bound materials, which use glass to make electrical contact to the cell.

[00043] “Comparable” as used herein when referring to light conversion efficiency, means a $\pm 0.6\%$ absolute difference in light conversion efficiency. Test-to-test variability may account for the majority of this variation. Test-to-test variability derives from the accumulated influences that may include changes in silicon wafer quality, wafer processing, paste printing and firing and/or measurement variance. Within a single test, where all wafers originate from the same source and are processed into cells and are tested concurrently, “Comparable light conversion efficiency” refers to within a $\pm 0.2\%$ absolute difference in same. Accordingly the present invention provides a conductive composition, typically in the form of a thick-film silver paste which comprises a silver powder, an organic medium/organic vehicle and discrete inorganic additives in a free state comprising a thallium component and a tellurium component.

[00044] The conductive inventive paste compositions exhibit an excellent set of properties when used as, for example, an electrode-forming conductive paste in a device, such as for example a photovoltaic device, such as a solar cell. Solar cells having electrodes formed from the inventive paste compositions exhibit a markedly improved efficiency in converting light energy into electrical energy. When employed as glass frit component and/or as inorganic additive component, the thallium component may be a thallium containing compound, such as for example an organothallium compound, thallium (I) oxide, thallium (III) oxide, thallium(I) bromide, thallium(I) carbonate, thallium(I) oxalate, thallium(I) iodide,

thallium(I) fluoride, thallium(I) nitrate, thallium(I) sulfate, thallium(I) ethoxide, thallium(III) acetate, thallium(III) trifluoroacetate, thallium(I) hexafluorophosphate, thallium(I) 2-ethylhexanoate and/or thallium(I) hexafluoro-2,4-pentanedionate. The thallium component may also be elemental thallium, and a mixture of any of the above.

[00045] When employed as glass frit component and/or as inorganic additive component, the tellurium component may be one or more of telluric acid, diisopropyl telluride, tellurium ethoxide, tellurium isopropoxide, antimony telluride, barium telluride, bismuth telluride, lanthanum telluride, lead (II) telluride, lithium telluride, manganese(II) telluride, manganese(IV) telluride, molybdenum telluride, nickel tellurate, nickel telluride, rhenium telluride, rhodium telluride, silver telluride, thallium telluride, titanium telluride, tungsten telluride, zinc telluride, tellurium bromide (TeBr_4) tellurium chloride (TeCl_4) tellurium iodide (TeI_4), and tellurium oxide (TeO_2). The tellurium component may also be elemental tellurium, and a mixture of any of the above.

[00046] The composition may include the tellurium component in an amount of about 0.1 to 0.75wt%.

[00047] The composition may include about 0.01wt% to about 5wt% of thallium component and preferably about 0.01 wt% to about 1.0wt% of same.

[00048] The inorganic additive may include a compound or material selected from a chalcogenide, a pnictogenide, or a halide, Ag_2Te , AgAsF_6 , Ag_3AsO_4 , AgBF_4 , AgBr , AgCl , AgClO_4 , AgF , AgF_2 , AgHF_2 , AgI , Ag_2MoO_4 , AgPF_6 , AgPO_4 , AgReO_4 , Ag_2SO_4 , Ag_2S , AgSbF_6 , AgVO_3 , Ag_2WO_4 , Al_2O_3 , As_2O_3 , AuTe_2 , BaO , B_2O_3 , BaF_2 , BaO , Bi , BiBr_3 , BiCl_3 , BiF_3 , $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, BiI_3 , Bi_2MoO_6 , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, Bi_2O_3 , $\text{Bi}(\text{OH})_3$, BiSb , Bi_2Se_3 , Bi_2S_3 , Bi_2Te_3 , BiVO_4 , $\text{Bi}_2(\text{WO}_4)_3$, C_2O_3 , CaO , CdO , CoO , CuO , Cu_2O , Ga_2O_3 , In_2O_3 , KAg_4I_5 , LaF_3 , La_2O_3 , Li_2O , Li_3PO_4 , MgO , Mn_2O_5 , MnO_2 , Mo_2O_3 , NiO , P_2O_5 , Pb , PbBr_2 , PbCl_2 , PbF_2 , PbHPO_4 , PbI_2 , PbO , PbSO_4 , PbSe , PbS , PbSb , PbTe , $\text{Pb}(\text{VO}_3)_2$, ReO_2 , ReO_3 , Re_2O_7 , RuO_2 , Sb_2O_3 , SeO_2 , SO_2 , SO_3 , SiO_2 , SnO_2 , SrF_2 , SrO , Tb_2O_3 , Tb_4O_7 , TeBr_4 , TeCl_4 , TeI_4 , TeO_2 , TiO_2 , TlF , Tl_2O_3 , OsO_4 , V_2O_5 , WO_3 , Y_2O_3 , ZnO , ZnTe , ZrO_2 , and combinations thereof.

[00049] Preferably the inorganic additive comprises a one or more of a lead compound, a bismuth compound, a thallium component, a tellurium component, and combinations thereof. Preferably the inorganic additive comprises lead oxide, bismuth oxide, thallium oxide, and tellurium oxide.

[00050] In one aspect, the inventive conductive paste compositions include between about 0.1wt% to about 5.0wt% inorganic additive. More preferably, the inventive conductive paste compositions include inorganic additive in an amount of about 0.5wt% to about 4.0wt%.

[00051] In one aspect, the inventive paste composition includes about 0.05wt% to about 2.5wt% lead oxide, preferably between about 0.1 wt% to about 0.75wt% lead oxide.

[00052] In one aspect, the inventive paste composition includes about 0.05 wt% to about 2.5wt% tellurium oxide, preferably between about 0.1 wt% to about 2.0wt% tellurium oxide, more preferably about 0.1wt% to about 0.75wt% tellurium oxide.

[00053] In one aspect, the inventive paste composition includes about 0.01wt% to about 2.5wt% bismuth oxide and preferably about 0.05% to about 0.5wt% bismuth oxide.

[00054] In one aspect, the inventive paste compositions include about 0.01wt% to about 5.0wt% of glass frit, preferably about 0.05wt% to about 2.5wt% of glass frit, more preferably about 0.1wt% to about 2wt% glass frit, even more preferably 0.1wt% to about <0.5wt% of glass frit, based on the total weight of the conductive paste composition. As indicated above, the inventive paste compositions may be glass free or be essentially glass free.

[00055] Typically glass frits are added to the paste compositions to etch through the insulating oxide-, nitride- or carbide-based anti-reflective coating (ARC), and layer(s) on the surface of the silicon wafer.

[00056] When glass frit is included in the conductive paste compositions, one or more of the following may be present in the glass frit: Ag_2Te , AgAsF_6 , Ag_3AsO_4 , AgBF_4 , AgBr , AgCl , AgClO_4 , AgF , AgF_2 , AgHF_2 , AgI , Ag_2MoO_4 , AgPF_6 , AgPO_4 , AgReO_4 , Ag_2SO_4 , Ag_2S , AgSbF_6 , AgVO_3 , Ag_2WO_4 , Al_2O_3 , As_2O_3 , AuTe_2 , BaO , B_2O_3 , BaF_2 , BaO , Bi , BiBr_3 , BiCl_3 ,

BiF₃, Bi₄Ge₃O₁₂, BiI₃, Bi₂MoO₆, Bi₂Mo₃O₁₂, Bi₂O₃, Bi(OH)₃, BiSb, Bi₂Se₃, Bi₂S₃, Bi₂Te₃, BiVO₄, Bi₂(WO₄)₃, C₂O₃, CaO, CdO, CoO, CuO, Cu₂O, Ga₂O₃, In₂O₃, KAg₄I₅, LaF₃, La₂O₃, Li₂O, Li₃PO₄, MgO, Mn₂O₅, MnO₂, Mo₂O₃, NiO, P₂O₅, Pb, PbBr₂, PbCl₂, PbF₂, PbHPO₄, PbI₂, PbO, PbSO₄, PbSe, PbS, PbSb, PbTe, Pb(VO₃)₂, ReO₂, ReO₃, Re₂O₇, RuO₂, Sb₂O₃, SeO₂, SO₂, SO₃, SiO₂, SnO₂, SrF₂, SrO, Tb₂O₃, Tb₄O₇, TeBr₄, TeCl₄, TeI₄, TeO₂, TiO₂, TlF, Tl₂O₃, OsO₄, V₂O₅, WO₃, Y₂O₃, ZnO, ZnTe, and ZrO₂

[00057] In one aspect, the glass frit comprises a lead compound, a tellurium compound, a bismuth compound and/or a thallium compound. In another aspect, the glass frit includes both lead oxide and tellurium oxide, in another aspect the glass frit contains lead oxide, tellurium oxide, bismuth oxide and a thallium compound, e.g., thallium oxide.

[00058] In one aspect, the glass frit comprises about 5wt% to about 60wt% lead oxide, preferably about 10wt% to about 50wt% lead oxide.

[00059] In one aspect, the glass frit comprises about 20wt% to about 70wt% tellurium oxide, preferably about 10wt% to about 60wt% tellurium oxide.

[00060] In one aspect, the glass frit comprises about 5wt% to about 20wt% bismuth oxide, preferably about 10wt% to about 15wt% bismuth oxide.

[00061] In one aspect, the glass frit comprises about 1wt% to about 60wt% thallium oxide, preferably about 1wt% to about 50wt% thallium oxide.

[00062] In one aspect, the inventive conductive paste composition includes silver powder as the conductive material. The silver powder may have an average specific surface area (SSA) of about 0.6m²/g to about 1.5m²/g and preferably has a particle size D50 of about 0.1μm to about 5μm, and more preferably of about 0.5 μm to about 2μm.

[00063] The silver powder is not limited in morphology and may be spherical, elliptical, etc. and typically may be thermally sintered to form a conductive network during a solar cell metallization firing step.

[00064] Furthermore the silver powder may be pre-coated with different surfactants to avoid particle agglomeration and aggregation. The surfactant may be a straight-chain, or branched-chain fatty acid, a fatty acid ester, fatty amide or mixtures thereof.

[00065] Two or more silver powders may be included in the inventive conductive paste compositions. When this is the case, a higher silver particle packing density may be attained, and the proximity of the silver particles to each other facilitates silver densification during the firing process. This results in a more connected conduction path, which may improve the solar cell efficiency.

[00066] The silver powder preferably has a purity of greater than 99.5%. Impurities such as Zr, Al, Fe, Na, Cl, K, and Pb may be present. Preferably, the impurity concentration of any one impurity is less than about 100ppm.

[00067] The conductive paste compositions according the present invention may include silver powder in an amount of about 40wt% to about 98wt%, preferably about 70wt% to about 95wt%, and more preferably about 87wt% to about 93wt%.

[00068] The conductive paste compositions include about 1 wt% to about 10wt% of the organic medium, preferably about 2wt% to about 8wt% of organic medium, and more preferably about 4wt% to about 6wt% of organic medium.

[00069] In one aspect, the organic medium includes resin, rosin and/or a solvent.

[00070] In one aspect, the resin is selected from one of acrylic resin, epoxy resin, phenol resin, alkyd resin, cellulose polymers, polyvinyl alcohol, rosin, and combinations thereof. Preferably, the resin is hydroxypropylcellulose (HPC), hydroxyethylcellulose (HEC), or a combination thereof.

[00071] In one aspect, the organic medium comprises about 0.2wt% to about 2 wt % resin or rosin, preferably about 0.5wt% to about 1.5 wt % resin or rosin.

[00072] The solvent may be Texanol® (common name: 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), propanol, isopropyl alcohol, ethylene glycol, diethylene glycol derivatives, toluene, xylene, dibutyl carbitol, terpineol, and mixtures thereof.

[00073] The solvent may also be dimethylethanolamine (2-(dimethylamino) ethanol, 2-aminoethanol (ethanolamine), 1, 2-propanediol (propylene glycol), 1, 3-butanediol, diethylene glycol, dipropylene glycol, aniline, water, glycerol, 1, 5-pentanediol, benzyl alcohol, 3-methylphenol (m-Cresol), and mixtures thereof.

[00074] In one aspect, the solvent has a surface tension greater than 35 dyne/cm, and the organic medium includes about 2wt% to about 80wt% of solvent.

[00075] The conductive paste compositions may further comprise a thixotropic agent which may be cellulose polymer, ethyl cellulose, hydroxyethyl cellulose, castor oil, hydrogenated castor oil, an amide modified castor oil derivative, a fatty amide, and combinations thereof.

[00076] Suitable thixotropic agents can be obtained from Rockwood Additives, Cray Valley, or the Troy Corporation.

[00077] The conductive paste compositions may also include a dispersant, for example, a long-chain fatty acid, such as, for example, a stearic acid with a functional amine group, acid ester, alcohol groups, and combinations thereof.

[00078] Suitable commercially available dispersants include BYK 108, BYK 111, Solsperse 66000 and Solsperse 27000, which can be obtained from Akzo Nobel, Byk, Lubrizol or Elementis.

[00079] For rheology modification of the inventive conductive paste compositions, one or more long chain alcohols may be included therein. Examples of such products include the Isofol® products commercially available from Sasol.

[00080] As indicated, one inventive aspect is that the inventive compositions are conductive paste compositions. The conductive paste compositions may have a viscosity of about

50Pa*s to about 250Pa*s at 10 reciprocal seconds and 25°C, using a 20mm diameter, 0 degree cone and plate system. Viscosity tests can be made with an AR-2000 Rheometer, as sold by TA Instruments, or an equivalent piece of equipment.

[00081] Another inventive aspect of the present disclosure is a method for making the inventive conductive paste compositions described herein.

[00082] Yet another inventive aspect of the present disclosure is a coated substrate comprising a substrate coated with the inventive conductive paste compositions described herein. Still yet another inventive aspect is a method of preparing a coated substrate with the inventive conductive paste compositions described herein.

[00083] In one aspect, the substrate may comprise semiconductor material, such as, for example, a silicon-containing semiconductor material. In another aspect, the semiconductor material is a silicon wafer that is employed as a substrate.

[00084] The inventive conductive paste compositions may be used to provide front contact electrodes for crystalline silicon solar cells wherein the substrate is a silicon wafer.

[00085] The process for preparing a coated substrate comprises

- a) applying a conductive paste composition according to the present invention to a surface of the substrate and
- b) drying the composition.

[00086] The conductive paste compositions may be prepared by forming an organic vehicle by combining organic resins, rosins and solvents, and mixing the organic vehicle with one or more of dispersants, thixotropic agents, and alcohols.

[00087] The consistency of the organic vehicle is usually in the form of paste with a viscosity preferably between 50 to 250Pa*s at 10 reciprocal seconds on a cone and plate system measured using a TA Rheometer or equivalent piece of equipment.

[00088] During the firing of the silicon wafer, it is desirable that the organic resins and rosins burn off during the firing, thereby leaving no residues on the wafer. The organic resins and rosins included in the organic medium may be chosen to attain this outcome.

[00089] The solvent should be able to dissolve the resins, rosins, and thixotropic agents, and preferably is capable of aiding the print quality conductive paste compositions. The solvent should evaporate during the subsequent drying step.

[00090] In another inventive aspect, described is a process for making a solar cell having electrodes printed thereon. The process comprises applying a coating of the inventive conductive paste composition onto the front side surface of a silicon wafer as the anode side. The coated silicon wafer is then fired. In another inventive aspect, the process for making a solar cell further comprises applying overlapping layers comprising aluminum and silver to the back side surface of the silicon wafer as the cathode side. The coated silicon wafer is then fired. The number of overlapping layers may be two (2).

[00091] The inventive conductive paste composition may be deposited on a silicon wafer by screen printing same through a stainless steel mesh screen. Stroke movement across the screen provides a high shear rate that thins the viscoelastic conductive paste composition as it rolls over and passes through micro-channels of mesh pattern of the screen. The size of the micro-channels is mesh type dependent. Mesh size may be about 200 wires to about 400 wires per inch. It is desirable that the fine grid lines, or “fingers”, be as narrow as possible to leave more open area for sunlight collection, while also being wide enough to maintain good print quality. The height of the printed fingers may be about 10 microns to about 35 microns. Taller fingers that are continuous, without roughness or valleys, may advantageously reduce the resistance to current, and also may advantageously improve the efficiency of the solar cell.

[00092] In one aspect in which the inventive conductive paste compositions are used in the manufacture of crystalline silicon solar cells, solar cell manufacturers may begin with doped silicon wafers of either p-type or n-type.

[00093] With regard to a p-type wafer, the wafer may be doped with p-type elements such as boron at concentrations of approximately about 10^{16} atoms/cm³. The wafer is preferably chemically cleaned to reduce impurities that could impact the optical or electrical properties of the silicon. The wafer may then be chemically textured to make it less reflective, thereby improving its light capturing capabilities. The wafer is then exposed to an n-type dopant, such as phosphorus, in either a gaseous or liquid state. The n-type dopant diffuses into the silicon wafer at temperatures up to 1000°C. Following diffusion, a surface “phos-glass” layer is chemically removed to expose the doped silicon surface underneath. Phosphorus concentrations remaining at the surface of the wafer are on the order of about 1 to about 10×10^{20} atoms/cm³, or about 1 phosphorous atom for every 1,000 to 10,000 silicon atoms.

[00094] The phosphorous concentration drops off below the surface, as is common to a diffusion profile in a solid, until it reaches the same concentration as the boron dopant, typically at a depth of about 100nm to about 300nm. The depth of this net-zero charge is the location of the diode, whereby electrical charges preferentially flow in one or the other direction based on the sign of the charge. In this way, the conductive electrons are captured by the emitter to diffuse to the anode.

[00095] Preferably, a step to provide electrical isolation is performed since the top, bottom and side edges may have the n-type dopant diffused into them. The “positive” side may be isolated from the “negative” sides of the cell by chemically removing the doped material from the edges of the wafer and from the back-side of the cell.

[00096] The optical and electrical qualities of the wafer may be improved by depositing dielectric materials such as, for example, H:SiN_x and/or SiO_x on the light receiving surface(s) of the wafer at a total thickness of about 70 angstroms to about 120 angstroms. A film of this material may serve as an anti-reflective coating (ARC) to the silicon. The hydrogen from the ARC layer may passivate dangling electric bonds at the surface and grain boundaries of the silicon.

[00097] At this point the wafer has properties of a working solar cell. When light shines on the wafer, electrical current will flow and a voltage difference can be measured between the

opposing wafer surfaces. To extract the current and voltage (power) from the cell, electrodes are screen printed onto the wafer.

[00098] A conductive paste employed in providing back bus bars is printed onto a minor area on the backside of the wafer (e.g., cell). The back bus bar paste is then dried by heating the cell to about 250°C, which volatilizes the solvents in the paste and results in their removal therefrom.

[00099] A less conductive paste, for example, an aluminum paste, is printed on the remaining backside area of the wafer. The printed aluminum paste layer overlaps the edges of the bus bar paste so that current delivered to the bus bar pads may disperse to the full rear face of the cell. The aluminum paste is then dried.

[000100] A conductive paste composition in accordance with the present invention is screen printed in a grid-like pattern on the front (e.g., light-exposure) side of the cell. Narrow silver grid lines on the screen, which are preferably less than 40µm wide, are narrowly spaced at a separation of about 1.4mm to maximize the amount of light incident on the silicon while reducing the in-plane resistance of electrons that will flow through the emitter on their way to being collected by the silver anode material.

[000101] The combination of silver powders and organic ingredients is intended to print through the narrow passages without interrupting the fine lines formed from the steel mesh of the screen. Having a sufficient amount of silver be transferred in continuous lines so that the grid lines themselves give minimal resistance to the current flow is the objective. To attain sufficient transfer of silver and to minimize resistance and line spreading, a high aspect ratio, e.g., line height divided by line width, of the fine lines should be maintained. With line widths of about 40µm, these heights should exceed about 12µm to deliver an aspect ratio (AR) of about ≥ 0.3 .

[000102] The rheology of the organic vehicle should provide shear thinning and settling properties without excessive spreading after the inventive conductive paste composition is applied to the wafer. Using binder materials may provide particle-to-particle cohesion that keeps the conductive paste composition from breaking apart ("binder", as used herein, refers

to the organic components of the organic vehicle system that result in particle-to-particle interaction. This may include the resins, rosins and thixotropes). Cohesion reduces the shading of the cell by limiting spreading and retaining straight line edges. The selection of the chain length of the binder material, its degree of substitution of hydroxyl groups and the percent loading of these binders can impact the line spreading and influence how clean the line edges are.

[000103] Following the drying of the conductive paste composition on the front side of the wafer, the wafer may be “fast fired” in which it reaches peak temperature near 800°C. The wafer is then rapidly cooled, e.g., in less than one minute, to room temperature. During this firing step, the aluminum paste reaches a eutectic point with the silicon and functions as a dopant to form a p+ back surface electric field, which drives electrical current in the preferred direction. Also, the amorphous dielectric anti-reflection coating bonds to the silicon. During the firing step, electrodes are formed between the wafer and the inventive conductive paste composition. The organic binder in the conductive paste volatilizes, and excess carbon is taken away by the oxygen provided by materials in the conductive paste composition.

[000104] Additives that flow to the surface of the silicon wafers etch through the insulating oxide and/or nitride ARC layers. The matrix of additives and glass that remain among the metal increases the cohesive network strength of the fired conductive paste composition. The network aids in the adhesion properties to the interconnect wires that will be soldered to the bus bar sections of the finished cell. The conductive powders either sinter into bulk metals, form colloids suspended in the additive and glass matrix at the interface with the silicon, or recrystallize onto the surface of the silicon. The silver crystallites provide the pathway for electrical current to move from the silicon into the bulk silver of the overlying silver grid. The fired silver grid acts as an electrical current collector and feeds the current to the printed front bus bars pads.

[000105] Conduction across the silicon/metal/glass/metal portion of the electrode is related to the efficiency of the solar cell in converting light into electrical power. Reducing the thickness of the glassy layer should reduce circuit resistance and therefore improve solar cell efficiency. By including inorganic additives in the inventive conductive paste compositions in lieu of glass, thereby reducing the amount of glass in the paste and by extension in the

electrode after formation thereof on the silicon wafer, it is believed that a reduction in the thickness of the glassy layer is achieved. Further, the composition of the inorganic additive in the conductive paste composition may impact the magnitude of colloidal silver particle loading, solubility of the silver in the inorganic additive, and the segregation influences of the silver to crystallize onto the silicon surface. For example, the segregation influence can be observed upon removal of the paste, in the density and size of silver islands that appear on the surface of the wafer. A high density and small size is the preferred result. Conductivity across this region is measured as contact Resistance (R_C), which is inversely proportional to the fill factor (FF). Power in the solar cell is calculated by multiplying the short circuit current (I_{SC}) by the open circuit voltage (V_{OC}) by the FF ($(I_{SC}) \times (V_{OC}) \times (FF)$). Cell efficiency is determined by normalizing the power to the cell area.

[000106] While the present inventive conductive paste compositions are described in relation to photovoltaic devices such as solar cell, they have other useful applications. For example, they can find use in the preparation of optically reflective applications, sealing glass pastes, etchant pastes, conductive pastes used for shielding purposes, and carrying electrical current in electronic circuit or inductive applications.

[000107] The invention is further described by the examples given below.

EXAMPLES

Example 1: Procedure for Making Ag-Containing Conductive Paste Compositions

[000108] Step 1: A formulation for an organic medium is shown in Table 1. The organic medium is made by dissolving the resins and rosins in the solvent solution (ingredients 1-4) at 60°C while mixing. After returning to room temperature, the thixotropic agent (ingredient 5) is added to the mixture and the mixture is slowly brought to 60°C while mixing. It is held at 60°C for 30 minutes before cooling.

Table 1. Vehicle formulation used in pastes discussed in the following Examples.

	Ingredient	wt. %
1	2,2,4-Trimethylpentanediol diisobutyrate	41.0
2	2-(2-Butoxyethoxy)ethyl acetate	34.0

3	Ester of Hydrogenated rosin	9.0
4	Ethyl cellulose 48.0-49.5 Ethoxyl %	3.0
5	Micronized amide wax rheology modifier	13.0
	Total	100.0

[000109] Step 2: The organic medium is mixed with the dispersant, additives and glass identified in Table 2 (ingredients 1-8) until the blend is homogenous.

Table 2. Silver paste formulation used in conductive paste compositions discussed in the following Examples.

	Ingredient	wt. %
1	Table 1 Organic Medium	4.859
2	Dispersant	1.4
3	Zinc oxide, ZnO	0.3
4	Lithium phosphate, LiPO ₄	0.15
5	Bismuth oxide, Bi ₂ O ₃ , nano-powder (36nm)	A
6	Lead oxide, PbO	B
7	Tellurium oxide, TeO ₂	C
8	Glass	1.691 Minus (A+B+C) – see Table 3
9	Ag powder	90.6
10	Withheld solvent and/or vehicle	1.0
	Total	100.0

[000110] Step 3: The silver powder (ingredient 9) is then added and mixed until the powder is wet out and no clumps remain.

[000111] Step 4: The paste viscosity is tested on a TA Rheometer at 10 reciprocal seconds.

[000112] Step 5: The viscosity of the paste is adjusted using ingredient 10 of Table 2 according to the following: the amount of solvent, 2,2,4-trimethylpentanediol diisobutyrate is

added based upon the measured viscosity. Approximately 0.1wt% of the solvent lowers the viscosity by 10Pa-s. Adequate solvent is added to reach the target viscosity of 140Pa-s (± 10) at 10 reciprocal seconds using a zero degree cone and plate on an AR-2000EX rheometer from TA Instruments or similar. The vehicle has minimal impact on the paste viscosity. The remainder of the 1% withheld material comes from the vehicle, which is added at an appropriate amount to bring the paste up to 100wt%.

[000113] Step 6: The mixture from Step 5 is then processed in multiple passes on a three-roll mill where particles in the mixture are further de-agglomerated and dispersed. Using the 4th scratch method for measuring the ‘fineness of grind’, the paste should reach preferred particle size of $< 15\mu\text{m}$. The preferred viscosity of the conductive paste compositions thus prepared at 10/s and 25°C is about 100Pa*s to about 200Pa*s, more preferably about 130Pa*s to about 150Pa*s as measured using a zero degree cone and plate on an AR-2000EX rheometer from TA Instruments.

Example 2: Fabrication of Solar Cells and Electrical Performance Testing

[000114] In the test examples given below, the silicon wafers used are mono-crystalline, 125mm x 125mm, and have an emitter sheet resistance of 80 ± 10 Ohm/square. Preparation includes the following steps.

- 1) 1.0g of Al paste is screen printed on the entire back-side of each silicon wafer except for a margin of about 1.5mm around the edge. The screen parameters used for printing Al paste are: 325mesh, 0.9mil wire diameter, $10\mu\text{m}$ emulsion-over-mesh (EOM), and a 45° bias. The squeegee shore hardness is 80. Cells are then dried in a BTU International D914 dryer with a belt speed of 90 inches per minute, ipm, and zone temperatures settings of 310°C, 290°C, and 285°C.
- 2) The conductive paste composition is screen printed on the front surface of the silicon wafers. The screen printing parameters are: 360mesh, 0.6mil wire diameter, and $15\mu\text{m}$ EOM and a 22.5° bias. The squeegee shore hardness is 70. Fine finger line openings on the screen are held at $45\mu\text{m}$. The cells are dried at a belt speed of 165 inches per minute (imp) with zones 1-3 set at the respective temperatures of 340°C, 370°C and 370°C.
- 3) The metallized wafers are fired in a BTU International PV309 firing furnace at a belt speed of 200ipm and zones 1-4 set at 850°C, 790°C, 880°C and 1000°C.

[000115] A Solar Simulator/I-V tester from PV Measurements Inc. is used to measure the electrical performance metrics of open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), fill factor (FF), efficiency (Eff), and series and shunt resistances (R_S , R_{SH}). The illumination of the lamp is calibrated using a sealed calibration cell with the measured characteristics adjusted to the standard AM1.5 spectral conditions at $1000\text{mW}/\text{cm}^2$. During testing, cells are positioned on a vacuum chuck under the lamp with the chuck temperature maintained at 25°C . Both dark and light I-V curves are collected by sweeping voltage between -0.2V up to $+1.2\text{V}$ and measuring the current output. The results are obtained using commercially available computer software.

[000116] A Suns-Voc tester, available from Sinton Instruments, is used to evaluate shunting and recombination mechanisms that may be associated to the metallization pastes. Cells are placed onto a base plate probe and the top-side bus bar is contacted with a probe. The cell voltage is measured as the cell is subjected to a variable light intensity pulse, thus providing a voltage versus light intensity curve. Sinton software calculates cell performance metrics from this data. The relevant metrics reported below include the pseudo-efficiency (Ps-Eff), ' $0.1\text{ Sun } V_{OC}$ ' and the electrical current recombination metric ' J_{O2} '.

Example 3: Additives Delivering Low-Resistance Electrical Contact and High-Efficiency Cell

[000117] Glasses were prepared by mixing varied amounts of PbO , TeO_2 , Bi_2O_3 , and Tl_2O_3 . One kilogram of the oxide mixtures were heated in alumina crucibles to 900°C for one hour and the melt was sparged with oxygen. The melted glass mixture was then poured into deionized water to quench it into a frit. The material was ball milled with zirconia media to lower the particle size distribution to a D50 value below $2.0\mu\text{m}$. The media was then removed and the remaining powder was dried.

[000118] Conductive paste compositions are made according to the process set forth in Steps 1 thru 6 of Example 1. Table 3 provides the amount of additives used in each of the pastes as designated by the variables 'A', 'B' and 'C' for ingredients 5, 6, and 7 in Table 2. Conductive paste compositions were made with one or more glasses, the compositions of which are reported in Table 4. The glass component follows the recipe of ingredient 8 in Example 1.

[000119] Paste 98A is a reference paste with a glass loading of 1.68wt%. Pastes 98B to 98P are used to evaluate different pathways to supplant glass with additives. Whether in bound or free states, as glass or additive forms, the wt% of the Bi_2O_3 , PbO , TeO_2 and Tl_2O_3 were held constant in the paste compositions shown in Table 3. The impact from the total amount of glass replaced, and how the ratio of free to bound material impacts the electrical performance were evaluated.

[000120] The amount of inorganic additives in pastes 98B to 98P ranges from 1.519 wt% to 0.15 wt% and as free components they are present from 0.23wt% to 1.76wt%. The free to bound ratios (for example, the wt% bismuth oxide as additive divided by wt% bismuth oxide as glass) for Bi_2O_3 , PbO and TeO_2 are also shown in Table 3. For the non-reference pastes 98B thru 98P, the free to bound Bi_2O_3 ranges from 0.12 to 10.21, for PbO it goes from 0.00 to infinity and for TeO_2 it spans 0.00 to 14.58.

Table 3. Inorganic Additives in the Formulations

	Additive Wt% (Free)				Glass Wt% (Bound)					Free to Bound Ratio			Wt% Total Additives cited + Glass
	A = Bi ₂ O ₃	B = PbO	C = TeO ₂	Total Wt %	Bi ₂ O ₃	PbO	TeO ₂	Tl ₂ O ₃	Total Wt%	Bi ₂ O ₃	PbO	TeO ₂	
Paste													
98A	0.011	-	-	0.011	0.207	0.664	0.72	0.084	1.680	0.05	-	-	1.691
98B	0.183	0.664	0.573	1.421	0.035	-	0.151	0.084	0.271	5.22	∞	3.78	1.691
98C	0.199	0.664	0.678	1.541	0.020	-	0.047	0.084	0.150	10.21	∞	14.58	1.691
98D	0.168	0.603	0.521	1.291	0.051	0.061	0.204	0.084	0.400	3.28	9.91	2.55	1.691
98F	0.168	0.555	0.567	1.291	0.050	0.109	0.157	0.084	0.400	3.35	5.11	3.61	1.691
98G	0.138	0.486	0.420	1.043	0.081	0.178	0.305	0.084	0.648	1.69	2.73	1.38	1.691
98H	0.149	0.486	0.497	1.132	0.070	0.178	0.228	0.084	0.560	2.13	2.73	2.18	1.691
98J	0.060	0.190	0.164	0.414	0.158	0.474	0.561	0.084	1.277	0.38	0.40	0.29	1.691
98K	0.065	0.189	0.194	0.448	0.154	0.474	0.531	0.084	1.243	0.42	0.40	0.37	1.691
98L	0.184	0.552	0.673	1.409	0.035	0.112	0.052	0.084	0.282	5.27	4.95	12.98	1.691
98M	0.184	0.622	0.603	1.409	0.035	0.042	0.122	0.084	0.282	5.27	14.94	4.95	1.691
98N	0.023	0.149	-	0.172	0.196	0.515	0.725	0.084	1.519	0.12	0.29	-	1.691
98P	0.025	-	0.159	0.183	0.194	0.664	0.566	0.084	1.508	0.13	-	0.28	1.691

[000121] Table 4 shows the unit conversion between the wt% in the conductive paste composition and the relative wt% and mol% present in the glass.

Table 4. Glass Formulations, Re-Stated In Terms of Relative Weight And Molar Percentages

Paste	Wt% Glass in paste	Wt% in Glass					Mol% in Glass				
		Bi ₂ O ₃	PbO	TeO ₂	Tl ₂ O ₃	Total	Bi ₂ O ₃	PbO	TeO ₂	Tl ₂ O ₃	Total
98A	1.68%	12%	40%	43%	5%	100%	5%	37%	56%	2%	100%
98B	0.27%	13%	0%	56%	31%	100%	6%	0%	79%	15%	100%
98C	0.15%	13%	0%	31%	56%	100%	8%	0%	56%	36%	100%
98D	0.40%	13%	15%	51%	21%	100%	6%	15%	69%	10%	100%
98F	0.40%	13%	27%	39%	21%	100%	6%	28%	56%	10%	100%
98G	0.65%	13%	27%	47%	13%	100%	6%	26%	62%	6%	100%
98H	0.56%	12%	32%	41%	15%	100%	6%	31%	56%	7%	100%
98J	1.28%	12%	37%	44%	7%	100%	6%	34%	57%	3%	100%
98K	1.24%	12%	38%	43%	7%	100%	6%	36%	56%	3%	100%
98L	0.28%	12%	40%	18%	30%	100%	7%	46%	30%	17%	100%
98M	0.28%	12%	15%	43%	30%	100%	6%	15%	63%	15%	100%
98N	1.52%	13%	34%	48%	6%	100%	6%	31%	61%	2%	100%
98P	1.51%	13%	44%	38%	6%	100%	6%	42%	50%	3%	100%

Table 5. Average Electrical Performance Metrics for 10 Cells of Each of the 98 Series Conductive Paste Compositions

Electrical Performance Metrics										
Paste	I _{sc} (A)	V _{oc} (V)	FF (%)	Eff (%)	R _s (Ohm)	R _{sh} (Ohm)	I _{REV} @ - 12V (A)	Ps- Eff (%)	0.1 sun V _{oc} (V)	J _{O2} (nA/cm ²)
98A	5.78	0.637	77.5	18.45	1.04	10032	-0.10	19.4	0.566	3.74
98B	5.79	0.637	77.3	18.45	1.09	6323	-0.20	19.4	0.566	2.57
98C	5.80	0.637	76.9	18.36	1.17	6064	-0.19	19.4	0.566	2.21
98D	5.80	0.637	77.4	18.46	1.09	7411	-0.18	19.5	0.566	1.72

98G	5.78	0.637	77.5	18.43	1.06	8317	-0.13	19.4	0.566	3.29
98H	5.78	0.637	77.5	18.43	1.06	8943	-0.13	19.4	0.566	2.28
98J	5.79	0.637	77.6	18.48	1.05	12103	-0.10	19.5	0.566	2.77
98K	5.82	0.637	77.5	18.56	1.06	12438	-0.08	19.5	0.567	1.97
98L	5.78	0.637	77.2	18.36	1.13	8806	-0.11	19.4	0.566	1.38
98M	5.81	0.637	77.5	18.54	1.06	9911	-0.16	19.5	0.567	1.35
98N	5.79	0.637	77.3	18.41	1.10	13749	-0.09	19.4	0.566	3.83
98P	5.80	0.637	77.5	18.51	1.06	10783	-0.09	19.5	0.567	3.34

[000122] Table 5 reports the average measured electrical response for ten (10) cells prepared from each conductive paste composition. Since efficiency, Eff, is proportional to the product of I_{SC} , V_{OC} and FF, it is important to note that the intended primary impact from the paste is on the FF. The function of modifying the paste is to lower the contact resistance portion of the series resistance, R_s , which in turn impacts the FF. While other factors such as R_{SH} and J_{02} can impact the FF, it was observed that R_s drives the FF values in this study through the strong correlation shown in Figure 1. Therefore, particular attention is paid to the R_s response from paste to paste, as it is the key indicator for contact resistance. By delineation as the R_s value decreases, the contact resistance is improved, such that smaller R_s numbers are preferred.

[000123] In comparing the wt% of glass to electrical performance between Tables 3 and 5, there is no correlation that indicates using more glass improves performance. Electrical performance does not rely on the amount of glass but rather on the interaction of the compositions of the additives and the glass. Thus, indicating the feasibility of replacing glass materials with additives as a practical means of achieving good electrical contact to silicon solar cells.

[000124] The free to bound ratios for the additives and the glass components were considered. From the electrical response values reported in Table 5 and the free to bound ratios reported in Table 3, the V_{OC} is 0.637V for all conductive paste compositions and variations in I_{SC} are minor compared to those from FF. Similarly, variations in Ps-Eff and J_{02} are similar for each result. Therefore, the electrical performance metrics are evaluated based solely on the series resistance, R_s . Increasing the free to bound ratio for Bi_2O_3 has no negative impact up to at least a ratio of 5 as observed in conductive paste compositions 98B

and 98M, and possibly higher. Similarly, the free to bound ratio for PbO has no restrictions from a value of 0.12 in paste 98N to a full replacement of bound PbO in pastes 98B and 98C. Comparing the R_s values observed in 98C and 98L to that of 98M, it appears that the free to bound ratio for TeO_2 exhibits good results (similar to comparative example 98A) at a ratio of up to 12, and possibly higher. The free to bound ratio observations above are limited to the confines of the inorganic systems evaluated and are not intended to indicate generalized limitations.

Example 4: Lowering the Amount of Glass in Conductive Paste Compositions

[000125] Comparable series resistance can be delivered when additives are used wholly or in part in place of glass in pastes, as shown in this example. In the conductive paste compositions of this example, the free to bound loading is varied to identify how performance is impacted.

[000126] The Example 4 pastes are made identically to the recipe provided in Example 1. The formulation is outlined in Table 6 and the values for the variables, A, B, C, X and Y are provided in Table 7.

Table 6. Conductive Paste Compositions used in Example 4

	Ingredient	wt. %
1	Table 1 Vehicle	5.12
2	Dispersant	1.4
3	Zinc oxide, ZnO	0.3
4	Lithium phosphate, LiPO_4	0.15
5	Bismuth oxide, Bi_2O_3 , nano-powder (36nm)	A
6	Lead oxide, PbO	B
7	Tellurium oxide, TeO_2	C
8	Glass	X
9	Ag powder	92.03 - Y
10	Deficient (solvent and/or vehicle)	1.0
	Total	100.0

[000127] Conductive paste compositions were prepared in which the glass amount varied from 0.55wt% to 0.00wt%, with the bound glass components being replaced by free inorganic additives. The total amount of additives and glass is not held constant like in the 98 series of pastes. The range of free to bound ratios for the Bi_2O_3 and TeO_2 are expanded compared to the 98 series while the free to bound PbO still ranges from zero to infinity.

[000128] The same glass is used for all pastes, which was also used for paste 98M of Example 3. The silver wt% was adjusted in order to hold the solids loading constant for all pastes, where the total ‘solids’ comprise ingredients 3 thru 10 in Table 6. Maintaining a constant solids load helps normalize the printability of the pastes to minimize paste to paste differences in I_{SC} .

Table 7. Wt% and Free To Bound Ratios for the Conductive Paste Compositions of Example 4

Paste	Additives Wt%				Glass Wt%				Free to Bound Ratio				Y = Total Wt% Additives + Glass (A+B+C+X)
	A = Bi ₂ O ₃	B = PbO	C = TeO ₂	Total wt%	Bi ₂ O ₃	PbO	TeO ₂	Ti ₂ O ₃	X=Total wt%	Bi ₂ O ₃	PbO	TeO ₂	
113 Ref	0.011	-	-	0.011	0.207	0.664	0.725	0.084	1.680	0.05	-	-	1.691
98M	0.184	0.622	0.603	1.409	0.035	0.042	0.122	0.084	0.282	5.27	14.94	4.95	1.691
113A	0.143	0.590	0.573	1.306	0.034	0.040	0.118	0.082	0.274	4.21	14.57	4.85	1.580
113B	0.116	0.424	0.479	1.018	0.061	0.073	0.213	0.147	0.494	1.90	5.81	2.25	1.512
113C	0.129	0.507	0.526	1.162	0.047	0.057	0.166	0.114	0.384	2.72	8.94	3.18	1.546
113D	0.156	0.673	0.621	1.450	0.020	0.024	0.071	0.049	0.165	7.69	27.69	8.75	1.614
113F	0.170	0.756	0.668	1.594	0.007	0.008	0.024	0.016	0.055	25.07	93.33	28.24	1.648
113G	0.177	0.797	0.692	1.666	-	-	-	-	-	∞	∞	∞	1.666

[000129] From the electrical response values reported in Table 8, the V_{OC} and I_{SC} are similar for all conductive paste compositions while the paste-to-paste differences in FF appear to be primarily responsible for the changes to cell efficiency (Eff). Nonetheless, the efficiencies obtained are comparable, thus indicating the success of the approach toward using Free rather Bound oxides to form comparably good electrical contacts to solar cells.

Table 8. Electrical Performance Values for the Conductive Paste Compositions of Example 4

Electrical Performance Metrics										
Paste	I_{SC} (A)	V_{OC} (V)	FF (%)	Eff (%)	R_s (Ω m)	R_{SH} (Ω m)	I_{REV} @ -12V (A)	Ps-Eff (%)	0.1 sun V_{OC} (V)	J_{O2} (nA/cm ²)
113 Ref ^f	5.74	0.633	77.73	18.23						
98M ^l	5.76	0.633	77.77	18.32						
113A	5.76	0.633	77.77	18.33	0.99	7265	-0.19	19.21	0.561	9.16
113B	5.76	0.633	77.97	18.39	0.98	9093	-0.15	19.27	0.562	6.77
113C	5.76	0.633	77.98	18.37	0.98	7605	-0.15	19.27	0.562	6.67
113D	5.76	0.633	77.69	18.29	1.00	6419	-0.25	19.19	0.561	10.24
113F	5.76	0.632	77.63	18.26	1.01	8185	-0.15	19.19	0.560	10.21
113G	5.76	0.632	77.33	18.20	1.02	9005	-0.16	19.12	0.559	14.16

[000130] The 113 Ref is a trial-adjusted extrapolation of the comparative example paste 98A. The extrapolation for 98M values is based on average I_{SC} and V_{OC} values from the 113 series and using the FF from the similar paste 113A. The values input for 113 Ref are determined by translating the values from 98A with the same normalization factors used to adjust 113A values to 98M.

[000131] Table 8 shows that the conductive paste compositions of the present invention, which replace all or part of the glass (bound) with inorganic oxide additives (free), exhibit comparable series resistance properties.

[000132] In addition to making electrical contact, an additional function of the conductive paste composition may be to provide a means to interconnect the solar cells. This entails

printing large area solder pads onto the faces of the cell. These solder pads act as bus bars in which electricity can enter and leave a cell. The glass in the paste has historically played a major part in determining the adhesion strength between the bus bar and ribbons that inter-connect the cells.

[000133] Standard 180° peel strength methods are used to test adhesion between the ribbons and the bus bars of the solar cells using an Instron load cell. The fired paste constitutes the bus bars. Four pastes with different amounts of glass, and Free to Bound ratios were tested. The adhesion strength (N), i.e., Newtons) was averaged across each of eight bus bars tested for each paste. Figure 2 shows the adhesion between the tabbing ribbons and bus bars of multiple cells measured for pastes 113A, B, G, and F, and shows the distribution of the eight data points for each paste and reports the mean value for each paste along with the wt% glass in each paste. The results surprisingly indicate that the loading level of glass, or lack thereof, does not impact this adhesion. Therefore replacing Bound with Free state material does not degrade the secondary function of the pastes made with zero glass.

Example 5: Changing the Ratio of TeO_2 to Tl_2O_3 in the Conductive Paste Compositions

[000134] Conductive paste compositions were prepared in which the amounts of Tl_2O_3 and TeO_2 were varied from composition to composition, and the performance characteristics of the compositions was assessed based on the ratio of TeO_2 to Tl_2O_3 .

[000135] Conductive paste compositions were prepared as described in Example 1 using the components and amounts thereof set forth in Table 9. Glass frit was prepared as described in Example 3. Solar cells were prepared from these pastes as set forth in Example 2. The amounts of PbO and Bi_2O_3 in the glass were held constant, and as indicated, the amounts of TeO_2 and Tl_2O_3 , expressed as the ratio on a weight percentage basis of TeO_2 to Tl_2O_3 (wt% ratio) were varied, as shown in Table 10.

Table 9. Ingredients for Conductive Paste Compositions used in Example 5

	Ingredient	wt. %
1	Table 1 Vehicle	6.2
2	Dispersant	1.5
3	Additives; $\text{ZnO} + \text{Li}_3\text{PO}_4$	0.34

4	Glass containing $\text{Ti}_2\text{O}_3 + \text{TeO}_2 + \text{PbO} + \text{Bi}_2\text{O}_3$	1.96
5	Ag powder	89.0
6	Withheld solvent and/or vehicle	1.0
	Total	100.0

Table 10. Weight % of Inorganic Components in Example 5 Conductive Paste Compositions

Paste	TeO_2	Ti_2O_3	$\text{Bi}_2\text{O}_3 + \text{PbO}$	$\text{Li}_3\text{PO}_4 + \text{ZnO}$	$\text{TeO}_2:\text{Ti}_2\text{O}_3$
25A	19.699%	33.730%	32.183%	14.388%	0.58
25B	33.105%	20.342%	32.165%	14.388%	1.63
25C	34.435%	19.077%	32.101%	14.388%	1.81
25D	36.024%	17.585%	32.003%	14.388%	2.05
25F	36.925%	16.718%	31.969%	14.388%	2.21
25G	37.655%	15.686%	32.271%	14.388%	2.40
25H	39.039%	14.499%	32.074%	14.388%	2.69
25I	40.299%	13.711%	31.601%	14.388%	2.94
25J	53.010%	0.572%	32.030%	14.388%	92.64

Table 11. Mol % of Inorganics in the Example 5 Paste Compositions

Paste	TeO_2	Ti_2O_3	$\text{Bi}_2\text{O}_3 + \text{PbO}$	$\text{Li}_3\text{PO}_4 + \text{ZnO}$	$\text{TeO}_2:\text{Ti}_2\text{O}_3$
25A	27.047%	16.182%	40.060%	16.711%	1.67
25B	40.595%	8.716%	35.764%	14.925%	4.66
25C	41.781%	8.088%	35.393%	14.738%	5.17
25D	43.170%	7.363%	34.945%	14.521%	5.86
25F	43.938%	6.951%	34.711%	14.399%	6.32
25G	44.558%	6.486%	34.511%	14.446%	6.87
25H	45.706%	5.931%	34.152%	14.211%	7.71
25I	46.731%	5.556%	33.828%	13.886%	8.41
25J	56.102%	0.212%	30.844%	12.842%	265.13

Table 12. Weight % of Inorganics in the Glass of Example 5 Paste Compositions

Paste	TeO_2	Ti_2O_3	$\text{Bi}_2\text{O}_3 + \text{PbO}$	$\text{TeO}_2:\text{Ti}_2\text{O}_3$
25A	23.010%	39.399%	37.591%	0.58
25B	38.668%	23.761%	37.571%	1.63
25C	40.222%	22.283%	37.496%	1.81
25D	42.078%	20.540%	37.381%	2.05
25F	43.130%	19.528%	37.342%	2.21
25G	43.983%	18.322%	37.695%	2.40
25H	45.599%	16.936%	37.465%	2.69
25I	47.072%	16.016%	36.912%	2.94
25J	61.919%	0.668%	37.412%	92.64

Table 13. Mol % of Inorganics in the Glass of Example 5 Paste Compositions

Paste	TeO ₂	Tl ₂ O ₃	Bi ₂ O ₃ + PbO	TeO ₂ :Tl ₂ O ₃
25A	39.022%	23.347%	37.632%	1.67
25B	55.923%	12.007%	32.070%	4.66
25C	57.328%	11.097%	31.574%	5.17
25D	58.963%	10.057%	30.979%	5.86
25F	59.858%	9.470%	30.672%	6.32
25G	60.581%	8.818%	30.601%	6.87
25H	61.906%	8.034%	30.060%	7.71
25I	63.080%	7.499%	29.421%	8.41
25J	73.485%	0.277%	26.238%	265.13

[000136] From the electrical response values reported in Table 14, the V_{OC} and I_{SC} are similar for all conductive paste compositions. Pastes 25A and 25J, the outer ratios of TeO₂ to Tl₂O₃, e.g., 0.6 and 93 respectively, have larger values for series resistance, R_S, which cause the subsequent decrease in FF and Eff values. There is approximately a 0.2% drop in efficiency in the 25J (at a ratio of 93) compared to the pastes with TeO₂:Tl₂O₃ ratios between 1.3 and 2.9. This difference in efficiency provides an indication of the improvement believed to be due to including the thallium component. Similarly, the drop in efficiency observed from 25A relative to the other paste compositions is believed to be due to including the tellurium component. The inclusion of both a thallium component and a tellurium component in the conductive paste compositions improves the efficiency of the cell.

Table 14. Effect on Series Resistance and Fill Factor from Adjusting the Ratio of TeO₂ to Tl₂O₃ (Average of 10 Solar Cells)

Electrical Performance						
Paste	TeO ₂ :Tl ₂ O ₃	Isc	Voc	FF	Eff	Rs
25A	0.6	8.95	0.624	66.93	15.46	3.30
25B	1.3	8.97	0.626	79.65	18.48	0.635
25C	1.6	8.95	0.626	79.68	18.46	0.620
25D	2	8.94	0.627	79.69	18.44	0.627
25F	2.2	8.95	0.627	79.73	18.48	0.625
25G	2.4	8.94	0.626	79.68	18.44	0.616
25H	2.7	8.93	0.626	79.71	18.43	0.621
25I	2.9	8.93	0.626	79.73	18.43	0.623
25J	93	8.91	0.628	78.89	18.25	0.797

[000137] It was found that the presence of each of Tl_2O_3 and TeO_2 improves the series resistance of the conductive paste compositions. The improvement can be seen for example when the ratio of TeO_2 to Tl_2O_3 is in the range of 0.6 to 93 on a weight percentage basis. Due to the magnitude of the improvement, it may be that the lower contact resistance between the fired electrode paste and the silicon solar cell is the cause of the improvement. The presence of the Tl_2O_3 may lower glass transition temperature and flow properties, such that better electrical contacts can be made.

[000138] The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements on this invention that fall within the scope and spirit of the invention.

CLAIMS**WHAT IS CLAIMED IS:**

1. A conductive composition comprising:
a silver powder;
an organic medium;
an optional inorganic additive;
elemental thallium and/or a thallium containing compound;
elemental tellurium and/or a tellurium containing compound;
and optionally, a glass frit.
2. The composition of claim 1, wherein the elemental thallium and/or thallium containing compound is present in the composition as a component of the inorganic additive.
3. The composition of claim 1 or 2, wherein the elemental tellurium and/or tellurium containing compound is present in the composition as a component of the inorganic additive.
4. The composition of any preceding claim, wherein the elemental thallium and/or thallium containing compound is present in the composition as a component of the glass frit.
5. The composition of any preceding claim, wherein the elemental tellurium and/or tellurium containing compound is present in the composition as a component of the glass frit.
6. The conductive composition of any preceding claim, wherein the thallium containing compound is selected from an organothallium compound, thallium (I) oxide, thallium (III) oxide, thallium (I) bromide, thallium (I) carbonate, thallium (I) oxalate, thallium (I) iodide, thallium (I) fluoride, thallium (I) nitrate, thallium (I) sulfate, thallium (I) ethoxide, thallium (III) acetate, thallium (III) trifluoroacetate, thallium (I) hexafluorophosphate, thallium(I) 2-ethylhexanoate, thallium (I) hexafluoro-2,4-pentanedionate.

7. The conductive composition of any preceding claim, wherein the tellurium containing compound is selected from telluric acid, diisopropyl telluride, tellurium ethoxide, tellurium isopropoxide, antimony telluride, barium telluride, bismuth telluride, lanthanum telluride, lead (II) telluride, lithium telluride, manganese(II) telluride, manganese(IV) telluride, molybdenum telluride, nickel tellurate, nickel telluride, rhenium telluride, rhodium telluride, silver telluride, thallium telluride, titanium telluride, tungsten telluride, zinc telluride, tellurium oxide, tellurium bromide, tellurium chloride, and tellurium iodide.

8. The conductive composition of any preceding claim, wherein the elemental thallium and/or thallium containing compound comprises thallium oxide.

9. The conductive composition of any preceding claim, wherein the elemental tellurium and/or tellurium containing compound comprises tellurium oxide.

10. The conductive composition of any preceding claim, wherein the elemental thallium and/or thallium containing compound comprises thallium (III) oxide.

11. The conductive composition of any preceding claim, wherein the inorganic additive comprises one or more components selected from a chalcogenide, a pnictogenide, a halide, Ag_2Te , AgAsF_6 , Ag_3AsO_4 , AgBF_4 , AgBr , AgCl , AgClO_4 , AgF , AgF_2 , AgHF_2 , AgI , Ag_2MoO_4 , AgPF_6 , AgPO_4 , AgReO_4 , Ag_2SO_4 , Ag_2S , AgSbF_6 , AgVO_3 , Ag_2WO_4 , Al_2O_3 , As_2O_3 , AuTe_2 , BaO , B_2O_3 , BaF_2 , BaO , Bi , BiBr_3 , BiCl_3 , BiF_3 , $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, BiI_3 , Bi_2MoO_6 , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, Bi_2O_3 , $\text{Bi}(\text{OH})_3$, BiSb , Bi_2Se_3 , Bi_2S_3 , Bi_2Te_3 , BiVO_4 , $\text{Bi}_2(\text{WO}_4)_3$, C_2O_3 , CaO , CdO , CoO , CuO , Cu_2O , Ga_2O_3 , In_2O_3 , KAg_4I_5 , LaF_3 , La_2O_3 , Li_2O , Li_3PO_4 , MgO , Mn_2O_5 , MnO_2 , Mo_2O_3 , NiO , P_2O_5 , Pb , PbBr_2 , PbCl_2 , PbF_2 , PbHPO_4 , PbI_2 , PbO , PbSO_4 , PbSe , PbS , PbSb , PbTe , $\text{Pb}(\text{VO}_3)_2$, ReO_2 , ReO_3 , Re_2O_7 , RuO_2 , Sb_2O_3 , SeO_2 , SO_2 , SO_3 , SiO_2 , SnO_2 , SrF_2 , SrO , Tb_2O_3 , Tb_4O_7 , TiO_2 , TlF , Tl_2O_3 , OsO_4 , V_2O_5 , WO_3 , Y_2O_3 , ZnO , ZnTe , and ZrO_2 .

12. The conductive composition of any preceding claim, wherein one or more of a bismuth containing compound, a lead containing compound, a lithium containing compound, a zinc containing compound, a tellurium containing compound, a thallium containing

compound, and combinations thereof are present in the composition as components of the inorganic additive.

13. The conductive composition of any preceding claim, wherein one or more of bismuth oxide, lead oxide, lithium phosphate, zinc oxide, tellurium oxide, thallium oxide, and combinations thereof are present in the composition as components of the inorganic additive.

14. The conductive composition of any preceding claim, wherein the glass frit comprises one or more components selected from Ag_2Te , AgAsF_6 , Ag_3AsO_4 , AgBF_4 , AgBr , AgCl , AgClO_4 , AgF , AgF_2 , AgHF_2 , AgI , Ag_2MoO_4 , AgPF_6 , AgPO_4 , AgReO_4 , Ag_2SO_4 , Ag_2S , AgSbF_6 , AgVO_3 , Ag_2WO_4 , Al_2O_3 , As_2O_3 , AuTe_2 , BaO , B_2O_3 , BaF_2 , BaO , Bi , BiBr_3 , BiCl_3 , BiF_3 , $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, BiI_3 , Bi_2MoO_6 , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, Bi_2O_3 , $\text{Bi}(\text{OH})_3$, BiSb , Bi_2Se_3 , Bi_2S_3 , Bi_2Te_3 , BiVO_4 , $\text{Bi}_2(\text{WO}_4)_3$, C_2O_3 , CaO , CdO , CoO , CuO , Cu_2O , Ga_2O_3 , In_2O_3 , KAg_4I_5 , LaF_3 , La_2O_3 , Li_2O , Li_3PO_4 , MgO , Mn_2O_5 , MnO_2 , Mo_2O_3 , NiO , P_2O_5 , Pb , PbBr_2 , PbCl_2 , PbF_2 , PbHPO_4 , PbI_2 , PbO , PbSO_4 , PbSe , PbS , PbSb , PbTe , $\text{Pb}(\text{VO}_3)_2$, ReO_2 , ReO_3 , Re_2O_7 , RuO_2 , Sb_2O_3 , SeO_2 , SO_2 , SO_3 , SiO_2 , SnO_2 , SrF_2 , SrO , Tb_2O_3 , Tb_4O_7 , TiO_2 , TlF , Tl_2O_3 , OsO_4 , V_2O_5 , WO_3 , Y_2O_3 , ZnO , ZnTe , and ZrO_2 .

15. The conductive composition of any preceding claim, wherein one or more of a bismuth containing compound, a lead containing compound, a tellurium containing compound, a thallium containing compound, and combinations thereof are present in the composition as a component of the glass frit.

16. The conductive composition of any preceding claim, wherein one or more of bismuth oxide, lead oxide, tellurium oxide, thallium oxide, and combinations thereof are present in the composition as a component of the glass frit.

17. The conductive composition of any preceding claim, wherein the ratio on a weight basis of the elemental tellurium and/or tellurium containing compound to the elemental thallium and/or thallium containing compound in the conductive composition is about 0.6 to about 93.

18. The conductive composition of any preceding claim, wherein the ratio on a weight basis of tellurium oxide to thallium oxide in the conductive composition is about 0.6 to about 93.

19. The conductive composition of any preceding claim, wherein elemental thallium or the thallium containing compound is present in an amount of about 0.01 wt% to about 5wt%.

20. The conductive composition of any preceding claim, wherein elemental thallium or thallium containing compound is present in an amount of about 0.01wt% to about 1.0wt%.

21. The conductive composition of any preceding claim, wherein tellurium oxide is present in an amount of about 0.05wt% to about 2.5wt%.

22. The conductive composition of any preceding claim, wherein tellurium oxide is present in an amount of about 0.1 wt% to about 2.0wt%.

23. The conductive composition of any preceding claim, wherein the inorganic additive is present in an amount of about 0.1wt% to about 5.0wt%.

24. The conductive composition of any preceding claim, wherein the inorganic additive is present in an amount of about 0.5wt% to about 4.0wt%.

25. The conductive composition of any preceding claim, wherein lead oxide is present in an amount of about 0.05wt% to about 2.5wt%.

26. The conductive composition of any preceding claim, wherein lead oxide is present in an amount of about 0.1wt% to about 0.75wt%.

27. The conductive composition of any preceding claim, wherein bismuth oxide is present in an amount of about 0.01wt% to about 2.5wt%.

28. The conductive composition of any preceding claim, wherein bismuth oxide is present in an amount of about 0.05wt% to about 0.5wt%.

29. The conductive composition of any preceding claim, wherein glass frit is present in an amount of about 0.01wt% to about 5.0wt%.

30. The conductive composition of any preceding claim, wherein glass frit is present in an amount of about 0.1wt% to less than about 0.5wt%.

31. The conductive composition of any preceding claim, wherein the conductive composition is essentially glass free.

32. The conductive composition of any preceding claim, wherein tellurium oxide is present in the glass frit in an amount of about 20 wt% to about 70wt%.

33. The conductive composition of any preceding claim, wherein thallium oxide is present in the glass frit in an amount of about 1wt% to about 60wt%.

34. The conductive composition of any preceding claim, wherein thallium oxide is present in the glass frit in an amount of about 1wt% to about 50wt%.

35. The conductive composition of any preceding claim, wherein silver powder is present in an amount of about 40wt% to about 98wt %.

36. The conductive composition of any preceding claim, wherein the average specific surface area of the silver powder is about 0.6m²/g to about 1.5m²/g.

37. The conductive composition of any preceding claim, wherein organic medium is present in an amount of about 1wt% to about 10wt%.

38. The conductive composition of any preceding claim, wherein the organic medium comprises one or more of a resin, a rosin, and a solvent.

39. The conductive composition of claim 41, wherein the organic medium comprises a resin selected from acrylic resin, epoxy resin, phenol resin, alkyd resin, cellulose polymers, polyvinyl alcohol, rosin and mixtures thereof.

40. The conductive composition claim 42, wherein the resin is selected from hydroxypropylcellulose, hydroxyethylcellulose, and mixtures thereof.

41. The conductive composition of any preceding claim, wherein the conductive composition is a paste.

42. The conductive composition of claim 44, wherein the paste is an electrode-forming paste.

43. A substrate coated with the conductive composition of any one of the preceding claims.

44. A device comprising a substrate coated with the conductive composition of any one of claims 1-42.

45. The device of claim 44, wherein the device is a semiconductor.

46. The device of claim 45, wherein the semiconductor comprises silicon.

47. The device of claim 44, wherein the device is a photovoltaic device.

48. The device of claim 47, wherein the photovoltaic device comprises a silicon substrate.

49. The device of claim 47 or 48, wherein the photovoltaic device is a solar cell.

50. The device of any one of claims 43-49, wherein the substrate is a silicon wafer.

51. A process for preparing a coated substrate comprising:
applying the conductive composition of any one of claims 1-42 to a surface of the
substrate; and
drying the conductive composition.

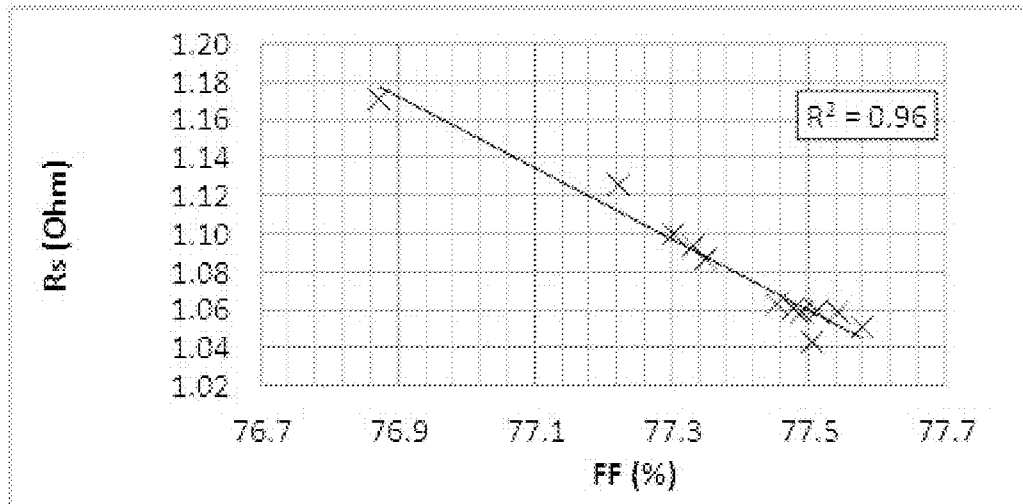
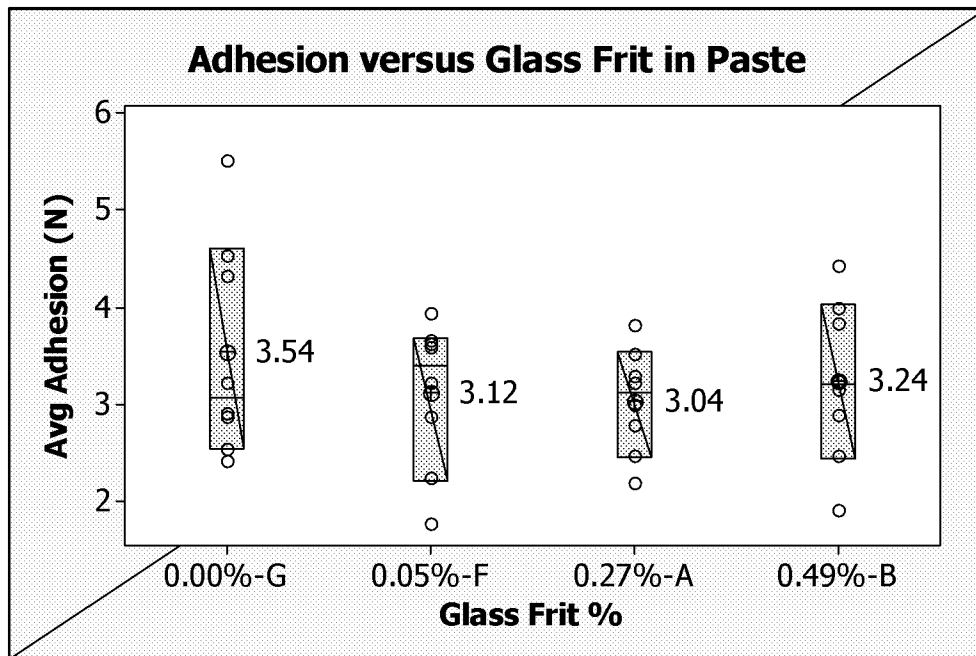
Figure 1

Figure 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/65738

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-51
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/65738

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01B 1/20; H01B 1/22; C01G 15/00; C01B 19/00 (2017.01)

CPC - H01B 1/20; H01B 1/22; C01G 15/00; C01B 19/00

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)

IPC(8) - H01B 1/20; H01B 1/22; C01G 15/00; C01B 19/00 (2017.01)

CPC - H01B 1/20; H01B 1/22; C01G 15/00; C01B 19/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and NPL (classification, keyword; search terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Pub West (US EP JP WO), Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent, Google Scholar, Free Patents Online; search terms: conductive, electroconductive, silver, powder, particle, particulate, thallium, Ti2O3, tellurium, TeO2, organic, solvent, resin, frit

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0277624 A1 (YANG et al.) 24 October 2013 (24.10.2013) para [0033], [0034], [0053], [0055], [0085], [0088]	1-3
X	US 2015/0072463 A1 (YANG et al.) 12 March 2015 (12.03.2015) para [0058], [0074], [0075], [0082], [0084], [0088], [0097]	1-3
X	US 4,933,030 A (DIETZ) 12 June 1990 (12.06.1990) col 4, l 43-44; col 6, l 19; col 6, l 65-68; col 13, Table 1	1-3
X, E	US 2016/0369111 A1 (MOYER et al.) 22 December 2016 (22.12.2016) the entire document	1-3
Y	WO 2015/024990 A1 (VISPA S.R.L.) 26 February 2015 (26.02.2015) the entire document	1-3
Y	US 5,336,644 A (AKHTAR et al.) 09 August 1994 (09.08.1994) the entire document	1-3

☐ Further documents are listed in the continuation of Box C.

* 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 application or patent 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

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Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
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