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(71) Applicant: **SUN CHEMICAL CORPORATION** [US/US]; 35 Waterview Boulevard, Parsippany, NJ 07054 (US).

(72) Inventors: **SUN, Bo**; 106 Bardonia Road, Bardonia, NY 10954 (US). **HE, Jin-an**; 8 Morgan Road, Parsippany, NJ 07054 (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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(54) Title: A SILVER PASTE CONTAINING ORGANOBISMUTH COMPOUNDS AND ITS USE IN SOLAR CELLS

(57) Abstract: The present invention is directed to a silver paste for a Si solar cell comprising an organobismuth additive and a solar cell having a silicon wafer with the silver paste on its front-side surface. The resultant cell exhibits improved efficiency.

A SILVER PASTE CONTAINING ORGANOBISMUTH COMPOUNDS AND ITS USE IN SOLAR CELLS

[0001] This application claims priority to U.S. Provisional Patent Application Serial No. 62/026,836 filed July 21st, 2014, 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 paste for a silicon (Si) solar cell comprising organobismuth compounds and a solar cell having a silicon wafer with the silver paste on its front-side surface. The solar cell exhibits improved efficiency resulting from the use of a separate organobismuth additive in the paste.

BACKGROUND TO THE INVENTION

[0003] Silicon solar cells are extensively used in the rapidly growing photovoltaic (PV) industry.

[0004] Silicon solar cells typically include a silicon wafer with a silver (Ag) paste screen-printed with a pattern on the front-side (facing the sunlight) of the silicon wafer. The silicon wafer also typically has two overlapping layers containing aluminum and silver respectively printed on the opposite (back-side) of the silicon wafer.

[0005] US 5,066,621 and US 5,336,644 are directed to sealing glass compositions containing metal oxides.

[0006] US 8,497,420 is directed to a thick film paste containing lead and tellurium oxides and their use in the manfacture of semiconductor devices.

[0007] US 2013/0037761 is directed to an electroconductive thick film paste comprising Ag for use in an electrode for a solar cell.

[0008] US 2012/0171810 describes paste compositions for an electrode of a solar cell which contains a conductive powder, an organic vehicle and glass frits.

[0009] US 2012/0138142 is directed to lead-free and cadmium-free paste compositions for use on contacts for solar cells.

[00010] US 2010/0294360 and US 2010/0294361 are directed to a process of forming a front-grid electrode on a silicon wafer with printed and dried metal pastes containing glass frits thereon.

[00011] US 2012/0312368 and US 2012/173875 describe an electroconductive thick film paste comprising Ag and Pb free bismuth based oxide both dispersed in an organic medium for the use in the manufacture of semiconductor devices.

[00012] US 2011/0147677 is directed to zinc containing glass compositions for use in conductive pastes for silicon semiconductor devices and photovoltaic cells.

[00013] WO 2012/0173875 is directed to a thick film paste containing bismuth based oxides and its use in the manufacture of semiconductor devices.

[00014] WO 2012/135551 describes high aspect ratio screen printable thick film paste wax compositions for positioning conductive lines on a solar cell device.

[00015] Finally Journal Article: Development of lead-free silver ink for front contact metallization Author(s): Kalio, A.; Leibinger, M.; Filipovic, A.; Kruger, K.; Glatthaar, M.; Wilde, J. is directed to solar energy materials and solar cells.

SUMMARY OF THE INVENTION

[00016] The present invention provides a composition for silicon solar cells comprising at least one Ag powder, at least one glass frit, at least one organic resin, at least one solvent and between 0.02 to 5.0 wt% of an organobismuth compound wherein the organobismuth compound is separate from the glass frits.

[00017] The present invention also provides a process for preparing a composition which comprises combining at least one Ag powder, at least one glass frit, at least one organic resin, at least one solvent and between 0.02 to 5.0 wt% of an organobismuth compound that is separate from the glass frits.

[00018] Additionally the present invention also provides a solar cell comprising a silicon wafer and the composition on the front-side surface of the silicon wafer.

[00019] Finally the present invention provides a process for making a solar cell comprising applying a coating of the composition onto the front-side surface of a silicon wafer.

[00020] 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.

DETAILED DESCRIPTION

[00021] It has now been found that the use of silver paste compositions with organobismuth compounds incorporated separately therein as additives and used for front-side silicon solar cell applications results in the production of solar cells with a higher cell efficiency and thus greater power output when exposed to sunlight.

[00022] Typically glass frits are added to the silver paste compositions when used in the production of solar cells to etch through the anti-reflective coating (ARC) on the front-side of a silicon wafer.

[00023] Furthermore when bismuth compounds have been used in such silver paste compositions they are typically incorporated into the silver paste by melting, at typically temperatures above 1000°C, the compound into glass frits, which are then subseqeuntly quenched and grinded.

[00024] However, it has now been found that adding an organobismuth compound as a separate and discrete additive which is not incorporated into glass frits imparts particularly advantageous properties to high efficiency front-side silver paste compositions.

[00025] The organobismuth compounds according to the present invention advantageously contain at least bismuth, carbon, hydrogen and oxygen.

[00026] Preferably, the compositions comprise between 0.02 to 2.5wt% of the organobismuth compound and advantageously between 0.1 to 1.5wt% of the organobismuth compound.

[00027] The organobismuth compound may be a liquid at room temperature or may be a solid. Where the organobismuth compound is a solid it typically has a particle size of between 5nm to 9μm and preferably a particle size of between 25nm to 3 μm.

[00028] Advantageoulsy, the organobismuth compound is a liquid at room temperature to facilitate processing.

[00029] The organobismuth compound is preferably selected from the group consisting of bismuth(III) subsalicylate, bismuth(III) citrate, bismuth(III) acetate, bismuth ethylhexanoate, bismuth hexafluoro-2,4-pentanedionate, bismuth(III) isopropoxide, bismuth trifluoromethanesulfonate hydride, bismuth (III) 2,2,6,6-tetramethyl-3,5-heptanedionate, triphenylbismuth, bismuth 2-ethylhexanoate monoisopropoxide, tris(1-methoxy-2-methyl-2-propoxy)bismuth, bismuth(III) tert-pentyloxide, bismuth(III) trifluoromethanesulfonate, bismuth subgallate hydrate, ammonium bismuth citrate, bismuth(III) 2-naphthol salt, bismuth(III) gallate basic, dichloritri(o-tolyl)bismuth, dichlorodiphenyl (p-tolyl) bismuth, dichlorotris(4-

chlorophenyl)bismuth and bismuth neodecanoate and combinations thereof, but is advantageously bismuth ethylhexanoate.

[00030] Typically the composition contains between 70 to 95 wt% of Ag powder, and more preferably between 80 to 92 wt%.

[00031] Usually the Ag powder has a purity of greater than 99.5% and typically contains impurities such as Zr, Al, Fe, Na, Zn, Pb at advantageously less than 100ppm.

[00032] The Ag powder(s) may be a mixture of one or more Ag powder(s) preferably with a particle size D50 between 0.1 to 5μm, more preferably between 0.5 to 2 μm.

[00033] Usually when two or more Ag powders are used a higher Ag particle packing density is achieved and the proximity of the Ag particles facilitates Ag sintering and percolation during the firing process. This results in a more connected and condensed electron conduction path which generally improves the solar cell efficiency.

[00034] The Ag powder(s) are not limited in morphology and may be spherical, elliptical, etc. and typically could be thermally sintered to form a conductive network during the solar cell metallization firing step.

[00035] Furthermore the Ag powder(s) may be pre-coated with different surfactants to avoid particle agglomeration and aggregation. The surfactant is advantageously a straight-chain, or branched-chain fatty acid, a fatty acid ester, fatty amide or a mixture thereof.

[00036] Additionally long-chain alcohols may also be used for rheology modification.

[00037] The composition usually comprises between 0.5 to 10 wt% of glass frits and preferably between 1 to 5 wt% of glass frits.

[00038] The glass frits may be formed from the group consisting of PbO, Al_2O_3, SiO_2, B_2O_3, Li_2O, TiO_2, ZnO, P_2O_5, V_2O_5, SrO, CaO, Sb_2O_3, SO_2, As_2O_3, Bi_2O_3, Tl_2O_3, Ga_2O_3, MgO, Y_2O_3, ZrO_2, Mn_2O_5, CoO, NiO, CuO, SrO, Mo_2O_3, RuO_2, TeO_2, CdO, In_2O_3, SnO_2, La_2O_3, BaO and mixtures thereof.

[00039] Additionally, the composition preferably contains between 0.2 to 2 wt% of organic resin and more preferably between 0.5 to 1.5 wt%.

[00040] Typically the resin is selected from acrylic resin, epoxy resin, phenol resin, alkyd resin, cellulose polymers, polyvinyl alcohol, rosin and mixtures thereof.

[00041] Advantageously the resins should burn off during the firing of the coated silicon wafer such that no residue remains thereon.

[00042] Additionally, the composition preferably contains between 0.2 to 20 wt% of solvent and more preferably between 2 to 8 wt%.

[00043] Typical solvents include texanol, propanol, isopropyl alcohol, ethylene glycol and diethylene glycol derivatives (glycol ether solvents), toluene, xylene, dibutyl carbitol, terpineol and mixtures thereof.

[00044] Preferably, the solvents include texanol, butyl carbitol and dibasic ester solvents such as DBE, DBE-6 and DBE-9, obtainable from Invista.

[00045] The solvent is effective for dissolving the resins, rosins, and thixotropic agents and is preferably capable of sustaining paste printing whilst subsequently evaporating thoroughly during the drying step.

[00046] The composition also typically contains an adhesion promoting agent, thixotropic agent and/or a dispersant.

[00047] Usually the composition contains between 0.1 to 0.7 wt% of an adhesion promoting agent, between 0.01 to 3.0 wt% of a dispersant and between 0.1 to 2.0 wt% and advantageously between 0.5 to 2.0 wt% of a thixotropic agent.

[00048] Typically the thixotropic agent is a cellulose polymer such as ethyl cellulose, hydroxyethyl cellulose, castor oil, hydrogenated castor oil, an amide modified castor oil derivative or a fatty amide. Suitable thixotropic agents include Thixatrol Max, Thixatrol ST and Thixatrol Pro.

[00049] Usually the dispersant is long-chain fatty acid such as stearic acid with functional amine, acid ester or alcohol groups. Suitable dispersants include BYK 108, BYK 111, Solsperse 66000 and Solsperse 27000.

[00050] The composition may also contain a metallic oxide additive such as ZnO, and typically contains between 2 to 10 wt% of metallic oxide.

[00051] In a preferred embodiment the Ag powder, the organobismuth and the glass frits are mixed with a varnish/vehicle.

[00052] A typical vehicle comprises between 3 to 20wt% of thixotropic agent, between 2 to 30wt% of resin and between 50 to 95wt% of solvent usually having a boiling point between 200 to 400°C.

[00053] Usually the front-side silver paste composition comprises between 3 to 10wt% of the vehicle.

[00054] The composition is usually in the form of paste and preferably has a viscosity of between 50 to 250Pa·S at 10 recipocal second.

[00055] The present invention also provides a process for making a solar cell which involves applying a coating of the composition onto the front-side surface of a silicon wafer. Furthermore

the process usually involves applying two overlapping layers containing aluminum and silver respectively to the back side surface of the silicon wafer. The coated silicon wafer is then fired.

[00056] The composition is usually deposited on a silicon wafer by screen/stencil printing. The stroke movement across the screen provides high shear rate to the composition through micro-channels of mesh pattern. The size of micro-channels is preferably 40 to 80microns for fingers, and preferably 1.0 to 2.0mm for bus bars. The fingers are preferably narrower in order to leave more open area for sunlight collection whilst the bus bars are preferably dashed rather than continuous due to the cost of Ag. The thickness of the printed finger lines is typically between 10 to 35microns. Advantageously the higher the printed fingers the better the finger's conductivity.

[00057] The manufacturing of silicon solar cells typically includes several steps namely;

i. the transfer of SiO_2 into a Si ingot;
ii. the transfer of the Si ingot to the Si wafer by sawing, etching, doping, ARC and other surface-treatments;
iii. screen-printing and drying the back side silver (Ag) paste on the back side of the wafer;
iv. screen-printing and drying aluminum (Al) paste on the back side of the wafer;
v. screen-printing and drying the front-side silver (Ag) paste on the front side of the wafer;
vi. co-firing the coated wafer in a furnace wherein the wafer goes through a temperature curve optimized for the overall efficiency of the device.

[00058] Thus the Al and Ag metals in the two back side coatings form a physical contact with the Si wafer through penetrating SiO_2 on the back side. Furthermore they also form a contact with each other through the overlapping area. The front side Ag paste penetrates the anti-reflection layer and reaches n-type Si beneath it and a good ohmic contact is formed between Ag lines and the n-Si emmiter during the firing process. The contact resistance between the Ag lines and the emitter for the current flow is preferred to be minimal to maximize the efficiency of the

device. In general, a thin layer of glass frits between the emitter and Ag traces is also preferred and results in higher efficiency.

[00059] The invention is further described by the examples given below.

EXAMPLES

[00060] The following examples illustrate specific aspects of the present invention and are not intended to limit the scope thereof in any respect and should not be so construed.

Example 1: Procedure for making Ag paste

Step 1

[00061] The varnish in Table 1 was made by dissolving rosin(s) and thixotropic agent(s) in a solvent (ingredients 1-3). The varnish is a mixture of solvent, thixotropic polymer, resins such as ethylene cellulose, polycarbonate, and rosin such as ester of hydrogenated rosin and hydrogenated castor oil. These can immerse glass frit(s), Ag powders and other solids, and make the paste fluidic enough to be capable of going through stainless-steel-mesh/emulsion channels with 30-100micron in channel width, 30-55micron in mesh thickness and 10-30micron in emulsion thickness, forming paste finger lines on the wafer. However, the varnish preferably allows the printed finger lines to have a thixotropy suitable to minimize the paste from spreading, thus more area is left for capturing sunlight to convert to electricity.

Table 1. Varnish Formulation for use with Examples A-F

	Ingredient	wt.%
1	Ester of Hydrogenated Rosin (Eastman)	11.5
2	Crayvallac Super (Arkema) (thixotropic agent)	14.1

	Ingredient	wt.%
3	Texanol	74.4
4	Dispersant (Altana BYK)	0.2
	Total	**100.0**

Step 2

[00062] The dispersant (ingredient 4) is then added into the above mixture and was aggressively mixed until it became uniform.

Table 2. Front-Side Silver Paste formulations

	Ingredient	Weight/g
1	Ag powder (Ames GoldSmith Corp.)	82.2
2	V2173 (3M Cerodyne Viox Inc.) Glass Frit	2.5
3	ZnO (HorseHead Corp.) Additive	5.5
4	Table 1 Varnish	7.8
5	Texanol	2.0
6	Elemental bismuth weight in organobismuth additives (Examples A-E)	0.18

For examples A, B, C, D and E the elemental bismuth in the organobismuth additives is 0.18g.

Step 3

[00063] The mixture from step (2) was aggressively mixed with glass frit(s), solvent and additives, including bismuth additives as needed (Table 2 – ingredients 2, 3, 4, 5, 6). The glass

frits are commercially available lead borosilicate from 3M Cerodyne Viox Inc. and a typical frit such as V2173, V2172, V0981 may be used alone or as the mixture of in the final paste.

Step 4

[00064] Ag powder(s) (ingredient 1) was then added to the step (3) mixture and mixed aggressively with DAC speed mixer from FlackTek Inc.

Step 5

[00065] The mixture from step (4) is then triple-roll milled to a preferred grind of 6-9μm. The preferred viscosity of the resulting pastes at 10/s is 50-250Pa*s, more preferably 70-150Pa*s as measured on AR-2000EX rheometer from TA Instruments.

[00066] The three main requirements of the paste are 1) electrical performance, mainly efficiency; 2) green strength (i.e. the lines will hold their integrity and will be resistant to smear during a finger rub test after drying and before firing; 3) ribbon adhesion after firing.

Table 3. Inventive Examples A-E; Comparative Example F – Comparison among different organobismuth compounds

Organobismuth Compound			Electrical Performance				
Ex.	structure	chemical name	Efficiency (%)	Rs (Ohm*cm2)	Voc (mV)	Jsc (mA/cm2)	F.F. (%)
A	$C_7H_5BiO_4$	Bismuth(III) subsalicylate	16.4	2.15	629.4	36.2	72.1
B	$C_6H_5BiO_7$	Bismuth(III) citrate	15.4	2.12	628.1	36.3	67.5
C	$C_6H_9BiO_6$	Bismuth(III) acetate	16.6	3.09	630.7	36.3	72.5
D	$C_{24}H_{45}BiO_6$	Bismuth ethylhexanoate	17.1	1.60	633.4	36.3	73.8

Organobismuth Compound			Electrical Performance				
Ex.	structure	chemical name	Efficiency (%)	Rs (Ohm*cm2)	Voc (mV)	Jsc (mA/cm2)	F.F. (%)
E	$C_{30}H_{57}BiO_6$	Bismuth neodecanoate	13.1	5.87	628.8	36.3	57.5
F	Without organobismuth additive		6.2	-	628.4	32.2	30.2

[00067] The above table provides a direct comparison of the resulting cell efficiency acquired with an Ag paste with various organobismuth compounds therein compared with the same Ag paste without organobismuth additive. Table 3 shows that Si wafer's efficiency is greatly enhanced by using organobismuth additives (A-E) in comparison with no organobismuth additive (F).

<u>Solar cell fabrication and test performance for pastes</u>:

[00068] A 5 inch mono-crystalline wafer with an emitter sheet resistance of 80 to 90 Ohm/square are used in this test and 3 steps as described below are used for preparation: 1) 1.0g of Al paste is screen-printed on the back-side of each Si wafers, it is then dried using BTU International PVD-600 drying furnace with the setting of belt speed = 90ipm, 310°C (Zone 1), 290°C (Zone 2), and 285°C (Zone 3). The screen used for printing is 325mesh, 23micron wire diameter, and 10micron emulsion, 45 degree bias, the squeegee used is 65-75 shore in hardness; 2) the front-side Ag paste is screen-printed on the front surface of the same wafer and it is dried in the same drying furnace with the setting of belt speed = 165ipm, 340°C (Zone 1), 370°C (Zone 2), and 370°C (Zone 3). The screen used for printing is 325mesh, 23micron wire diameter, and 16micron emulsion, 22.5 degree bias, the squeegee used is 65-75 shore in hardness; 3) the wafers are fired using BTU International PVD-600 firing furnace with the setting of belt speed belt speed = 200ipm, 850°C (Zone 1), 790°C (Zone 2), 790°C (Zone 3), and 1000°C (Zone 4). The electrical performance (open-circuit voltage Voc (V), efficiency, fill factor, series resistance and shunt resistance in the dark and under light) is measured using a Solar Simulator/I-V tester from PV Measurements Inc. The illumination of the lamp was calibrated using a sealed calibration

cell, and the measured characteristics were adjusted to the standard AM1.5G illumination conditions (1000 mW/cm^2). During testing, the cells were positioned on a vacuum chuck located under the lamp and the chuck temperature was maintained at 24°C +/-1 using a chiller. Both dark and light I-V curves were collected by sweeping voltage between -0.2V and +1.2V and measuring current. Standard solar cell electrical parameters were collected from the instrument including Cell efficiency (%), Series resistance (Rs), Shunt Resistance (Rsh) and Open Circuit Voltage (Voc), short-circuit current (Isc), and short-circuit current density (Jsc). The Cell efficiency η, is equal to the fill factor and is a key parameter in evaluating the performance of a solar cell. The fill factor is defined as the ratio of the maximum power from the solar cell to the product of Voc and Isc. Graphically, the fill factor is the division of the area of the largest rectangle which could fit between the I-V curve and I/V axes by Isc*Voc. The results were obtained using standard computer software available in the industry for measuring electrical parameters of solar cells.

[00069] 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

1. A composition for silicon solar cells comprising
   a) at least one Ag powder,
   b) at least one glass frit,
   c) at least one organic resin,
   d) at least one solvent,
   e) and between 0.02 to 5.0 wt% of an organobismuth compound wherein the organobismuth compound is separate from the glass frit(s).

2. A composition according to claim 1 comprising between 0.1 to 1.5 wt% of the organobismuth compound.

3. A composition according to claim 1 or 2 wherein the organobismuth compound is a liquid at room temperature.

4. A composition according to claim 1 or 2 wherein the organobismuth compound is a solid at room temperature.

5. A composition according to claim 4 wherein the organobismuth compound has a particle size of between 5nm to 9µm.

6. A composition according to claim 4 or 5 wherein the organobismuth compound has a particle size of between 25nm to 3µm.

7. A composition according to claim 1 or 2 wherein the organobismuth compound is selected from the group consisting of bismuth(III) subsalicylate, bismuth(III) citrate, bismuth(III) acetate, bismuth ethylhexanoate, bismuth hexafluoro-2,4-pentanedionate, bismuth(III) isopropoxide, bismuth trifluoromethanesulfonate hydride, bismuth (III) 2,2,6,6-tetramethyl-3,5-heptanedionate, triphenylbismuth, bismuth 2-ethylhexanoate

monoisopropoxide, tris(1-methoxy-2-methyl-2-propoxy)bismuth, bismuth(III) tert-pentyloxide, bismuth(III) trifluoromethanesulfonate, bismuth subgallate hydrate, ammonium bismuth citrate, bismuth(III) 2-naphthol salt, bismuth(III) gallate basic, dichloritri(o-tolyl)bismuth, dichlorodiphenyl (p-tolyl) bismuth, dichlorotris(4-chlorophenyl)bismuth and bismuth neodecanoate and combinations thereof.

8. A composition according to claim 7 wherein the organobismuth compound is bismuth ethylhexanoate.

9. A composition according to anyone of the preceding claims comprising an adhesion promoting agent, at least one resin, a thixotropic agent and/or a dispersant.

10. A composition according to claim 9 wherein the dispersant is a fatty acid.

11. A composition according to anyone of the preceding claims further comprising an organometal additive selected from the group consisting of organic compounds of zinc, vanadium, barium, and strontium, and combinations thereof.

12. A composition according to anyone of the preceding claims further comprising a metallic oxide additive.

13. A composition according to claim 12 wherein the metallic oxide additive is ZnO.

14. A composition according to anyone of the preceding claims comprising between 70 to 95 wt% of Ag powder.

15. A composition according to anyone of the preceding claims comprising between 80 to 92 wt% of Ag powder.

16. A composition according to anyone of the preceding claims wherein the Ag powder has a particle size D50 between 0.1 to 5µm.

17. A composition according to anyone of the preceding claims wherein the Ag powder has a particle size D50 between 0.5 to 2µm.

18. A composition according to anyone of the preceding claims comprising between 0.5 to 10 wt% of glass frits.

19. A composition according to anyone of the preceding claims comprising between 1 to 5 wt% of glass frits.

20. A composition according to anyone of the preceding claims wherein the glass frits are formed from PbO, Al_2O_3, SiO_2, B_2O_3, Li_2O, TiO_2, ZnO, P_2O_5, V_2O_5, SrO, CaO, Sb_2O_3, SO_2, As_2O_3, Bi_2O_3, Tl_2O_3, Ga_2O_3, MgO, Y_2O_3, ZrO_2, Mn_2O_5, CoO, NiO, CuO, SrO, Mo_2O_3, RuO_2, TeO_2, CdO, In_2O_3, SnO_2, La_2O_3, BaO and mixtures thereof.

21. A composition according to anyone of the preceding claims comprising between 0.2 to 2 wt% of organic resin.

22. A composition according to anyone of the preceding claims comprising between 0.5 to 1.5 wt% of organic resin.

23. A composition according to anyone of the preceding claims wherein the resin is selected from acrylic resin, epoxy resin, phenol resin, alkyd resin, cellulose polymers, polyvinyl alcohol, rosin and mixtures thereof.

24. A composition according to anyone of the preceding claims comprising between 2 to 20 wt% of solvent.

25. A composition according to anyone of the preceding claims comprising between 2 to 8 wt% of solvent.

26. A composition according to anyone of the preceding claims wherein the solvent is selected from texanol, propanol, isopropyl alcohol, ethylene glycol and diethylene glycol derivatives, toluene, xylene, dibutyl carbitol, terpineol and mixtures thereof.

27. A composition according to anyone of the preceding claims comprising between 0.1 to 0.7 wt% of an adhesion-promoting agent.

28. A composition according to anyone of the preceding claims comprising between 0.01 to 3.0 wt% of a dispersant.

29. A composition according to anyone of the preceding claims comprising between 0.5 to 2.0 wt% of a thixotropic agent.

30. A composition according to anyone of the preceding claims comprising between 2 to 10 wt% of metallic oxide.

31. A composition according to anyone of the preceding claims wherein the composition is in the form of a paste.

32. A process for preparing a composition according to anyone of claims 1 to 31 comprising combining a Ag powder, glass frits, at least one organic resin, at least one solvent and between 0.02 to 5.0 wt% of an organobismuth compound that is separate from the glass frits.

33. A process according to claim 32 comprising
    a) combining the organic resin and the solvent to form a varnish and

b) adding the Ag powder, the glass frits and the organobismuth compound to the varnish.

34. A process according to claim 33 wherein step (a) comprises adding a thixotropic agent.

35. A process according to claims 33 or 34 wherein step (a) comprises adding a dispersant.

36. A solar cell comprising a silicon wafer and a composition according to anyone of claims 1 to 31 on the front side surface of the silicon wafer.

37. A solar cell according to claim 36 wherein the silicon wafer has two overlapping layers one comprising Al and one comprising Ag on the back side surface of the silicon wafer.

38. A process for making a solar cell comprising applying a coating of the composition according to anyone of claims 1 to 31 onto the front side surface of a silicon wafer.

39. A process according to claim 38 further comprising applying two overlapping layers one comprising Al and one comprising Ag the back side surface of the silicon wafer.

40. A process according to claims 38 or 39 further comprising firing the coated silicon wafer.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 15/39530

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.: 6, 9-40
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 15/39530

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01B 1/02 (2015.01)
CPC - H01B 1/22; H05K 1/092; H05K 1/095

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): H01B1/02 (2015.01)
CPC: H01B1/22; H05K1/092; H05K1/095

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC: H01B1/16; H01L21/268 (keywords limited; search terms below)
USPC: 252/503,506,507,512,513,514,515,519.2; 438/57 (keywords limited; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST(PGPB,USPT,EPAB,JPAB); PatBase; Google Scholar; Google Patents
Search terms: silicon solar cell$2 organobismuth silver glass frits and "glass frits" paste powder "silver powder" resin organometallic "bismuth compound" "bismuth compounds"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0164777 A1 (Kleine Jaeger et al.) 28 June 2012 (28.06.2012), especially, para [0001], [0014], [0015], [0022], [0023], [0025], [0035], [0051] and [0063].	1-5, 7, 8
A	US 2010/0300522 A1 (Ginley et al.) 02 December 2010 (02.12.2010), especially, para [0025] and [0042].	1-5, 7, 8

☐ 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
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 September 2015 (12.09.2015)	06 OCT 2015

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774