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- **Lee, Jung Chul**
Gyeonggi-do (KR)
- **Oh, Jae Hwan**
Gyeonggi-do (KR)
- **Kim, Jae Ho**
Gyeonggi-do (KR)

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(74) Representative: **Hüttermann, Aloys**
Michalski Hüttermann & Partner
Patentanwälte
Neuer Zollhof 2
40221 Düsseldorf (DE)

(71) Applicant: **Cheil Industries Inc.**
Gyeongsangbuk-do 730-710 (KR)

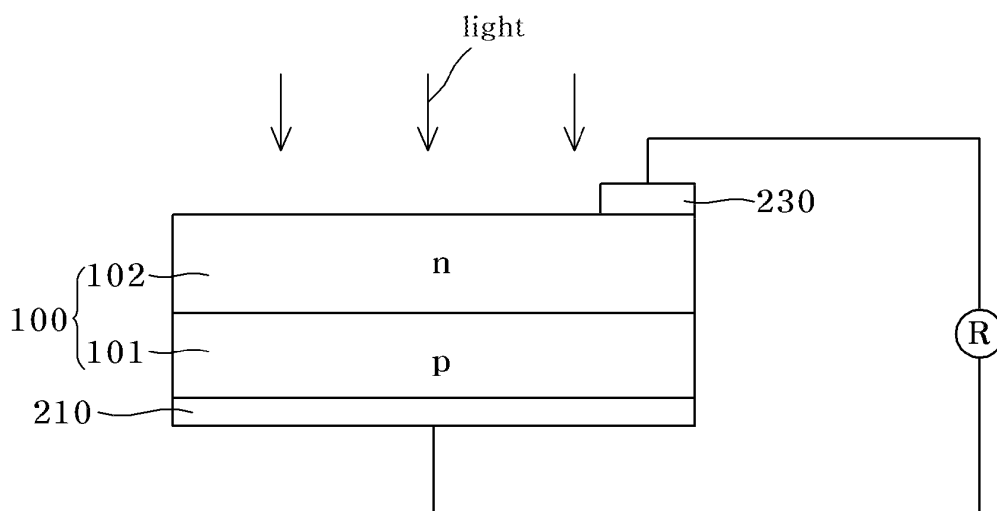
(72) Inventors:
• **Jung, Seok Hyun**
Gyeonggi-do (KR)

(54) **Paste for solar cell electrode and electrode using the same and solar cell using the same**

(57) Disclosed herein are pastes for solar cell electrodes exhibiting superior printability and conversion efficiency. The paste includes (a) a conductive powder, (b) a glass frit, (c) an organic vehicle, and (d) metal oxide particles comprising nanometer scale particles having an average particle diameter (D50) of 15 to 50 nm and mi-

cron scale particles having an average particle diameter (D50) of 0.1 to 2 μm . The present invention also discloses an electrode formed of the paste for solar cell electrodes, and a solar cell comprising the electrode, which has improved paste printability while exhibiting superior conversion efficiency.

Fig 1.



Description

Field of the Invention

[0001] The present invention relates to a paste for solar cell electrodes and solar cells using the same. More particularly, the present invention relates to a paste for solar cell electrodes, which includes nanometer and micron scale metal oxide particles and exhibits superior printability and conversion efficiency, and to solar cells using the same.

Description of Related Art

[0002] As fossil fuels such as oil and coal will soon run out, solar cells utilizing sunlight as an alternative energy source have attracted attention. A solar cell is formed to generate electric energy using the photovoltaic effect of a p-n junction which converts photons into electricity. In the solar cell, a front electrode and a rear electrode are formed on a front surface and a rear surface of a semiconductor wafer or substrate with the p-n junction, respectively. Then, the photovoltaic effect of the p-n junction is induced by sunlight entering the wafer and electrons generated by the photovoltaic effect of the p-n junction provide an electric current flowing to the outside through the electrodes. The electrodes of the solar cell are formed on the wafer by applying, patterning, and burning a paste for electrodes.

[0003] One standard for evaluating solar cell quality is conversion efficiency. The conversion efficiency of the solar cells is a value that indicates a conversion amount of incident light into electrical energy and is expressed as the ratio of the maximum output to incident energy. Characteristics of electrodes are an important factor in improving the conversion efficiency of the solar cells, and a paste for front electrodes configured to receive incident sunlight generally includes conductive particles, glass frit powders and a vehicle provided as a liquid carrier.

[0004] Recently, most attempts to improve the conversion efficiency of solar cells have focused upon these components of the paste.

[0005] Conventionally, however, Ag ions penetrate a silicon wafer during sintering after printing and drying a solar cell paste on front and rear sides of the wafer, such that the prepared solar cell suffers deterioration in series and parallel resistance due to low distribution of ions on the electrode, whereby the conversion efficiency of the solar cell cannot be significantly improved.

[0006] Another conventional method using 7 to 100 nm average diameter zinc oxide powder suffers disadvantages such as an increase in viscosity of pastes, pattern losses due to poor printability, and decrease in conversion efficiency.

[0007] Therefore, the inventors developed a paste for solar cell electrodes and a solar cell using the same, which has improved paste printability while exhibiting superior conversion efficiency.

Summary of the Invention

[0008] One aspect of the present invention provides a paste for solar cell electrodes. The paste for solar cell electrodes includes (a) a conductive powder, (b) a glass frit, (c) an organic vehicle, and (d) metal oxide particles comprising nanometer scale particles having an average particle diameter (D50) of ≥ 15 to ≤ 50 nm and micron scale particles having an average particle diameter (D50) of ≥ 0.1 to ≤ 2 μm .

[0009] The conductive powder may include at least one selected from the group consisting of silver (Ag), gold (Au), palladium (Pd), platinum (Pt), copper (Cu), chromium (Cr), cobalt (Co), aluminum (Al), tin (Sn), lead (Pb), zinc (Zn), iron (Fe), iridium (Ir), osmium (Os), rhodium (Rh), tungsten (W), molybdenum (Mo), nickel (Ni), and indium tin oxide (ITO).

[0010] The glass frit may include a leaded glass frit, a lead-free glass frit or a mixture thereof. Further, the glass frit may be selected from a crystallized glass frit, a non-crystallized glass frit, and a mixture thereof.

[0011] The organic vehicle may include an organic binder and a solvent.

[0012] The metal oxide particles may include at least one selected from the group consisting of zinc oxide (ZnO), lead oxide (PbO), copper oxide (CuO), silicon oxide (SiO_2), and titanium oxide (TiO_2) particles.

[0013] The metal oxide particles may include particles having a nanometer scale average particle diameter (D50), and particles having a micron scale average particle diameter (D50). The nanometer scale particles may have an average particle diameter (D50) of ≥ 15 to ≤ 50 nm, and preferably ≥ 20 to ≤ 40 nm, and the micron scale particles may have an average particle diameter (D50) of ≥ 0.1 to ≤ 2 μm , and preferably 0.5 to ≤ 1.5 μm . In one embodiment, the nanometer scale particles may be present in an amount of ≥ 5 to ≤ 50 wt% with respect to a total amount of the metal oxide particles.

[0014] In one embodiment, the paste for solar cell electrodes may include (a) ≥ 60 to ≤ 90 wt% of the conductive powder, (b) ≥ 1 to ≤ 10 wt% of the glass frit, (c) ≥ 8 to ≤ 20 wt% of the organic vehicle, and (d) ≥ 1 to ≤ 10 wt% of the nanometer and micron scale metal oxide particles. The paste for solar cell electrodes may further include additives, such as a plasticizer, a dispersant, a thixotropic agent, a viscosity stabilizer, an anti-foaming agent, a pigment, a UV stabilizer, an antioxidant, a coupling agent, etc., which may be added in amounts well known to those skilled in the art.

[0015] Another aspect provides an electrode formed of the paste.

[0016] A further aspect provides a solar cell including the electrode.

Brief Description of the Drawing

[0017]

FIG. 1 is a schematic view of a solar cell manufactured using a paste in accordance with an exemplary embodiment of the present invention.

Detailed Description of the Invention

[0018] According to one embodiment, a paste for solar cell electrodes includes (a) a conductive powder, (b) a glass frit, (c) an organic vehicle, and (d) nanometer and micron scale metal oxide particles.

(a) Conductive powder

[0019] The conductive powder may comprise a conductive organic material, a conductive inorganic material, or a combination thereof.

[0020] In one embodiment, the conductive powder is an inorganic powder, and preferably a metallic powder. Examples of the conductive powder may include, but are not limited to, silver (Ag), gold (Au), palladium (Pd), platinum (Pt), copper (Cu), chromium (Cr), cobalt (Co), aluminum (Al), tin (Sn), lead (Pb), zinc (Zn), iron (Fe), iridium (Ir), osmium (Os), rhodium (Rh), tungsten (W), molybdenum (Mo), nickel (Ni), and indium tin oxide (ITO). These conductive powders may be used alone or as an alloy of two or more kinds thereof. These conductive powders may also be used alone or in a combination of two or more kinds thereof.

[0021] In one embodiment, the conductive powder includes silver (Ag) particles and may further include nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn) or copper (Cu) particles.

[0022] The conductive powder may have a spherical shape, a flake shape, an amorphous shape, or a combination thereof. In one embodiment, the conductive powder may have a spherical shape to further improve fill factor, sintering density and UV transmittance.

[0023] The conductive powder may have an average particle diameter (D50) of ≥ 0.1 to ≤ 10 μm , preferably ≥ 0.2 to ≤ 7 μm , more preferably ≥ 0.5 to ≤ 5 μm , and still more preferably ≥ 1 to ≤ 3 μm . The average particle diameter was measured by Model 1064D (CILAS Co., Ltd.) after dispersing the conductive powder in isopropyl alcohol (IPA) with ultrasound waves at room temperature for 3 minutes.

[0024] The conductive powder may be present in an amount of 60 to ≤ 90 wt% with respect to the total weight of the paste. With the conductive powder in this range, it is possible to prevent deterioration in conversion efficiency due to an increase of resistance and to prevent difficulty in forming the paste due to a relative reduction in amount of the organic vehicle. The conductive powder is preferably present in an amount of ≥ 70 to ≤ 88 wt%, and more preferably ≥ 75 to ≤ 82 wt%.

(b) Glass frit

[0025] The glass frit may enhance adhesion between the conductive powder and the underlying substrate during a burning process and is softened upon sintering to further lower a sintering temperature.

[0026] The glass frit may comprise a crystallized glass frit or non-crystallized glass frit. The glass frit may be any of a leaded glass frit, a lead-free glass frit and a mixture thereof. For example, the glass frit may include, but are not limited to, at least one selected from zinc oxide-silicon oxide (ZnO-SiO_2), zinc oxide-boron oxide-silicon oxide ($\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$), zinc oxide-boron oxide-silicon oxide-aluminum oxide ($\text{ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$), bismuth oxide-silicon oxide ($\text{Bi}_2\text{O}_3\text{-SiO}_2$), bismuth oxide-boron oxide-silicon oxide ($\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$), bismuth oxide-boron oxide-silicon oxide-aluminum oxide ($\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$), bismuth oxide-zinc oxide-boron oxide-silicon oxide ($\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3\text{-SiO}_2$), and bismuth oxide-zinc oxide-boron oxide-silicon oxide-aluminum oxide ($\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$) glass frit.

[0027] The glass frit may have an average particle diameter (D50) of ≥ 0.1 to ≤ 5 μm , preferably ≥ 0.5 to ≤ 3 μm . Within this range, curing of a deep part through UV irradiation is not interrupted and generation of pinholes does not occur in a developing process when forming the electrodes. The average particle diameter was measured by Model 1064D (CILAS Co., Ltd.) after dispersing the glass frit in isopropyl alcohol (IPA) with ultrasound waves at room temperature for 3 minutes.

[0028] In one embodiment, the glass frit may have a transition point of ≥ 300 to $\leq 600^\circ\text{C}$, and preferably ≥ 400 to $\leq 550^\circ\text{C}$.

[0029] The glass frit may be present in an amount of ≥ 1 to ≤ 10 wt%, and preferably ≥ 1 to ≤ 7 wt% with respect to the total weight of the paste. Within the range, it is possible to prevent deterioration in conversion efficiency due to an improvement in resistance, sintering properties and adhesion of the conductive powder, while preventing an excessive

amount of glass frit from remaining after burning, which can cause an increase in resistance and deterioration in wettability.

(c) Organic vehicle (vehicle)

[0030] The organic vehicle may comprise an organic binder which provides liquid properties to the paste. In one embodiment, the organic vehicle (c) may comprise an organic binder and a solvent. Specifically, the organic vehicle (c) may include ≥ 5 to ≤ 40 wt% of the organic binder and ≥ 60 to ≤ 95 wt% of the solvent. In another embodiment, the organic vehicle (c) may include ≥ 5 to ≤ 30 wt% of the organic binder and ≥ 70 to ≤ 95 wt% of the solvent.

[0031] Examples of the organic binder include, but are not limited to, acrylic polymers obtained by copolymerization with hydrophilic acrylic monomers such as a carboxyl group; cellulose polymers, such as ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and hydroxyethyl hydroxypropyl cellulose, and the like. These binders may be used alone or in a mixture of two or more kinds thereof.

[0032] The solvent may be an organic solvent having a boiling point of 120°C or more. Examples of the solvent may include, but are not limited to, methyl cellosolve, ethyl cellosolve, butyl cellosolve, aliphatic alcohol, α -terpineol, β -terpineol, dihydro-terpineol, ethylene glycol, ethylene glycol mono butyl ether, butyl cellosolve acetate, texanol, etc. These solvents may be used alone or in a mixture of two or more kinds thereof.

[0033] The organic vehicle may be present in an amount of ≥ 8 to ≤ 20 wt% with respect to the total weight of the paste, and preferably ≥ 10 to ≤ 15 wt%. Within the range, it is possible to prevent inefficient dispersion or excessive increase in viscosity after preparation of the paste, which can lead to printing difficulty, and to prevent an increase in resistance and other problems that can occur during the burning process.

(d) Metal oxide particles

[0034] The metal oxide particles improve contact resistance of electrodes and promote crystallization of the paste.

[0035] The metal oxide particles may include, but are not limited to, at least one of zinc oxide (ZnO), lead oxide (PbO), copper oxide (CuO), silicon oxide (SiO_2), and titanium oxide (TiO_2).

[0036] The metal oxide particles may include a mixture of particles having a nanometer scale average particle diameter (D50) and particles having a micron scale average particle diameter (D50). In one embodiment, the nanometer scale metal oxide particles may have an average particle diameter (D50) of ≥ 15 to ≤ 50 nm, and preferably ≥ 20 to ≤ 40 nm. In one embodiment, the micron scale metal oxide particles may have an average particle diameter (D50) of ≥ 0.1 to ≤ 2 μm , preferably ≥ 0.1 to ≤ 1.5 μm . The average particle diameter was measured by Model 1064D (CILAS Co., Ltd.) after dispersing the metal oxide particles in isopropyl alcohol (IPA) with ultrasound waves at room temperature for 3 minutes. Within this range, the paste may have good fill factor and conversion efficiency.

[0037] The metal oxide particles formed of the nanometer scale particles and the micron scale particles may be present in an amount of ≥ 1 to ≤ 10 wt% with respect to the total weight of the paste, and preferably, in an amount of ≥ 1 to ≤ 8 wt%. Within this range, it is possible to prevent deterioration in resistance and conversion efficiency due to deterioration in sintering properties during the burning process, and to prevent poor printing due to an increase in resistance and viscosity of the paste.

[0038] Further, the nanometer scale particles may be present in an amount of ≥ 5 to ≤ 50 wt% with respect to the total weight of the metallic oxide particles, preferably ≥ 25 to ≤ 50 wt%, and still more preferably ≥ 25 to ≤ 40 wt%. Within this range, the specific surface area and volume of the metal oxide particles increase to provide more spaces for reaction with the glass frit, thereby providing desired effects.

[0039] The paste for solar cell electrodes may further include typical additives, as needed, to enhance flow properties, process properties, and stability. The additives may include, but are not limited to, a plasticizer, a dispersant, a thixotropic agent, a viscosity stabilizer, an anti-foaming agent, a pigment, a UV stabilizer, an antioxidant, a coupling agent, etc. These additives may be used alone or as a mixture of two or more kinds thereof. These additives are well known to those skilled in the art and are commercially available.

[0040] These additives may be added in an amount of ≥ 0.1 to ≤ 5 wt% with respect to the total weight of the paste, but this amount may be changed, as needed.

[0041] Other aspects of the invention provide an electrode formed of the paste for solar cell electrodes and a solar cell including the same. FIG. 1 shows a solar cell according to one exemplary embodiment of the invention.

[0042] Referring to FIG. 1, a rear electrode 210 and a front electrode 230 may be formed by printing and burning the paste on a wafer or substrate 100 that includes a p-layer 101 and an n-layer 102, which will serve as an emitter. For example, a preliminary process for preparing the rear electrode 210 is performed by printing the paste on the rear surface of the wafer 100 and drying the printed paste at 200 to 400°C for 10 to 60 seconds. Further, a preliminary process for preparing the front electrode 230 may be performed by printing the paste on the front surface of the wafer 100 and drying the printed paste. Then, the front electrode 230 and the rear electrode 210 may be formed by burning the wafer 100 at 400 to 900°C for 30 to 50 seconds.

[0043] Next, the invention will be described in more detail with reference to examples. However, it should be noted that these examples are provided for illustrative purposes and not intended to limit the scope of the invention.

[0044] Elaboration of details apparent to those skilled in the art will be omitted herein for clarity.

Examples

[0045] Specifications of components used in the following examples and comparative examples were as follows:

(a) Conductive powder: Spherical Ag powder having an average particle diameter (D50) of 2.0 μm (AG-4-8, Dowa HighTech Co., Ltd.)

(b) Glass frit

(b1) Low melting-point leaded glass frit having an average particle diameter of 1.0 μm and transition point of 451°C (Leaded Glass, PSL1004C, Particology Co., Ltd.)

(b2) Low melting-point lead-free glass frit having an average particle diameter of 1.7 μm and a transition point of 317°C (CSF-6, Phoenix PDE) (c) Organic vehicle: ethyl cellulose (Dow Chemical Co., Ltd., STD4) dissolved at 600 in terpineol (Nippon Terpine Co., Ltd.)

(d) Metal oxide particle

(d1) ZnO powder (Kanto Chemical Co., Ltd.) having an average particle diameter (D50) of 1.2 μm

(d2) ZnO powder (SB Chemical Co., Ltd.) having an average particle diameter (D50) of 30 nm

Examples 1 to 4

[0046] With the aforementioned ingredients prepared at a ratio given in Table 1, 0.3 parts by weight of dispersant BYK111 I (BYK-chemie), 0.3 parts by weight of thixotropic agent BYK430 (BYK-chemie), 0.1 parts by weight of anti-foaming agent BYK053 (BYK-chemie) were further added thereto and mixed therewith, followed by milling using a 3-roll mill, thereby preparing pastes for solar cell electrodes.

Comparative Example 1

[0047] The same process as in Example 1 was carried out except that the nanometer scale metal oxide particles were not used.

Comparative Example 2

[0048] The same process as in Example 1 was carried out except that the micron scale metal oxide particles were not used.

[0049] The using amounts of these components below are of parts by weight.

Table 1

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Conductive powder	Ag particle	80	80	80	80	80	80
Glass frit	Leaded	3	3	3	-	3	3
Glass frit	Lead-free	-	-	-	3	-	-
Vehicle	ethyl cellulose	1	1	1	1	1	1
	terpineol	11.3	11.3	13.3	11.3	11.3	11.3
Metal oxide particle	ZnO (30nm)	1	2	0.5	1	-	4
Metal oxide particle	ZnO (1.2 μm)	3	2	1.5	3	4	-
Additives	Dispersant	0.3	0.3	0.3	0.3	0.3	0.3

(continued)

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
5	Additives	Thixotropic agent	0.3	0.3	0.3	0.3	0.3
	Additives	Anti-foaming agent	0.1	0.1	0.1	0.1	0.1
10	total		100	100	100	100	100

[0050] Each of the pastes for solar cell electrodes prepared in Examples 1 to 4 and Comparative Examples 1 and 2 was deposited in a predetermined pattern on a front surface of a wafer by screen printing, and dried in a UV furnace. Then, an aluminum paste was printed over the rear surface of the wafer and dried by the same method. Cells prepared by this process was subjected to a burning process at 400 to 900°C for 30 to 50 seconds using a belt type furnace, and fill factor (FF, %) and conversion efficiency (eff, %) of each solar cell were measured using CT-801 (Pasan, Co., Ltd.). The results are shown in Table 2.

Table 2

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
FF (%)	74.1	71.5	72.2	73.15	60.8	51.3
Eff. (%)	17.1	16.675	16.625	17.005	13.3	11.21

[0051] As can be seen from these results, the pastes prepared by mixing the leaded or lead-free glass frit with nanometer scale and micron scale zinc oxide particles exhibited superior fill factors and conversion efficiency.

[0052] Such improvement in fill factor and conversion efficiency is believed to be due to promotion of paste crystallization by the glass frit and zinc oxide powder during a cooling process after drying and sintering the paste printed on the front and rear sides of the silicon wafer such that the paste is crystallized on a layer (or an emitter layer) of the silicon wafer to prevent silver (Ag) ions from entering the silicon wafer and to improve surface distribution of the silver ions.

[0053] Meanwhile, when the nanometer scale zinc oxide particles were mixed in an amount of 5 to 50 wt% with respect to the total weight of zinc oxide particles, the specific surface area and volume of the metal oxide particles increased to provide more spaces for reacting with the glass frit, thereby providing desired effects. However, when the mixed amount of the nanometer scale zinc oxide particles exceeded 50 wt% with respect to the total weight of zinc oxide particles, the metal oxide particles caused rapid increase in viscosity of the paste and in pattern loss resulting from poor printability due to excessive increase in specific surface area and volume and, thereby causing significant deterioration in fill factor and conversion efficiency.

[0054] Although some embodiments have been described in the present invention, these embodiments are given by way of illustration only and not intended to limit the scope of the invention. It should be understood that various modifications, changes, and equivalents thereof can be made by those skilled in the art without departing from the spirit and scope of the invention.

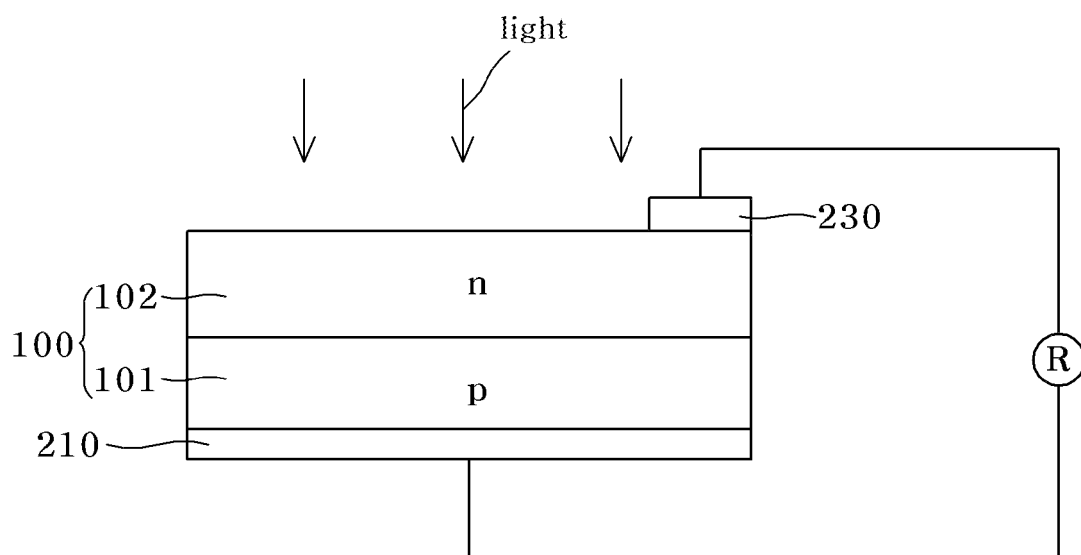
Claims

1. A paste for solar cell electrodes, comprising: (a) a conductive powder; (b) a glass frit; (c) an organic vehicle; and (d) metal oxide particles comprising nanometer scale particles having an average particle diameter (D50) of ≥ 15 to ≤ 50 nm and micron scale particles having an average particle diameter (D50) of ≥ 0.1 to ≤ 2 μ m.
2. The paste of claim 1, wherein said metal oxide particles comprise at least one selected from the group consisting of zinc oxide (ZnO), lead oxide (PbO), copper oxide (CuO), silicon oxide (SiO₂), and titanium oxide (TiO₂) particles.
3. The paste of claim 1, wherein said nanometer scale particles are present in an amount of ≥ 5 to ≤ 50 wt% with respect to a total weight of the metal oxide particles.
4. The paste of claim 1, wherein said conductive powder comprises at least one selected from the group consisting of

silver (Ag), gold (Au), palladium (Pd), platinum (Pt), copper (Cu), chromium (Cr), cobalt (Co), aluminum (Al), tin (Sn), lead (Pb), zinc (Zn), iron (Fe), iridium (Ir), osmium (Os), rhodium (Rh), tungsten (W), molybdenum (Mo), nickel (Ni), and indium tin oxide (ITO).

- 5 **5.** The paste of claim 1, wherein said glass frit comprises a leaded glass frit, a lead-free glass frit, or a mixture thereof.
6. The paste of claim 1, wherein said organic vehicle comprises an organic binder and a solvent.
- 10 **7.** The paste of claim 1, wherein said paste comprises (a) ≥ 60 to ≤ 90 wt% of the conductive powder, (b) ≥ 1 to ≤ 10 wt% of the glass frit, (c) ≥ 8 to ≤ 20 wt% of the organic vehicle, and (d) ≥ 1 to ≤ 10 wt% of the nanometer and micron scale metal oxide.
- 15 **8.** The paste of claim 1, further comprising: at least one type of additive selected from the group consisting of a plasticizer, a dispersant, a thixotropic agent, a viscosity stabilizer, an anti-foaming agent, a pigment, a UV stabilizer, an antioxidant, and a coupling agent.
- 20 **9.** An electrode formed of the paste for solar cell electrodes according to claim 1.
- 25 **10.** A solar cell comprising the electrode according to claim 9.
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- 55

Fig 1.





EUROPEAN SEARCH REPORT

Application Number
EP 10 19 5259

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 1 713 092 A2 (DU PONT [US]) 18 October 2006 (2006-10-18) * paragraph [0019] - paragraph [0039] * * claims 1-11 *	1-10	INV. H01B1/22
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			TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 19 March 2012	Examiner Kövecz, Monika
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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 10 19 5259

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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